

# Springer Tracts in Modern Physics

## Volume 228

Managing Editor: G. Höhler, Karlsruhe

Editors: A. Fujimori, Chiba  
J. Kühn, Karlsruhe  
Th. Müller, Karlsruhe  
F. Steiner, Ulm  
J. Trümper, Garching  
C. Varma, California  
P. Wölflé, Karlsruhe

Available online at  
**SpringerLink.com**

Starting with Volume 165, Springer Tracts in Modern Physics is part of the [SpringerLink] service. For all customers with standing orders for Springer Tracts in Modern Physics we offer the full text in electronic form via [SpringerLink] free of charge. Please contact your librarian who can receive a password for free access to the full articles by registration at:

[springerlink.com](http://springerlink.com)

If you do not have a standing order you can nevertheless browse online through the table of contents of the volumes and the abstracts of each article and perform a full text search.

There you will also find more information about the series.

# Springer Tracts in Modern Physics

---

Springer Tracts in Modern Physics provides comprehensive and critical reviews of topics of current interest in physics. The following fields are emphasized: elementary particle physics, solid-state physics, complex systems, and fundamental astrophysics.

Suitable reviews of other fields can also be accepted. The editors encourage prospective authors to correspond with them in advance of submitting an article. For reviews of topics belonging to the above mentioned fields, they should address the responsible editor, otherwise the managing editor. See also [springer.com](http://springer.com)

## Managing Editor

Gerhard Höhler

Institut für Theoretische Teilchenphysik  
Universität Karlsruhe  
Postfach 69 80  
76128 Karlsruhe, Germany  
Phone: +49 (7 21) 6 08 33 75  
Fax: +49 (7 21) 37 07 26  
Email: [gerhard.hoehler@physik.uni-karlsruhe.de](mailto:gerhard.hoehler@physik.uni-karlsruhe.de)  
[www-ttp.physik.uni-karlsruhe.de/](http://www-ttp.physik.uni-karlsruhe.de/)

## Elementary Particle Physics, Editors

Johann H. Kühn

Institut für Theoretische Teilchenphysik  
Universität Karlsruhe  
Postfach 69 80  
76128 Karlsruhe, Germany  
Phone: +49 (7 21) 6 08 33 72  
Fax: +49 (7 21) 37 07 26  
Email: [johann.kuehn@physik.uni-karlsruhe.de](mailto:johann.kuehn@physik.uni-karlsruhe.de)  
[www-ttp.physik.uni-karlsruhe.de/~jk](http://www-ttp.physik.uni-karlsruhe.de/~jk)

Thomas Müller

Institut für Experimentelle Kernphysik  
Fakultät für Physik  
Universität Karlsruhe  
Postfach 69 80  
76128 Karlsruhe, Germany  
Phone: +49 (7 21) 6 08 35 24  
Fax: +49 (7 21) 6 07 26 21  
Email: [thomas.muller@physik.uni-karlsruhe.de](mailto:thomas.muller@physik.uni-karlsruhe.de)  
[www-ekp.physik.uni-karlsruhe.de](http://www-ekp.physik.uni-karlsruhe.de)

## Fundamental Astrophysics, Editor

Joachim Trümper

Max-Planck-Institut für Extraterrestrische Physik  
Postfach 13 12  
85741 Garching, Germany  
Phone: +49 (89) 30 00 35 59  
Fax: +49 (89) 30 00 33 15  
Email: [jtrumper@mpe.mpg.de](mailto:jtrumper@mpe.mpg.de)  
[www.mpe-garching.mpg.de/index.html](http://www.mpe-garching.mpg.de/index.html)

## Solid-State Physics, Editors

Atsushi Fujimori

*Editor for The Pacific Rim*

Department of Physics  
University of Tokyo  
7-3-1 Hongo, Bunkyo-ku  
Tokyo 113-0033, Japan  
Email: [fujimori@wyvern.phys.s.u-tokyo.ac.jp](mailto:fujimori@wyvern.phys.s.u-tokyo.ac.jp)  
[http://wyvern.phys.s.u-tokyo.ac.jp/welcome\\_en.html](http://wyvern.phys.s.u-tokyo.ac.jp/welcome_en.html)

C. Varma

*Editor for The Americas*

Department of Physics  
University of California  
Riverside, CA 92521  
Phone: +1 (951) 827-5331  
Fax: +1 (951) 827-4529  
Email: [chandra.varma@ucr.edu](mailto:chandra.varma@ucr.edu)  
[www.physics.ucr.edu](http://www.physics.ucr.edu)

Peter Wölfle

Institut für Theorie der Kondensierten Materie  
Universität Karlsruhe  
Postfach 69 80  
76128 Karlsruhe, Germany  
Phone: +49 (7 21) 6 08 35 90  
Fax: +49 (7 21) 6 08 77 79  
Email: [woelfle@tkm.physik.uni-karlsruhe.de](mailto:woelfle@tkm.physik.uni-karlsruhe.de)  
[www-tkm.physik.uni-karlsruhe.de](http://www-tkm.physik.uni-karlsruhe.de)

## Complex Systems, Editor

Frank Steiner

Institut für Theoretische Physik  
Universität Ulm  
Albert-Einstein-Allee 11  
89069 Ulm, Germany  
Phone: +49 (7 31) 5 02 29 10  
Fax: +49 (7 31) 5 02 29 24  
Email: [frank.steiner@uni-ulm.de](mailto:frank.steiner@uni-ulm.de)  
[www.physik.uni-ulm.de/theo/qc/group.html](http://www.physik.uni-ulm.de/theo/qc/group.html)

R.E. Walstedt

# The NMR Probe of High- $T_c$ Materials



Springer

Russell E. Walstedt  
University of Michigan  
Department of Physics  
Ann Arbor, MI 48104, USA  
walstedt@umich.edu

---

R.E. Walstedt, *The NMR Probe of High- $T_c$  Materials*, STMP 228 (Springer, Berlin Heidelberg 2008), DOI 10.1007/978-3-540-75565-4

---

Library of Congress Control Number: 2007936864

Physics and Astronomy Classification Scheme (PACS):  
NMR STUDIES IN GENERAL 76.60.-K  
CUPRATE SUPERCONDUCTORS 74.72.-H

ISSN print edition: 0081-3869  
ISSN electronic edition: 1615-0430  
ISBN 978-3-540-75564-7 Springer Berlin Heidelberg New York

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilm or in any other way, and storage in data banks. Duplication of this publication or parts thereof is permitted only under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer. Violations are liable for prosecution under the German Copyright Law.

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

© Springer-Verlag Berlin Heidelberg 2008

The use of general descriptive names, registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Typesetting: by the authors and Integra using a Springer L<sup>A</sup>T<sub>E</sub>X macro package  
Cover design: eStudio Calamar S.L., F. Steinen-Broo, Pau/Girona, Spain

Printed on acid-free paper SPIN: 11935247 5 4 3 2 1 0

To Erwin, Vince, and Hiroshi

---

## Preface

To the old saying that if you want to learn something about a subject, teach a course on it, I would add the much more arduous option of writing a book about it. The upside, of course, is that you may gain a perspective on a long-time favorite subject which can be achieved in no other way. The fact is that the opportunity to write such a book as this is, indeed, a rare opportunity. This is especially so for someone who, by the calendar, is well into retirement years.

While high  $T_c$  itself is the *opportunity of a lifetime* for those of us who experienced it, and revisiting the old milestones in writing this monograph was a genuine nostalgia trip, it is also important to reflect on the purpose of such a book as this. Now that the great majority of experimental high- $T_c$  studies are finished, who could be interested in such a book? To give some kind of answer to this, let me pinpoint the 2006 M<sup>2</sup>S Conference in Dresden.<sup>1</sup> Not only was it at this conference that the idea for this book was hatched, but the conference itself evinced an astonishingly high level of interest in high- $T_c$  issues, especially the theoretical aspects. Since it is now a number of years since a review of high- $T_c$  studies with NMR has appeared, there may be a need on the part of theorists and other interested parties for an organized summary of results and of the ideas which have been advanced to bind them together.

The foregoing offers a partial answer to the “Why now?” question, but let me note that excellent answers to that question also emerge from the subject itself. Although many issues were settled as of 10 years ago, new ideas and even new phenomena have appeared since that time. Let me offer two examples. The confirmation by N. Curro and co-workers of a dynamical exponent crossover in the high-temperature phase diagram opens up a new arena of potential experimental activity. D. Pines and co-workers had predicted such an effect and other theorists, including C. Varma, had predicted a phase

---

<sup>1</sup> This was the *8th International Conference on Materials and Mechanisms of Superconductivity and High Temperature Superconductors*, Dresden, July 9–14, 2006.

boundary in that region. Another interpretive breakthrough is to be credited to A. Uldry and P.F. Meier, who in 2005 created a new, general method for analyzing relaxation ( $T_1$ ) data in terms of temperature-dependent spin-spin correlation coefficients for close-neighbor copper sites. Discussed at some length in this volume, this method rests on a very firm theoretical foundation. It has the great virtue that it separates spin-spin these correlation effects from the temperature dependence of the quasiparticle dynamics, itself, which theoretical modelers have been trying to get at. If this extraordinarily simple method had been “available” 15 years ago, I suggest that our understanding of these issues would be greatly advanced from where it is.

As for regrets, they come mainly under the heading of omissions. There are many excellent pieces of work which are not included, simply for want of time and space. The book was conceived of as a monograph and is in no sense an encyclopedia, not even within the narrow purview of high- $T_c$  NMR. As an example, I greatly regret omitting the large and fascinating subject of impurity doping in cuprates, from which we have nonetheless learned a lot.

Let me conclude by mentioning just a few of the people who have contributed, directly and indirectly, to the initiation and creation of this book. First let me thank Prof. Hiroshi Yasuoka, for bringing me to Tokai-mura in Japan for a 5-plus year extension of my career in solid-state NMR, and through which I also became involved in the European physics scene. Let me thank Prof. Dr. Frank Steglich for his support during my extensive visits to Dresden in 2006 and 2007. Invaluable support came from the Department of Physics at the University of Michigan in providing work space and the library facilities required for a project such as this. I want especially to thank Prof. Chandra Varma at the University of California at Riverside, for shepherding this book into existence through his role as editor for Springer Verlag and for his reading of much of the manuscript, giving penetrating, enlightening, and invaluable comments on the presentation. I also thank Jinan Yang for help with computer issues and with the preparation of the figures.

Ann Arbor, MI,

*Russell E. Walstedt*  
June 2007

---

# Contents

|          |                                                                                        |    |
|----------|----------------------------------------------------------------------------------------|----|
| <b>1</b> | <b>Introduction</b>                                                                    | 1  |
| 1.1      | The Basic Phenomenology of High- $T_c$ Materials                                       | 1  |
| 1.2      | Carrier Doping and the Master Phase Diagram                                            | 2  |
| 1.3      | The NMR Probe                                                                          | 4  |
| 1.4      | Outline of the Remaining Chapters                                                      | 6  |
| 1.4.1    | Summary of Chapter 2 – NMR Review                                                      | 6  |
| 1.4.2    | Summary of Chapter 3 – Preliminary Cuprate NMR                                         | 7  |
| 1.4.3    | Summary of Chapter 4 – The Pseudogap                                                   | 7  |
| 1.4.4    | Summary of Chapter 5 – $T_1$ Models                                                    | 8  |
| 1.4.5    | Summary of Chapter 6 – The Dynamical Susceptibility                                    | 9  |
|          | References                                                                             | 10 |
| <b>2</b> | <b>Introduction to NMR Studies of Metals, Metallic Compounds, and Superconductors</b>  | 13 |
| 2.1      | Basic NMR Phenomenology                                                                | 13 |
| 2.1.1    | The Basic Hamiltonian for NMR Spectra                                                  | 14 |
| 2.1.2    | Observation of NMR/NQR Signals                                                         | 17 |
| 2.1.3    | Definition and Interpretation of NMR parameters: $T_2$                                 | 19 |
| 2.1.4    | Definition and Interpretation of NMR parameters:<br>The shift tensor $K_{\alpha\beta}$ | 21 |
| 2.1.5    | Definition and Interpretation of NMR parameters: $T_1$                                 | 23 |
| 2.2      | NMR Probe of sp-Band Metals and Type I Superconductors                                 | 32 |
| 2.2.1    | NMR Shifts and Relaxation in Simple Pauli Paramagnets                                  | 33 |
| 2.2.2    | The Moriya Theory of Exchange Enhancement<br>in Simple Metals                          | 36 |
| 2.2.3    | NMR in the Superconducting State of Simple Metals                                      | 38 |
| 2.3      | Static and Dynamic Magnetism in d-band Metals                                          | 44 |
| 2.3.1    | The d-Electron HF Interactions                                                         | 45 |
| 2.3.2    | Orbital Shift and Susceptibility                                                       | 46 |
| 2.3.3    | Spin-Lattice Relaxation Effects for d-Band Electrons                                   | 50 |
| 2.3.4    | NMR Studies of 3d Metals as Type-II Superconductors                                    | 53 |

|            |                                                                                                                                 |           |
|------------|---------------------------------------------------------------------------------------------------------------------------------|-----------|
| 2.3.5      | $T_1$ Phenomenology for Type-II Superconductors . . . . .                                                                       | 58        |
| References | . . . . .                                                                                                                       | 63        |
| <b>3</b>   | <b>The Superconducting Cuprates: Preliminary Steps</b>                                                                          |           |
|            | <b>in their Investigation via NMR . . . . .</b>                                                                                 | <b>67</b> |
| 3.1        | Cuprate Structures and Doping Effects: LSCO and YBCO . . . .                                                                    | 68        |
| 3.1.1      | LSCO: A superconductor with $T_c(\text{max}) \simeq 40\text{ K}$ . . . . .                                                      | 68        |
| 3.1.2      | The 92 K Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) . . . . .                                                | 70        |
| 3.1.3      | Physical Models of Itinerant Quasiparticles in Cuprates . . . .                                                                 | 71        |
| 3.2        | Early NMR/NQR Studies: The Early Predominance of YBCO . . . .                                                                   | 72        |
| 3.2.1      | NMR Shift and Relaxation of the $^{89}\text{Y}$ in YBCO7 . . . . .                                                              | 73        |
| 3.2.2      | Establishing the Site Assignment for the Cu(1) and<br>Cu(2) NQR Spectra . . . . .                                               | 75        |
| 3.2.3      | Variation of the $^{89}\text{Y}$ shift $K_{89}(x)$ with $x$ for YBCO6+ $x$ . . . .                                              | 76        |
| 3.2.4      | Physical Models for the Relaxation of $^{63}\text{Cu}(2)$ in<br>YBCO7 . . . . .                                                 | 79        |
| 3.2.5      | Introduction of the <i>Spin Hamiltonian</i> Model for the<br>$\text{Cu}^{2+}$ . . . . .                                         | 79        |
| 3.2.6      | Experimental Breakthrough: Oriented Powder Samples . . . . .                                                                    | 80        |
| 3.3        | The Mila-Rice-Shastry Model: A Universal HF Tensor for the<br>Cuprates . . . . .                                                | 81        |
| 3.3.1      | General Definition of the HF Tensors . . . . .                                                                                  | 82        |
| 3.3.2      | Extracting the Cu(1,2) HF tensors for YBCO7<br>from Shift and Susceptibility Data Using the Spin<br>Hamiltonian Model . . . . . | 84        |
| 3.3.3      | Quantum Chemistry of YBCO7 and the Hyperfine<br>Tensor . . . . .                                                                | 87        |
| 3.3.4      | $T_1$ Ratios and Electron Spin Correlation Effects . . . . .                                                                    | 90        |
| 3.4        | Incorporating $^{17}\text{O}$ and $^{89}\text{Y}$ data into the Mila-Rice-Shastry<br>Picture . . . . .                          | 92        |
| 3.4.1      | Measurements of $T_1$ for $^{17}\text{O}$ in YBCO7 . . . . .                                                                    | 97        |
| 3.4.2      | The One-Band, Two-Band Debate: $^{89}\text{Y}$ and $^{17}\text{O}(2,3)$<br>NMR in YBCO . . . . .                                | 98        |
| 3.5        | Formulation of $T_1$ in Terms of $\chi''(q, \omega)$ and $\mathbf{q}$ -Dependent HF<br>Couplings . . . . .                      | 99        |
| 3.5.1      | Derivation of Dynamical Susceptibility $T_1$ Equation . . . . .                                                                 | 99        |
| 3.5.2      | The Fluctuation-Dissipation Theorem . . . . .                                                                                   | 101       |
| 3.6        | A d-Wave Model for the NMR Shift and $T_1$ at $T < T_c$ . . . . .                                                               | 104       |
| 3.6.1      | The NMR Shift Behavior for $T < T_c$ . . . . .                                                                                  | 105       |
| 3.6.2      | The Monien-Pines Calculations of NMR Shifts below $T_c$ . . . .                                                                 | 107       |
| 3.6.3      | Calculating the Relaxation Decay Curve . . . . .                                                                                | 108       |
| References | . . . . .                                                                                                                       | 112       |

|          |                                                                                           |     |
|----------|-------------------------------------------------------------------------------------------|-----|
| <b>4</b> | <b>Pseudogap Effects in Cuprate NMR Studies</b>                                           | 115 |
| 4.1      | The Pseudogap in Oxygen-Deficient YBCO7-x                                                 | 117 |
| 4.1.1    | HF Parameters for YBCO6.63 from Scaling of Shift Data                                     | 120 |
| 4.1.2    | A Simple Model Theory of Spin Dynamics for YBCO6.63                                       | 126 |
| 4.1.3    | INS Data for the Pseudogap of Underdoped YBCO                                             | 128 |
| 4.1.4    | A Comprehensive $T_1$ Data Set for YBCO6.63                                               | 130 |
| 4.2      | Pseudogap Phenomenology with Other Probes                                                 | 134 |
| 4.2.1    | Pseudogap Effects in the Electronic Specific Heat                                         | 134 |
| 4.2.2    | ARPES Studies of Pseudogapped Cuprates                                                    | 136 |
| 4.3      | Pseudogap Behavior of $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y248)                          | 138 |
| 4.3.1    | NMR Shift and Relaxation Behavior in Y248                                                 | 139 |
| 4.3.2    | Measuring the Pseudogap Isotope Effect in Y248 with NMR                                   | 143 |
| 4.3.3    | Theory of the Pseudogap by Varma                                                          | 146 |
| 4.3.4    | Effect of Zn impurities on the Pseudogap in Y248                                          | 147 |
| 4.4      | “Pseudogap-like” Effects in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO:x)             | 148 |
| 4.4.1    | Spin Susceptibility Scaling for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$                  | 149 |
| 4.4.2    | Behavior of the $^{17}\text{O}$ and $^{63}\text{Cu}$ NMR Shifts in LSCO:x                 | 152 |
| 4.4.3    | $^{63}\text{Cu}$ NQR spectra and Contrasting $T_1$ Behaviors in LSCO:x                    | 153 |
|          | References                                                                                | 156 |
| <b>5</b> | <b>Relaxation Models for Cuprate NMR</b>                                                  | 159 |
| 5.1      | The Uldry-Meier Parameterization Model                                                    | 160 |
| 5.1.1    | Basic Formulation of the UM Analysis                                                      | 161 |
| 5.1.2    | The Uldry-Meier Analysis of YBCO7                                                         | 163 |
| 5.1.3    | The Uldry-Meier Analysis of YBCO6.63                                                      | 167 |
| 5.1.4    | The Uldry-Meier Analysis of $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y248)                    | 169 |
| 5.2      | The Millis, Monien, and Pines Model for $T_1$ in Cuprates                                 | 172 |
| 5.3      | $T_1$ Model for YBCO Using INS Data for $\chi''(q, \omega)$                               | 179 |
| 5.3.1    | The Gaussian Model Susceptibility                                                         | 180 |
| 5.3.2    | Comparison with the UM Analysis Results for YBCO7                                         | 184 |
| 5.4      | A Small-U Hubbard Model of Cuprate Spin Dynamics                                          | 187 |
| 5.4.1    | Basic Formulation of the Dynamic Susceptibility                                           | 187 |
| 5.4.2    | Remarks on the Hubbard Model Calculations                                                 | 189 |
| 5.5      | The Large-U Hubbard Model of Si, Levin et al                                              | 192 |
| 5.6      | Relaxation via Orbital Currents proposed by Varma                                         | 195 |
| 5.7      | Relaxation of Planar $^{63}\text{Cu}$ and $^{17}\text{O}$ at $T < T_c$                    | 199 |
| 5.7.1    | $\chi''(\mathbf{q}, \omega)$ for the Small-U Hubbard Model at $\mathbf{T} < \mathbf{T}_c$ | 201 |
| 5.7.2    | $T_1$ and Spin-Spin Correlations below $T_c$ : The UM Analysis                            | 207 |
|          | References                                                                                | 210 |

|          |                                                                                                |     |
|----------|------------------------------------------------------------------------------------------------|-----|
| <b>6</b> | <b>Dynamic Susceptibility Studies for the Cuprates</b>                                         | 213 |
| 6.1      | The Indirect Spin-Spin Coupling Theory of Pennington and Slichter                              | 214 |
| 6.1.1    | Some General Properties of the Indirect Spin-Spin Coupling                                     | 216 |
| 6.1.2    | The Gaussian model of Indirect Spin-Spin Coupling in YBCO                                      | 217 |
| 6.1.3    | Measuring Indirect Spin-Spin Coupling via Spin-Echo Decay                                      | 218 |
| 6.1.4    | Behavior and Interpretation of Indirect Couplings in YBCO and Y248                             | 219 |
| 6.2      | The Bulut-Scalapino Calculation of $1/T_{2g}$ for $T < T_c$                                    | 224 |
| 6.3      | Coordinated Interpretation of NMR and INS Data for LSCO                                        | 227 |
| 6.3.1    | Review of INS Data for Optimally-Doped LSCO                                                    | 228 |
| 6.3.2    | Interpretation of $^{63}\text{Cu}$ and $^{17}\text{O}$ $T_2$ Data with INS Data for $\chi'(q)$ | 236 |
| 6.4      | The Sokol-Barzykin-Pines Scaling Theory of $\chi(q, \omega)$                                   | 242 |
| 6.4.1    | Phase Diagram and Basic Relationships for $T_1$ , $T_{2g}$                                     | 242 |
| 6.4.2    | The Dynamical Crossover Study by Curro et al: Y248                                             | 245 |
|          | References                                                                                     | 250 |
| <b>A</b> | <b>Appendices</b>                                                                              | 253 |
| A.1      | Some Basic Properties of Spin Echoes                                                           | 253 |
| A.1.1    | Basic Derivation of the Two-Pulse Spin Echo                                                    | 253 |
| A.1.2    | Modelling Spin-Echo Decay                                                                      | 257 |
| A.2      | The Gaussian Decay Time $T_{2g}$ for Indirect Spin-Spin Coupling                               | 257 |
| A.2.1    | Indirect Coupling with a Gaussian Susceptibility                                               | 258 |
| A.3      | Spin Echo Decay via Spin-Lattice Relaxation                                                    | 260 |
|          | References                                                                                     | 261 |
|          | <b>Index</b>                                                                                   | 263 |

# Introduction

The discovery of high-temperature superconductors among hole-doped  $\text{CuO}_2$  structures was one of those rare events in the scientific sphere which launches a whole new world of activity for hundreds of theorists and experimentalists alike. It is now more than twenty years since the New York City APS meeting dubbed the “Woodstock of Physics” witnessed the announcement of the original high- $T_c$  results [1], but the level of activity on this topic remains extraordinarily high.

For the nuclear magnetic resonance (NMR) probe, the high- $T_c$  materials have offered a panorama of new phenomenology to be analyzed and categorized in ways which had not previously come into use. It is the purpose of this volume to give a systematic account of many of the phenomena which have come to light in the process. The style of presentation is intended to be partly historical, partly tutorial for the non-specialist, and partly a review. There is by now a very large number of well-established ideas and effects descriptive of the cuprates to be addressed. However, there is also the feeling, even twenty years on, that this monograph offers only a snapshot of a vigorous and ongoing enterprise.

We begin by presenting in this introductory chapter a broad perspective on the phenomenology and materials to be addressed, as well as on the NMR probe itself in the context of the cuprates. This is followed by an organizational synopsis of the remaining chapters.

## 1.1 The Basic Phenomenology of High- $T_c$ Materials

The concept of a half-filled “conduction band” which cannot conduct on account of on-site Coulomb repulsion forces was inaugurated in 1949 by N.F. Mott – the “Mott insulator” [2]. Mott, who discussed the case of  $\text{NiO}$ , commented, “Experiments on the conductivity of cupric salts would be of great interest” [2]. Nearly forty years later a “cupric salt”, with a modest amount of hole-doping in the conduction plane, emerged as a superconductor,

and “high- $T_c$ ” was born. Just how such a system conducts – and superconducts – then became the investigative preoccupation of hundreds, possibly thousands of researchers around the world for many years to follow.

The basic process whereby the entire system of localized,  $S = \frac{1}{2}$ ,  $\text{Cu}^{2+}$  moments becomes a set of itinerant quasiparticles with the addition of a far smaller number of mobile hole “carriers” is one of great fascination, upon which even now there seems to be no clear theoretical consensus. As a basic mechanism, however, the Zhang-Rice singlet picture [3] provides at least a conceptual framework. Since the quasiparticles which result are known (through NMR studies) to pair off at low temperatures into a ground state of magnetically inert Cooper-pair singlets, the resulting scenario of fully itinerant character for the solitary holes on the  $\text{Cu}^{2+}$  sites seems at this point incontrovertible.

Furthermore, these quasiparticles are known to possess a Fermi surface, with respect to which angle-resolved photoemission studies (ARPES) can be used to measure the superconducting energy gap. However, in many cases, gapping is found to occur in the normal state as well [4, 5, 6], in what is known as the “pseudogap” [7]. Many of the high- $T_c$  systems also exhibit poor, but metallic-like conduction in the normal state, characterized by a non-Fermi-liquid temperature dependence  $\rho \propto T$  instead of the usual  $T^2$ .

While the cuprates exhibit certain metallic attributes, they also clearly possess some features characteristic of the undoped insulating host, namely a powerful antiferromagnetic (AFM) exchange interaction between nearest-neighbor  $\text{Cu}^{2+}$  moments. The effects of these AFM couplings have emerged from virtually all inelastic neutron scattering (INS) studies of the cuprates, and are a major feature of theoretical modelling and experimental fits to nuclear relaxation data as well (see Sect. 1.3).

## 1.2 Carrier Doping and the Master Phase Diagram

There are by now hundreds of host structures known which contain  $\text{CuO}_2$  quadratic layers that superconduct under suitable doping conditions. A partial list is given in the review by Hazen [8]. In this volume, in order to limit the extent of material to be covered, we focus on the three principal systems  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (LSCO:x),  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO7-x), and the related stoichiometric compound  $\text{YBa}_2\text{Cu}_4\text{O}_8$  (Y248). These three were chosen, because they emerged early on as systems easy to synthesize and characterize. As a consequence, there is an extensive literature built up around them both in terms of experimental data and, naturally, of theoretical modelling as well. Even with our purview narrowed to these three systems, there are unfortunately many interesting studies which had to be omitted.

One of the most important characteristics of the YBCO7-x and LSCO:x are their phase diagrams, plotted with coordinates  $T$  vs.  $\delta$ , where  $\delta$  represents the doping level of carriers in the  $\text{CuO}_2$  planes. An early version of the cuprate

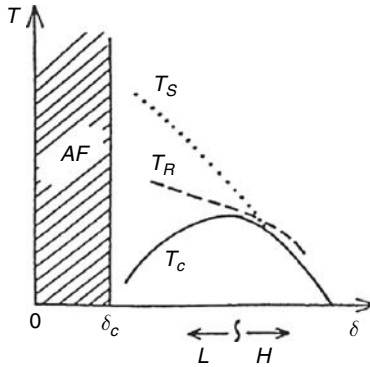


**Fig. 1.1.** The temperature vs.  $\delta$  phase diagram of a typical cuprate structure, where  $\delta$  is the number of hole carriers per formula unit. In the case of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , one has  $\delta \sim x$ . For very small values of  $\delta$  there is an antiferromagnetically ordered region. To the right of that is a roughly parabolic region of superconducting behavior which is centered on  $\delta \simeq 0.15$ . See text for additional discussion. Reprinted figure from T. Tanamoto, H. Kohno, and H. Fukuyama, *J. Phys. Soc. Japan* **62**, 717 (1993). Copyright 1993 Physical Society of Japan

phase diagram is shown in Fig. 1.1, where the superconducting phase lies under a dome extending from  $\delta = 0.05$  up to  $\delta \sim 0.35$ . At lower  $\delta$  values there is an AFM phase which as  $\delta \rightarrow 0$  occurs at  $T_N \simeq 325 \text{ K}$ . The lines extending above and to the left of the superconducting dome represent, in the present instance, maxima in the spin susceptibility and in the nuclear relaxation curves, respectively [9]. In versions of this phase diagram discussed in Chaps. 4 and 6, these lines have other interpretations as well, such as the pseudogap temperature or the crossover between the tetragonal and orthorhombic phases in LSCO, etc. – see Sect. 1.4).

There is, in principle, a phase diagram similar to Fig. 1.1 for every cuprate structure. It happens for LSCO: $\Delta$  that the hole doping level can be varied across the entire superconducting range by varying  $\delta$ . In YBCO7- $x$ , on the other hand, the doping is controlled via the oxygen content. At  $x = 0$  (YBCO7) the structure is stoichiometric and the hole-doping level is  $\sim 0.33$  per Cu ion, which is just slightly above optimal doping [10, 11]. As  $x$  is increased, the doping diminishes all the way into the AFM insulating phase. However, the overdoped phase which would correspond to negative values of  $x$  simply does not exist.

The stoichiometric compound Y248 is structurally similar to YBCO7, but with an extra chain layer. It has a very stable oxygen content up to relatively high temperatures, but its doping level giving  $T_c \simeq 84 \text{ K}$  cannot be altered without decomposition. It has been an attractive system for study and will be discussed in Chaps. 4, 5 and 6.

Characterization of samples for experimental investigation is a matter of great importance, since a large body of reliable data for mainstream

structures is on hand. Sample characterization includes morphology of the sample material, x-ray crystallography for phase purity, superconducting diamagnetism (Meissner effect) including the value and sharpness of  $T_c$ , and magnetic susceptibility for excessive local moment content. The NMR and NQR studies themselves include sample characterization tests, to be mentioned in Sect. 1.3 to follow.

For articles discussing structures and a variety of bulk and other measurements, see the reviews edited by D.M. Ginsburg [12].

### 1.3 The NMR Probe

The NMR probe is a local, real-space probe, where the behavior of nuclear spins can be monitored on a site-by-site basis. The magnetic hyperfine (HF) interaction of a nucleus couples it to magnetic entities in its immediate environment. This interaction rarely goes beyond nearest-neighbors, though dipolar interactions may have some effects beyond that range. One of the remarkable HF effects in cuprates is the extraordinarily large coupling of  $^{63,65}\text{Cu}$  with neighboring ( $\text{Cu}^{2+}$ ) electron spin moments, which is comparable with on-site interactions. There is, however, an intervening  $\text{O}^{2-}$  ligand, so this is a second-neighbor interaction. Such an effect was unprecedented. The effect of HF couplings is also strongly affected by site symmetry, where strong, but equal couplings to antiferromagnetically correlated neighbor spins may be rendered ineffective. Such effects are well known for insulating antiferromagnets (e.g.  $^{19}\text{F}$  in  $\text{KMnF}_3$ ).

The measurements performed and type of data received are also very much conditioned by the properties of the naturally occurring nuclear species in the system investigated. Thus, the 100% abundant,  $I = \frac{1}{2}$ ,  $^{89}\text{Y}$  in YBCO7, with its nearly isotropic NMR shift, total absence of quadrupole effects, and weak, but adequate relaxation times was the subject of the first NMR study on cuprates to be published [13]. The  $^{63,65}\text{Cu}$  isotopes with  $I = \frac{3}{2}$ , (nearly) axial site symmetry, and very substantial quadrupolar energies which allow both NMR and NQR to be performed, were quick to follow [14, 15, 16, 17].

Studies of  $^{17}\text{O}$ , which only appeared after an interval of many months, were hampered by the fact that  $^{17}\text{O}$  is present in only trace quantities in natural oxygen. Further, it is too expensive to incorporate into the sample synthesis and has to be diffusively exchanged into sample materials at an elevated temperature. Such a process is critically dependent on diffusion rates in any given material. In  $\text{LSCO:x}$ , for example, diffusion is fast and single crystals of moderate size are easily doped with  $^{17}\text{O}$ . For YBCO7-x, however, this is only feasible with powders and crystals of the smallest size. With Y248 it is also very difficult, requiring lengthy high-temperature anneals [18]. Nonetheless,  $^{17}\text{O}$  doping eventually became a routine element of technique.

## *A Sampling of NMR Measurements and their Interpretation*

We give a brief survey of types of NMR observations made and their significance for the behavior of cuprate materials. First, the NMR spectrum is fundamental and is a major element of sample characterization. The width and distribution of NMR/NQR resonance lines tells a great deal about the phase purity and microscopic quality of sample material. If there are crystallographically inequivalent sites, they usually have different spectra. Quadrupolar frequency shifts and broadening and their field/frequency dependence can usually be analyzed to yield values of coefficients from the HF Hamiltonian. These matters are reviewed in some detail in Chap. 2.

The NMR shift, which is measured as a frequency shift proportional to the applied field, is fundamentally a measure of the various terms in the magnetic polarization of the sample, conveyed to the nuclear spins by HF coupling fields. The NMR shift is an important source of information on intrinsic susceptibilities. For example, the decay of the spin susceptibility in the superconducting state can usually only be measured via the NMR shift, where direct magnetic measurements would be swamped by the much larger diamagnetic response.

There are various contributions to NMR shifts in metals. The s-contact shift, for which we reserve the term “Knight shift” [19], is a mainstay effect in sp-band and d-band metals. In cuprates this term is oddly absent. In its place are the core-polarization shift, orbital shift, dipolar shift, and even “spin-orbit shift”, a second-order effect which arises in the spin Hamiltonian model. There are also very important transferred HF fields giving rise to NMR shifts, originating in the Mila-Rice [20] and Shastry [21] treatments of cuprate quantum chemistry. NMR shift measurements are a very important tool for determining the HF parameters, since any such determination is independent of model assumptions required for the dynamics.

NMR dynamics, as represented by the spin-lattice relaxation time  $T_1$ , are a key diagnostic of quasiparticle dynamics in metals and in cuprates in particular.  $T_1$  is linked to  $\chi''(\mathbf{q}, \omega)$  via the fluctuation dissipation theorem [22, 23]. In cuprates,  $T_1$  measurements have been interpreted (for the first time!) through theoretical modeling of  $\chi''(\mathbf{q}, \omega)$ . What makes this process particularly interesting is the interplay between the strong AFM fluctuation effects, which typically produce an AFM peak near  $\mathbf{q} = (\pi, \pi)$ , and the transferred HF couplings at  $^{17}\text{O}(2,3)$  and  $^{89}\text{Y}$  in, e.g. YBCO7-x, which allow their relaxation processes to avoid the AFM peak. Meanwhile, the  $^{63}\text{Cu}(2)$  are quite sensitive to the AFM peak. In effect one has, then, a “ $\mathbf{q}$ -space spectrometer” for quasiparticle fluctuations. These effects occupy a substantial fraction of the discussion in this volume.  $T_1$  measurements are also very sensitive to the difference between s-wave and d-wave gap characteristics in the superconducting state. Calculations of d-wave  $T_1$  characteristics below  $T_c$  were among the first strong evidences for d-wave singlet character of quasiparticle pairing in cuprates [24, 25].

A second relaxation time, the spin-echo decay time  $T_{2g}$ , has taken on a major significance in the effort to characterize the dynamic susceptibility of cuprate compounds. This decay time is actually used to measure a *static interaction* which occurs in cuprates, namely a c-axis indirect spin-spin coupling of the form  $\mathcal{H}_{zz} = \sum_{ij \neq} \alpha_{ij} I_{zi} I_{zj}$ , which was first identified by Pennington et al. [26]. How this comes about is discussed in Appendix A.1 and in Chap. 6 of the book. Interpretation of  $\mathcal{H}_{zz}$  in terms of  $\chi'(\mathbf{q}, 0)$  for  $\mathbf{q}$  in the vicinity of  $(\pi, \pi)$  was established by the Pennington–Slichter model calculation [27]. Through measurements of  $T_{2g}$  the indirect coupling has become a major element in characterizing the strength of AFM fluctuations in cuprates. In addition, the interpretation of  $T_{2g}$  in the superconducting state by Bulut and Scalapino [24] again provided dramatic evidence in favor of d-wave pairing several years before it was widely accepted by the research community.

The foregoing is just a sampling of interesting effects which have come to light through NMR studies of cuprate superconductors. We refer the interested reader to sources on the fundamental principles of NMR [28, 29], on NMR studies of conventional metals and superconductors [30, 31, 32], as well as on NMR of high- $T_c$  superconductors [33, 34, 35, 36, 37, 38]. We now give a brief summary of the remaining chapters.

## 1.4 Outline of the Remaining Chapters

This section gives a brief summary of the content of Chaps. 2–6.

### 1.4.1 Summary of Chapter 2 – NMR Review

In Chap. 2 we give a review of the elements of NMR technique and interpretation, where basic definitions of key NMR parameters are given and some of the pitfalls and complexities associated with powder samples are discussed. The use of spin echoes – the standard tool for conducting NMR measurements – is described, with a detailed derivation including spin echo decay mechanisms presented in Appendix A.1. This leads into a summary of basic relaxation mechanisms for simple metals, including the Moriya theory of electron–electron interaction effects [22] and the BCS-based interpretation of the spin-paramagnetic shift and  $T_1$  behaviors in the superconducting state. The Anderson–Farrell resolution of spin-orbit coupling effects for  $T < T_c$  is covered in some detail. These effects were struggled over for many years, but almost all problems were finally resolved.

Discussion of the foregoing is extended to d-band metals, including the discovery and establishment of orbital shifts and relaxation effects. The interpretation of NMR spectra and relaxation effects in the mixed state of type-II superconductors is discussed at some length, with data from the literature. Many of the associated problems have cropped up again with the cuprates. The discussion of, e.g. the  $V_3X$ ’s is offered as a foundation for understanding cuprate mixed-state NMR.

### 1.4.2 Summary of Chapter 3 – Preliminary Cuprate NMR

Chapter 3 gives an account of the early stages of high- $T_c$  NMR research. In the first two years, almost all studies were done with either random powder samples or microcrystals with very low signal amplitude. There was an intense focus on YBCO7, because of its high  $T_c$  ( $\sim 90\text{ K}$ ) and because of its relative ease of preparation. In random powders,  $^{63}\text{Cu}(2)$  NMR spectra (just the  $-\frac{1}{2} \leftrightarrow \frac{1}{2}$  transition) were  $\sim 5\text{ kG}$  wide in an 8T laboratory NMR magnet, taking several days of signal averaging to perform a single scan.  $T_1$  measurements on the  $^{63,65}\text{Cu}$  were done mainly with NQR, once the frequencies had been extracted from NMR spectra.

$^{63}\text{Cu}(2)$  NMR shifts persisting into the superconducting state were identified as Van Vleck orbital shifts. The anisotropy and magnitude of these shifts fit well with a simple *spin Hamiltonian* model of the copper ionic state, which appears to resemble that of a  $\text{Cu}^{2+}$  ion in an insulating host for the purpose of analyzing HF effects. This picture has held up even until now. Moreover, the  $d_{x^2-y^2}$  ground state orbital dictates that the normally dominant orbital  $T_1$  mechanism effectively vanishes in the cuprates. In Sect. 5.6 a proposal for its revival via the *marginal Fermi liquid theory* is presented [39].

The apparent vanishing of the c-axis spin HF field led to the Mila-Rice proposal: A massive transferred HF coupling from  $nn$   $\text{Cu}^{2+}$  ions nearly  $4\text{ \AA}$  away. This unprecedented HF term made sense of the  $T_1$  and NMR shift data for the  $^{63}\text{Cu}(2)$ . Their watershed paper, including calculated quantum chemistry, provided a framework for interpretation of cuprate NMR data which has held up ever since [20].

The chapter closes with an account of the first interpretation of  $T_1$  data in the superconducting state using d-wave pairing with BCS theory, by Monien and Pines [24]. This landmark result gave a clear indication of the correctness of d-wave and the inadmissibility of s-wave, even though it would be five more years before the correctness of this picture was widely accepted.

### 1.4.3 Summary of Chapter 4 – The Pseudogap

Even before the Mila-Rice resolution of anomalous NMR shift behavior appeared, workers had begun to explore the highly unusual behavior in the underdoped region of the phase diagram in Fig. 1.1. There it was found that low-frequency fluctuations which drive the  $T_1$  process, as well as the uniform susceptibility, were beginning to collapse at temperatures far above  $T_c$ . It was as though the superconducting energy gap was beginning to develop at some  $T^*$  well above  $T_c$  in anticipation of the actual transition to superconductivity. In the spirit of “spin-charge separation”, an idea that dominated early thinking on cuprate quasiparticle behavior [40], this effect was at first dubbed the “spin gap”. There was a tacit assumption that charge states were unaffected. Nonetheless, the spin pseudogap was soon recognized as a universal feature of the underdoped phases. Moreover, in a most astonishing bit of prescience,

the appearance of such a precursive energy gap in the cuprates had actually been predicted by Friedel [7], who coined the term “pseudogap”.

Pseudogap characteristics via NMR shift and  $T_1$  data are documented in detail for several compounds in Chap. 4. Several years after the spin fluctuation properties of pseudogap systems were well established, it came to light through both electronic specific heat and ARPES measurements that charge properties were also profoundly altered in pseudogap systems. In this chapter we also review these effects briefly. With ARPES one finds that certain regions of the Fermi Surface, e.g. the quadratic axes, are gapped while the diagonal regions are not. Since the dynamic susceptibility is a summation over the Fermi surface, this means that the gap reflected by  $\chi''(\mathbf{q}, \omega)$  may vary significantly with  $\mathbf{q}$ . It follows that pseudogap  $T_1$  behavior can be quite different at the  $^{63,65}\text{Cu}$  site from what it is at the  $^{17}\text{O}$  sites. These differences are clearly observed in a number of cases discussed.

The pseudogap behavior of LSCO: $x$  is particularly interesting. In what was actually the first pseudogap behavior to be reported [41], the remarkable scaling of susceptibilities for different  $x$  values in this system was at first interpreted with a model suited to 2D insulating antiferromagnets. This is possible, since the latter systems exhibit a susceptibility temperature maximum which resembles pseudogap behavior. The disparate behaviors of  $1/T_1T$  for the  $^{63,65}\text{Cu}$  and the  $^{17}\text{O}$  also clearly tag this system as having a pseudogap. The low- $T$   $\chi_0(T) \propto T^{1/2}$  behavior of LSCO: $x$  is in accord with the Varma theory of pseudogap behavior [39], as is that of Y248 [42].

#### 1.4.4 Summary of Chapter 5 – $T_1$ Models

From the earliest days of high- $T_c$  NMR one of the main challenges has been to understand the disparate behaviors of  $T_1$  at various lattice sites. In addressing this question, there are several important branching points in the flow diagram of deduction so to speak. Magnetic dipole processes are assumed to be predominant. First, then, one must decide whether spin fluctuations alone will suffice to explain everything, or whether orbital relaxation, severely inhibited by the  $d_{x^2-y^2}$  ground-state orbitals, will play a role as well. Many workers have opted for the spin fluctuation picture, while the existence of a possible orbital mechanism has been pointed out by Varma [39]. A summary of the latter calculation is given in Sect. 5.6.

In the purely spin-dynamical picture, one must next decide whether a single dynamical variable per  $\text{Cu}^{2+}$  site, namely the itinerant  $S = \frac{1}{2}$  hole, is sufficient, or do the doped-in hole carriers form a second dynamical entity? The general approach to this question has been to see whether a complete account of the data can be given with one variable per site. Several  $T_1$  modeling efforts based on the latter assumption are described in Chap. 5, where it is presumed with Moriya [22] that any successful scenario can be expressed in terms of  $\chi''(\mathbf{q}, \omega)$ . Three of these employ the random-phase approximation in order to incorporate the (mandatory) electron-electron interactions, and

one is simply based on the shape and width of the the AFM peak in  $\chi''(\mathbf{q}, \omega)$  determined by INS studies.

Quite recently, however, a novel, but related approach was pioneered by Uldry and Meier [43], in which they attempt to systematize  $T_1$  data on several cuprates using electronic spin–spin correlations as parameters which vary with  $T$  and in which there is a universal spin fluctuation frequency (correlation time), also a function of  $T$ , which applies to all  $T_1$  processes. The other central assumption is that the HF Hamiltonian has the Mila–Rice form

$$\mathcal{H}_{HF} = \sum_{\alpha} \sum_i S_{i\alpha} \left[ A_{\alpha} + B \sum_{j(nn)} I_{j\alpha} \right] \quad (1.4.1)$$

for the planar  $^{63,65}\text{Cu}$  nuclei, with similar forms for the ligands. With these ingredients all of the data are fitted in a self-consistent way. The form (1.4.1) and the admissibility of the spin–spin correlations and correlation time as temperature–dependent parameters are the main assumptions here. A theoretical basis for this scheme is derived using  $\chi''(\mathbf{q}, \omega)$  in Chap. 3. It yields an internally consistent picture, in which the dynamically–derived HF constants basically agree with those derived from the shift. This scheme is useful for evaluating theoretical models as well as for analyzing experimental data.

### 1.4.5 Summary of Chapter 6 – The Dynamical Susceptibility

In this chapter three topics related to modeling and characterization of  $\chi(\mathbf{q}, \omega)$  are presented and discussed. First, large indirect spin–spin couplings in cuprates were noted early on and modeled quantitatively by Pennington and Slichter [25]. Further, the strength of indirect spin–spin couplings  $\mathcal{H}_{zz}$  noted above can be measured by means of spin-echo decay if the entire nuclear spin transition observed can be inverted by the spin echo refocussing pulse ( $\theta_2 \simeq \pi$ ). Measurements of this type have been carried out on a number of systems, yielding a quantitative measure of  $\chi'(\mathbf{q}, 0)$   $\mathbf{q} = (\pi, \pi)$ . This has become an important source of input data for the dynamical susceptibility.

Another major data source for  $\chi''(\mathbf{q}, \omega)$  is INS. The compound LSCO: $x$  with  $x \simeq 0.15$  became an important test case for  $\chi''(\mathbf{q}, \omega)$ . This system bears the distinction of having been measured with INS *in absolute units* over most of the first Brillouin zone (all known structure), over energies ranging from 1–200 meV, and at temperatures ranging from below  $T_c$  to nearly 300 K [44]. The dynamical susceptibility determined in this way was found to be highly incommensurate. These data were used to calculate  $T_1$  for  $^{63,65}\text{Cu}$  and for  $^{17}\text{O}$ , with interestingly mixed results. The NMR data behave as though the discommensurations were either much smaller or simply not there at all.

The final section of Chap. 6 offers a brief review of the behavior of  $T_1$  and  $T_{2g}$  in the normal state region above and principally on the left side of the superconducting dome in Fig. 1.1. Sokol, Barzykin, and Pines have proposed

a crossover in the value of the dynamical exponent from  $z = 1$  (quantum critical phase) to  $z = 2$  (non-scaling region) [45, 46]. The line dividing these two behaviors is suggested to take place where the correlation length  $\xi(T) = 2a$  ( $a$  = lattice constant). This idea has been tested up to 700 K on the cuprate Y248 by Curro et al [47]. A clear transition from  $z = 1$  to 2 was found at  $T = 500$  K, giving support to this scaling theory.

## References

1. J.G. Bednorz, K.A. Mueller, Z. Phys. **B64**, 189 (1986) 1
2. N.F. Mott, Proc. Phys. Soc. London Sect. A**62**, 416 (1949) 1
3. F.C. Zhang, T.M. Rice, Phys. Rev. **B37**, 3759 (1988) 2
4. J.M. Harris, Z.-X. Shen, et al., Phys. Rev. **B54**, R15665 (1996) 2
5. A.G. Loeser et al., Science **273**, 325 (1996) 2
6. H. Ding et al., Nature (London) **382**, 51 (1996) 2
7. J. Friedel, Physica C**153–155**, 1610 (1988) 2, 8
8. R.M. Hazen, in *Physical Properties of High Temperature Superconductors*, Vol. II, ed. by D.M. Ginsburg (World Scientific, Singapore, 1990), p. 121 2
9. T. Tanamoto, H. Kohno, H. Fukuyama, J. Phys. Soc. Japan **62**, 717 (1993) 3
10. T. Graf, G. Triscone, J. Muller, J. Less-Common Met. **159**, 349 (1990) 3
11. M. Horvatić, T. Auler, C. Berthier, Y. Berthier, et al., Phys. Rev. **B47**, 3461 (1993) 3
12. D.M. Ginsberg (ed.), *Physical Properties of High Temperature Superconductors I* (World Scientific, Singapore, 1989) and *Physical Properties of High Temperature Superconductors II* (World Scientific, Singapore, 1990) 4
13. J.T. Markert, T.W. Noh, S.E. Russek, R.M. Cotts, Sol. St. Comm. **63**, 847 (1987) 4
14. D. Brinkmann, L. Pauli, J. Roos, H. Zimmermann, Phys. Lett. A**124**, 112 (1987) 4
15. W.W. Warren, Jr., R.E. Walstedt, et al., Phys. Rev. Lett. **59**, 1860 (1987) 4
16. H. Lütgemeier, M.W. Pieper, Sol. St. Comm. **64**, 267 (1987) 4
17. I. Furo, A. Jánossy, L. Mihály, et al., Phys. Rev. **B36**, 5690 (1987) 4
18. M. Bankay, M. Mali, J. Roos, D. Brinkmann, Phys. Rev. **B50**, 6416 (1994) 4
19. W.D. Knight, Phys. Rev. **76**, 1259 (1949); C.H. Townes, C. Herring, W.D. Knight, Phys. Rev. **77**, 852 (1950) 5
20. F. Mila, T.M. Rice, Physica C**157**, 561 (1989) 5, 7
21. B.S. Shastry, Phys. Rev. Lett. **63**, 1288 (1989) 5
22. T. Moriya, J. Phys. Soc. Japan **18**, 516 (1963) 5, 6, 8
23. V. Jaccarino, in *Physics of Solids*, International School of Physics “Enrico Fermi”, Course XVIII (Academic Press, New York, 1966) 5
24. H. Monien, D. Pines, Phys. Rev. **B41**, 6297 (1990) 5, 6, 7
25. N. Bulut, D.J. Scalapino, Phys. Rev. **B45**, 2371 (1992) 5, 9
26. C.H. Pennington, D.J. Durand, C.P. Slichter, Phys. Rev. **B39**, 274 (1989) 6
27. C.H. Pennington, C.P. Slichter, Phys. Rev. Lett. **66**, 381 (1991) 6
28. A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1983) 6
29. C.P. Slichter, *Principles of Magnetic Resonance*, 3rd edn. (Springer-Verlag, New York, 1992) 6

30. J. Winter, *Magnetic Resonance in Metals* (Clarendon Press, Oxford, 1971) 6
31. A. Narath, *Hyperfine Interactions*, ed. by A.J. Freeman and R.B. Frankel (Academic Press, New York, 1967), p. 287 6
32. D.E. MacLaughlin, "Magnetic Resonance in the Superconducting State", in *Solid State Physics*, Vol. 31, ed. by H. Ehrenreich, F. Seitz, D. Turnbull (Academic Press, New York, 1976), p. 1 6
33. C.H. Pennington, C.P. Slichter, In *Physical Properties of High Temperature Superconductors*, Vol. II, ed. by D.M. Ginsberg (World Scientific, Singapore, 1990), p. 269 6
34. R.E. Walstedt, W.W. Warren, Jr., *Science* **248**, 1082 (1990) 6
35. C.P. Slichter, in *Strongly Correlated Electron Systems*, ed. by K.S. Bedell et al., (Addison – Wesley, Reading, MA, 1993), p. 427 6
36. D. Brinkmann, M. Mali, in *NMR Basic Principles and Progress*, Vol. 31 (Springer Verlag, Berlin, 1994), p. 171 6
37. C. Berthier, M.H. Julien, M. Horvatić, Y. Berthier, *J. Phys. I France* **6**, 2205 (1996) 6
38. C.P. Slichter, in *Handbook of High Temperature Superconductivity*, ed J.R. Schriber, J.S. Brooks (Springer Science+Business Media, New York, 2007), p. 215 6
39. C.M. Varma: *Phys. Rev. Lett.* **77**, 3431 (1996) 7, 8
40. P.W. Anderson, *Science* **235**, 1196 (1987) 7
41. D.C. Johnston, *Phys. Rev. Lett.* **62**, 957 (1989) 8
42. G.V.M. Williams, et al., *Phys. Rev. Lett.* **80**, 377 (1998) 8
43. A. Uldry, P.F. Meier, *Phys. Rev. B* **72**, 094508 (2005) 9
44. G. Aeppli, T.E. Mason, et al., *Science* **278**, 1432 (1997) 9
45. A. Sokol, D. Pines, *Phys. Rev. Lett.* **71**, 2813 (1993) 10
46. V. Barzykin, D. Pines, *Phys. Rev. B* **52**, 13585 (1995) 10
47. N. Curro, T. Imai, C.P. Slichter, B. Dabrowski, *Phys. Rev. B* **56**, 877 (1997) 10

*This page intentionally blank*

---

# Introduction to NMR Studies of Metals, Metallic Compounds, and Superconductors

The field of high- $T_c$  NMR developed in a context of many years of NMR studies of conventional superconductors as well as of d-band transition metals, alloys, and intermetallic compounds. It is therefore appropriate to begin this volume with a brief review not only of the NMR probe, itself, but of the general physical phenomena probed by NMR in transition metal systems, in both the normal and superconducting states. The published literature on this subject matter is, of course, vast, and the references cited here will necessarily be rather limited. We begin by citing the standard works on nuclear magnetism by Abragam [1] and Slichter [2], where almost all basic NMR phenomena are derived and discussed. These sources also present an extensive guide to the early literature, which the interested reader will find highly informative. For NMR of metallic systems, there are thorough reviews by Narath [3] and Winter [4] and for early NMR studies on superconductivity, there is a detailed and informative review by MacLaughlin [5]. We shall also have recourse to the treatments of superconductivity by Tinkham [6] and Schrieffer [7]. Relevant reviews of high- $T_c$  NMR studies will be cited at the beginning of Chap. 3.

## 2.1 Basic NMR Phenomenology

We begin with a brief review of current NMR technique and its capabilities. The basic data one usually hopes to acquire with resonance methods consist of the spectral shape and features, the frequency shift tensor  $\mathbf{K}_{\alpha\beta}$ , and the relaxation times  $T_1$  and  $T_2$ . The acquisition and interpretation of these elements of data will be the preoccupation of most of this volume. Here we wish simply to introduce them, and in this Sect. 2.1 the basic measurement and interpretation of these parameters will be reviewed. Some additional discussion of NMR phenomenology is given in the Appendices.

### 2.1.1 The Basic Hamiltonian for NMR Spectra

The basic nuclear spin Hamiltonian for spectra is given by (2.1.1), including both the Zeeman term representing the effect of an applied field  $\mathbf{H}$  and a quadrupolar term representing the interaction of the nuclear quadrupole moment with the electrical field gradient (EFG) tensor  $V_{uv} = \frac{\partial^2 V}{\partial u \partial v}$  at the nuclear site in question (see [1], Ch. VI).

$$\mathcal{H}_{spec} = -\gamma \hbar \mathbf{I} \cdot (\hat{\mathbf{1}} + \hat{\mathbf{K}}) \cdot \mathbf{H} + \frac{e^2 q Q}{4I(2I-1)} [3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2)], \quad (2.1.1)$$

where  $\hat{\mathbf{K}}$  is the NMR shift tensor and  $\hat{\mathbf{1}}$  is the unit tensor. In this equation we use conventional notation, where  $q = |\frac{\partial^2 V}{\partial Z^2}| = V_{ZZ}$  is the principal component of the EFG tensor, and the EFG asymmetry parameter is defined as  $\eta = (V_{XX} - V_{YY})/V_{ZZ}$ . The  $(X, Y, Z)$  are the principal axes of the tensor, where we define  $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$  and note that Laplace's equation gives  $V_{XX} + V_{YY} + V_{ZZ} = 0$ . It follows that  $0 \leq \eta \leq 1$ . If we permit the parameters  $\hat{\mathbf{K}}$ ,  $q$ , and  $\eta$  to be distributed, then  $\mathcal{H}_{spec}$  will generate the vast majority of NMR spectra found in practice.

Although (2.1.1) is frequently quoted, it has the disadvantage that it assumes that the quantization axis is along the principal axis of the EFG tensor. Since one often works with the field along *some* principal axis of the EFG, it is useful to generalize (2.1.1) for an arbitrarily chosen principal axis. In principal axis coordinates, the quadrupolar Hamiltonian becomes [1]

$$\mathcal{H}_Q = \frac{eQ}{2I(I+1)} \sum_{\alpha} V_{\alpha\alpha} I_{\alpha}^2. \quad (2.1.2)$$

In terms of the  $V_{\alpha\alpha}$ , (2.1.1) becomes in traceless form [2]

$$\begin{aligned} \mathcal{H}_{spec} = & -\gamma \hbar \mathbf{I} \cdot (\hat{\mathbf{1}} + \hat{\mathbf{K}}) \cdot \mathbf{H} + \frac{eQ}{4I(2I-1)} [V_{\alpha\alpha}(3I_{\alpha}^2 - I(I+1)) \\ & + \frac{1}{2}(V_{\beta\beta} - V_{\gamma\gamma})(I_+^2 + I_-^2)], \end{aligned} \quad (2.1.3)$$

where  $\alpha$  is the quantization axis and  $(\alpha, \beta, \gamma)$  are an arbitrary permutation of  $(X, Y, Z)$ . In this form it is clear that first-order splittings will be proportional to  $|V_{\alpha\alpha}|$ , and the second-order splittings will be proportional to  $(V_{\beta\beta} - V_{\gamma\gamma})^2$ .

While (2.1.1) and (2.1.3) are useful for generating spectra, it should be noted that a number of other terms are necessary for a complete description of NMR phenomena. Some of the omissions are (a) terms to represent fixed internal hyperfine (HF) fields which may occur in ordered magnetic systems, (b) spin and orbital fluctuation terms which drive  $T_1$  processes, (c) dipolar and indirect spin-spin coupling terms which generate  $T_2$  processes, and (d) radiofrequency (*rf*) excitation terms. Such terms will be invoked when the need arises.

We make a number of general remarks about the use of (2.1.1) and (2.1.3) to generate and analyze spectra.

- Experiments are usually carried out in one of two limiting cases, namely,  $H = 0$ , so that quadrupolar energies alone determine the spectrum (NQR), and secondly, the *high field limit*  $\gamma H \gg \frac{e^2 q Q}{4\hbar I(2I-1)}$ , wherein the quadrupolar terms may be treated with perturbation theory.
- For  $I = \frac{1}{2}$  the nuclear quadrupole moment  $Q$  vanishes identically, according to the Wigner–Eckart theorem (e.g. see [2], Ch.10).
- For nuclear spin sites with cubic symmetry, one has  $V_{XX} = V_{YY} = V_{ZZ} = 0$ , greatly simplifying the spectrum as with  $I = \frac{1}{2}$ . For quadrupolar nuclei, the effects of stray EFG's in nominally cubic structures may still play a role in the spectrum, however. Crystalline disorder caused by impurities, dislocations, etc., often cause a distribution of stray EFG's to occur at the nuclei of interest. Thus, one often finds *cubic* NMR lines with *complete first-order broadening*, so that only the  $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$  transition is easily resolved. Such cases will be discussed as they arise.
- In the almost universally encountered high-temperature limit defined by  $\hbar\gamma H \ll k_B T$ , Boltzmann factors are always small compared with unity. The sign of  $qQ$  in (2.1.1) is immaterial to the spectra and is, in fact, indeterminate. For convenience, we shall always take  $qQ$  to be positive. Note also that the term “ $-I(I+1)$ ” in (2.1.1) has been inserted only to render the quadrupole tensor traceless. It plays no role in the spectral transition frequencies and may be omitted or replaced by some other quantity for calculational convenience.
- In the most frequently occurring cases of non-cubic site symmetry, i.e. tetragonal or trigonal, the EFG symmetry is termed “axial”, giving  $V_{XX} = V_{YY}$ . Thus,  $\eta = 0$  and the quadrupolar Hamiltonian is greatly simplified. We shall focus primarily on this case and comment on how the results are affected if  $\eta > 0$ .
- In the high-field limit with  $\eta = 0$ , we comment briefly on how the EFG term affects the spectrum. If we let the angle between  $\mathbf{H}$  and the EFG principal axis  $Z$  be  $\theta$ , then the simplest case is when  $\theta = 0$ . The eigen-energies then have the exact form  $E_m = -\hbar\gamma H(1 + K)m + \hbar\nu_Q m^2/2$ , where  $\nu_Q = \frac{3e^2 q Q}{2\hbar I(2I-1)}$ ,  $m$  is the  $\langle I_z \rangle$  quantum number, and we have assumed a scalar shift  $K$ . In such a case, the energy levels are shifted as shown in Fig. 2.1. In the spectrum shown, the  $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$  transition is not affected by the  $\nu_Q$  term, and the  $(\pm m \leftrightarrow \pm(m+1))$  transitions are displaced by  $\pm\nu_Q$ ,  $\pm 2\nu_Q, \dots$ , for  $m = \frac{1}{2}, \frac{3}{2}, \dots$ , respectively, as shown in the figure. The lines displaced by  $\pm n\nu_Q$  are known as *first-order satellites*.
- For  $\theta \neq 0$  the eigenfrequencies can often be estimated satisfactorily with second-order perturbation theory (see [1], Ch. VI). The first-order resonance frequencies become

$$\nu_L + \nu_{\pm n}^{(1)} = \nu_L \pm n\nu_Q(3\cos^2\theta - 1)/2, \quad (2.1.4)$$

$n = 1, 2, \dots$ . Here,  $n = 1$  corresponds to the  $(\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2})$  transitions and  $n > 1$  corresponds to transitions with progressively higher values of  $m$ .

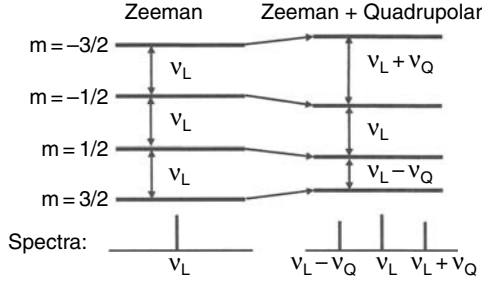


**Fig. 2.1.** On the left, the nuclear Zeeman term gives uniformly spaced energy levels and a single NMR line. On the right, first-order quadrupole splittings produce “first-order satellites” from the  $(\pm 1/2 \leftrightarrow \pm 3/2)$  transitions. The  $(-1/2 \leftrightarrow 1/2)$  transition is not affected to first order

In the case of powder samples with a uniform distribution of  $\theta$  over the unit sphere, the first-order quadrupole shift stated above gives rise to an intensity distribution over frequencies ranging from  $\nu_L - n\nu_Q/2$  to  $\nu_L + n\nu_Q$  if the  $\theta = 0$  satellite displacement is  $n\nu_Q$ . The normalized distribution function is

$$\rho_q(\nu) = [6n\nu_Q(\nu - \nu_L + n\nu_Q/2)]^{-\frac{1}{2}}, \quad (2.1.5)$$

so that the  $\theta = 0$  line at frequency  $n\nu_Q$  becomes a powder pattern with a square-root singularity at  $\nu = \nu_L - n\nu_Q/2$ . Here, the Larmor frequency  $\nu_L = \gamma H(1 + K)$ . We note that  $m$  is no longer strictly a good quantum number, so there are second-order frequency shifts as well. Interestingly, the second-order frequency shifts of the satellites at  $\pm n\nu_Q(3\cos^2\theta - 1)$  are equal, so that the second-order correction to their pairwise separation  $2n\nu_Q(3\cos^2\theta - 1)$  vanishes. If  $\eta > 0$ , however, the singularities all disappear and the peak at that position becomes progressively broader as  $\eta$  increases.

- For the often-used  $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$  transition, the frequency to second order is given by

$$\nu_{\pm\frac{1}{2}}^{(2)} = \nu_L - \frac{\nu_Q^2}{16\nu_L} \left[ I(I+1) - \frac{3}{4} \right] \sin^2\theta (9\cos^2\theta - 1). \quad (2.1.6)$$

In the case of a random powder sample, (2.1.4) and (2.1.6) give rise to characteristic *powder patterns* which are easy to recognize. Such a pattern is shown in Fig. 2.2, where a small amount of Gaussian broadening has been added. In cases where  $\eta > 0$ , these powder patterns are altered significantly. Also, if there is shift anisotropy  $K(\theta)$  with a range comparable to the second-order quadrupole shift of the  $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$  transition, its powder-pattern shape will also be altered significantly, whereas the first-order peaks will all reflect the shift value  $K(\pi/2)$ . Further discussion of these effects is given below.

- When  $H = 0$  we have the case of *nuclear quadrupole resonance* (NQR). The nuclear spin energies are determined entirely by  $Q$ ,  $I$ , and the local

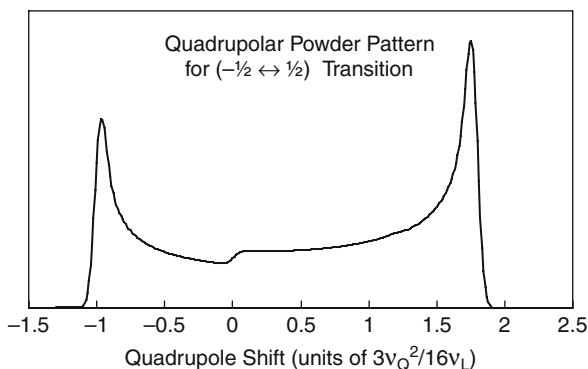


**Fig. 2.2.** Quadrupolar powder pattern for the  $(-1/2 \leftrightarrow 1/2)$  transition based on the second-order quadrupolar energy given in 2.1.6 (axial case). Minimal Gaussian broadening has been applied. The coefficient given is for  $I = 3/2$ . For arbitrary half-integral  $I$  the coefficient becomes  $(4I(I+1) - 3)\nu_Q^2/64\nu_L$

EFGs. If  $\nu_Q$  (see item 6 above) is large enough, i.e. in the MHz range, then NQR spectroscopy is feasible. Considering the case of  $\eta = 0$ , (2.1.1) then shows that  $E_{|m|+1} - E_{|m|} = (2|m| + 1)\nu_Q$ . Thus, there is a series of  $I - \frac{1}{2}$  NQR lines at frequencies  $\nu_Q, 2\nu_Q, \dots$ . The  $m$ -levels are doubly degenerate, since  $E_m$  is independent of the sign of  $m$ . The two parallel transitions produce identical signals under the usual excitation conditions<sup>1</sup>. If  $\eta > 0$ , the levels are still doubly degenerate, but the transition frequencies are now a function of  $\eta$ . If there are two or more NQR frequencies, their ratio can be used to determine  $\eta$ .

### 2.1.2 Observation of NMR/NQR Signals

In the early days of solid-state NMR, it was customary to employ continuous wave methods to observe NMR signals. Techniques such as the marginal oscillator and the popular crossed-coil *rf* bridge spectrometer manufactured by Varian Associates were used to obtain a wealth of useful NMR data. Compared with pulsed NMR this method has, however, a number of inherent drawbacks. It is not useful for severely broadened lines, it cannot distinguish between static and dynamic line broadening, so it cannot measure  $T_2$ , nor a

<sup>1</sup> It is possible to separately excite, e.g. the  $(1/2, 3/2)$  and the  $(-1/2, -3/2)$  transitions, using circularly polarized *rf* pulses (M.J. Weber and E.L. Hahn, Phys. Rev. **120**, 365 (1960)). However, for most measurements, there is no advantage in doing so.

short value of  $T_1$ , to name just a few. Thus, it gradually gave way to pulse methods for solid-state NMR studies<sup>2</sup>.

### The Spin Echo

The *spin echo*[9] is used almost universally for measurement and observation of NMR/NQR signals in solids. Typically, short, medium-power *rf* pulses applied at the frequency of a  $|\Delta m| = 1$  transition of the Hamiltonian  $\mathcal{H}_{spec}$  are followed by a spin-echo signal as shown in Fig. 2.3. The *rf* fields are applied transverse to the axis of spin quantization. The first pulse produces a precessing, transverse nuclear magnetization proportional to the instantaneous spin polarization at the time it is applied. The precessing moment following the first pulse often decays in a time of the order of the pulse width, as shown in the figure, and is usually unobservable because of the “dead time” of the receiver. Such a decay time is known as  $T_2^*$ <sup>3</sup>. A second *rf refocussing* pulse at time  $\tau$  causes the precessing moment to reappear briefly at time  $2\tau$  as shown. Using digital electronic methods, such spin echo signals are recorded, noise averaged, and stored for manipulation and analysis. A basic calculation of the spin echo response is presented and discussed in Appendix A.1, including a simple treatment of spin echo decay processes.

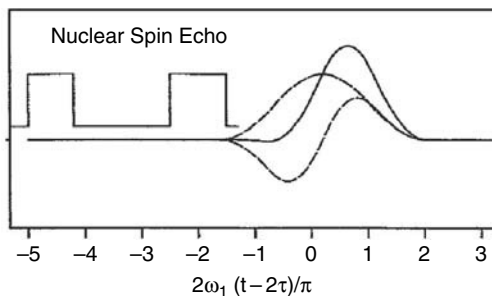


**Fig. 2.3.** A simulated spin echo signal is shown (*solid curve*), corresponding to the  $(0.8\pi/2, \pi/2)$  pulse pair (shown) applied to a broad, inhomogeneous distribution of NMR frequencies. The echo is the sum of two contributions which are symmetric and antisymmetric, respectively, (*dashed lines*) with respect to the center point of the echo. The latter point is at time  $2\tau + t_{w2} - t_{w1}$  from the leading edge of the first pulse, where  $\tau$  is the time interval between the leading edges of the pulses and  $t_{w1}, t_{w2}$  are the respective pulse widths [8]

<sup>2</sup> There are certain advantages to *cw* technique, however. If  $T_2$  is shorter than a few  $\mu s$ , spin echoes may become unobservable, whereupon *cw* methods become the only way to observe an NMR signal.

<sup>3</sup>  $T_2^*$  is often a reflection of the inhomogeneous linewidth  $\Delta H$ , in which case  $T_2^* \sim 1/\gamma\Delta H$ . If such broadening is severe, then  $T_2^*$  will be determined by the length and shape of the exciting *rf* pulse. In the latter case it is usually unobservable because of amplifier dead time.

We touch here briefly on an important point regarding spin-echo spectroscopy. This is the frequency resolution of this technique, which is discussed in detail in Appendix A.1. Since the NMR signals are excited using pulse fields  $H_1$  of typically 100 Gauss amplitude, one might suppose that these large fields would limit the available frequency resolution to  $\sim \gamma H_1$ . However, this is not the case. It is straightforward to demonstrate that the total area under the spin echo waveform is proportional to the line intensity at the frequency of excitation to within a very narrow bandwidth. The resolution obtained in this way is formally independent of the magnitude of the excitation field  $H_1$ . See Appendix A.1 for details.

The question of observability of spin-echo signals is an important one for the NMR spectroscopist. We note here that solid-state NMR signals are typically of the order of microvolts, with expected raw signal-to-noise ratios which are typically of the order of unity or less. Thus, one cannot overemphasize the importance of digital signal averaging methods to the success of modern pulsed NMR technique. The great majority of solid-state NMR studies reported nowadays have used digital signal averaging to improve the signal-to-noise ratio. It is also possible to estimate the available NMR signal strength given reasonable estimates of the experimental parameters. A detailed discussion of such matters is beyond the purview of the present volume.

### 2.1.3 Definition and Interpretation of NMR parameters: $T_2$

The relaxation time  $T_2$  represents a fairly complex realm of phenomenology in NMR. Put most simply,  $T_2$  is the transverse decay time for nuclear magnetization. But there are several fundamentally different mechanisms for  $T_2$  processes as well as two major categories of  $T_2$  effects, namely (i)  $T_2$  for the free-induction signal excited by a single pulse and (ii)  $T_2$  for spin echoes. For both of these, homogeneous broadening refers to the effect of local spin-spin interactions such as dipolar [1], pseudo-dipolar [10], and RKKY [11]. Often, however, NMR lines are statically broadened by disorder and other spurious effects, such that free induction signals are not observable.

In contrast, one can nearly always observe the spin echo, which typically does not “see” inhomogeneous broadening. The spin echo is a signal observed when two *rf* pulses are applied at a time interval  $\tau$ . At time  $2\tau$  from the first pulse a signal appears which has typically a much longer decay time than the free induction. For the spin echo,  $T_2$  is the decay time constant of the echo amplitude  $\mathcal{E}(2\tau)$  as the pulse separation  $\tau$  is increased. A simulated spin echo is shown in Fig. 2.3.

A basic discussion of spin echo formation and decay mechanisms is given in Appendix A.1. In high- $T_c$  materials, indirect spin-spin couplings are particularly important. A new and useful formulation of indirect spin-spin couplings in terms of dynamical susceptibilities has been given by Pennington and Slichter[12]. This calculation is discussed in detail in Chap. 6. The

measurement of the latter indirect spin-spin couplings via spin-echo decay is analyzed in some detail in Appendix A.1.

It is interesting that one can write down a formally exact solution to the spin echo decay problem. The following expression represents the variation of the spin echo amplitude at time  $2\tau$  for *rf* pulses applied at 0 and  $\tau$ :

$$\mathcal{E}(2\tau) = \text{Tr} \left[ I_x e^{i\mathcal{H}_i^* \tau} e^{i\theta_2 I_y} e^{i\mathcal{H}_i^* \tau} I_x e^{-i\mathcal{H}_i^* \tau} e^{-i\theta_2 I_y} e^{-i\mathcal{H}_i^* \tau} \right] / \text{Tr}(I_x^2), \quad (2.1.7)$$

where the spin system  $\mathbf{I} = \sum_i \mathbf{I}_i$  is being excited with pulses along the  $y$  axis which are assumed for simplicity to be uniform over the entire resonance line. Thus, the initial magnetization lies along the  $x$  axis and the *refocussing pulse* is given a pulse angle  $\theta_2$ . The interaction Hamiltonian  $\mathcal{H}_i$  represents all pairwise interaction terms between the spins  $\mathbf{I}_i$  as well as with and among any other nuclear species in the system considered. All such terms have been transformed into a reference frame rotating at the frequency of the applied *rf* pulses,  $\mathcal{H}_i^* = \exp(i\omega I_z \tau) \mathcal{H}_i \exp(-i\omega I_z \tau)$ , and any *non-secular* time-dependent terms which result are dropped. Included in  $\mathcal{H}_i$  is a truncated Zeeman term which might be written  $\mathcal{H}_Z = -\sum_i [\gamma H(1 + K_i) - \omega] I_{iz}$ . If locally non-uniform, the latter term would have a very important effect on  $\mathcal{E}(2\tau)$  in that it inhibits flip-flop fluctuation processes among the  $\mathbf{I}_i$ . It is slightly ironic that an inhomogeneous term such as this is frequently necessary for the observation of a spin echo.

An expression such as (2.1.7) is not often useful for direct evaluation. However, it can be used to argue the basic features of many special cases of echo decay. We give here a few simple examples. It is the essence of spin echo formation that a term such as  $\mathcal{H}_Z^*$  mentioned above has no direct effect on echo amplitude. Any other term in  $\mathcal{H}_i^*$  which is static and is unaffected by the  $\theta_2$  pulse will also have no direct effect on echo amplitude. Many spin-spin coupling terms cause fluctuations among the spins  $\mathbf{I}_i$  or among spins which are coupled to the  $\mathbf{I}_i$ . These will cause the echo to decay, and will present many highly complicated sub-cases. A simple example of this behavior is analyzed in Appendix A.1.

A case of interest which arises in cuprate NMR is the simple case where all spin flip-flop interactions are blocked by local inhomogeneities. There would be no echo decay process except for the fact that the spins  $\mathbf{I}_i$  are inverted (with a substantial probability) by the  $\theta_2$  pulse. The typically Gaussian echo decay  $\mathcal{E}(2\tau) \simeq \exp[-(2\tau)^2/2T_{2g}^2]$  found in this case can then be used to measure the indirect spin-spin coupling, as mentioned above.

The other important contributor to spin-echo decay is the spin-lattice interaction, which modifies the expression (2.1.7) with a multiplicative factor  $\exp(-2\tau/T_{1E})$ . The decay constant  $T_{1E}$  is a parameter of some complexity and is therefore discussed in detail in Appendix A.2.  $T_{1E}$  is only equal to  $T_1$  in the case where  $T_1$  is isotropic and  $I = \frac{1}{2}$  for the nuclei observed, or for  $I > \frac{1}{2}$  in the highly unusual case that all  $|\Delta m| = 1$  transitions are degenerate and are contributing to the echo signal. For a more typical case of half-integral  $I > \frac{1}{2}$ , where the  $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$  transition is being observed, then  $1/T_{1E} = (I + \frac{1}{2})^2/T_1$

(isotropic  $T_1$ ) [13]. It is usually important to account for the effect of  $T_1$  in spin echo decay in cuprate NMR studies. Expressions derived for this purpose are given in Appendix A.2.

#### 2.1.4 Definition and Interpretation of NMR parameters: The shift tensor $\mathbf{K}_{\alpha\beta}$

NMR frequency shifts are useful for characterizing a resonance line as well as analyzing different components in the magnetic susceptibility of a metallic compound. NMR shifts are useful probes, because they always reflect one or more components of magnetic polarization in the system, such as spin or Van Vleck paramagnetism. There can, of course, be magnetic polarization without a palpable NMR frequency shift, but there is no magnetic NMR shift without a source of polarization, i.e. susceptibility, to drive it. There are complications, of course, when there are fixed sources of internal magnetic polarization, such as in the *mixed state* of a type-II superconductor. Such cases are considered in Sect. 2.3. In general, we have omitted consideration of cases which involve magnetic ordering. Shifts, then, are defined to be linear in the applied magnetic field  $H$ . Analysis of shifts can be quite complex with random powder samples when the shift is anisotropic, and even more so if they are combined with inherently anisotropic quadrupolar splittings. Such cases occur frequently, and it is important to know how to analyze and characterize them.

##### *Defining the NMR Shift*

In general terms, the NMR shift is a measure of how the magnetic induction  $B$  differs at a nuclear site in a metallic specimen from its value in free space when the sample is removed. In practice, shifts are referred to bare values of the nuclear gyromagnetic ratio  $\gamma$ , where  $\gamma$  is the ratio

$$\gamma = \frac{\mu}{\hbar I} \quad (2.1.8)$$

of the nuclear magnetic moment  $\mu$  to its angular momentum  $\hbar I$ . “Bare” values of  $\gamma$  are measured in compounds or other environments which are as magnetically neutral as possible. For nuclei of elements which are highly active magnetically, defining  $\gamma$  can be difficult and somewhat arbitrary. On the other hand, even compounds lacking a form of paramagnetism almost always have so-called chemical shifts, which are typically of the order of tens or hundreds of *ppm*. Such shifts are orbital in origin and have been discussed in detail in [2], Chap. 4.

NMR shifts in metals are typically two orders of magnitude larger than chemical shifts, so that the latter are often ignored. In high- $T_c$  compounds, however, we shall see that, e.g. for  $^{17}\text{O}$  and  $^{89}\text{Y}$ , chemical shifts will play a role in the discussion. In d-band metals, however, the NMR shift is dominated by

the spin-paramagnetic and Van Vleck terms mentioned earlier. In Sect. 1.2 we discuss a detailed formulation of these effects as well as methods for analyzing NMR shift data. Here we focus on defining and measuring the shift tensor.

Given a suitable reference  $\gamma$ , then, the NMR shift  $K$  is defined with respect to a change in the resonant frequency  $\nu_{res} = \gamma H(1 + K)$ , or

$$K = \frac{\nu_{res}}{\gamma H} - 1. \quad (2.1.9)$$

Since a lot of NMR spectroscopy is done by scanning the magnetic field, it is important to note that the fractional shift in the resonant field, which is  $-K/(1 + K)$ , not only has the opposite sign, but a palpably different magnitude than  $K$  if the shift is large. The unmistakable hallmark of an NMR frequency shift or of a spectrum of shifts for a powder is that they scale precisely with the applied field. If this is not the case, then one is dealing with quadrupole effects or other complications.

### *The NMR Shift: Tensor or Scalar?*

In practice, most shifts are characterized as scalar parameters. However, formally the NMR frequency shift tensor  $\mathbf{K}_{\alpha\beta}$  is defined to be the  $\alpha$  component of the internal field at the nuclear spin divided by the  $\beta$  component of the applied field ([1], Ch. VI). In general, then, the induced, internal shift field is not parallel to the external field. This can be a complication in the interpretation of large shift effects. However, in cases where the shift anisotropy is 1% or less, it is a good approximation to replace the shift tensor with a scalar shift given by  $K(\theta, \phi) = K_X \sin^2\theta \cos^2\phi + K_Y \sin^2\theta \sin^2\phi + K_Z \cos^2\theta$ , where the  $K_{X,Y,Z}$  are the principal values of the shift tensor and  $(\theta, \phi)$  give the orientation of the field  $\mathbf{H}$  in the principal axis coordinates. Another approach, which involves no approximation, is to confine shift measurements on oriented powder or single crystal samples to field orientations along the principal axes. The (X,Y,Z) axes will generally coincide with crystalline axes of symmetry.

In metals with cubic crystal structure or with single crystals, then, shift measurements are usually straightforward. If microscopic disorder is reasonably low, then line-broadening effects will be 0.01% or less and a 1% shift can be reliably measured to good accuracy. If the nuclear site is non-cubic, however, there is the possibility of an anisotropic shift as well as the virtual certainty of quadrupolar shifts and broadening for  $I > \frac{1}{2}$ . For such cases it is very helpful to have either single crystals or oriented powders for non-cubic systems<sup>4</sup>. Otherwise, data will have to be obtained by analyzing powder patterns, i.e. broadened spectra which result from a sample made up of randomly

---

<sup>4</sup> Oriented powder samples are samples with anisotropic susceptibilities which have been induced to form partially-to-fully ordered dominant magnetic axes in a magnetic field. This technique was of great importance for NMR and susceptibility studies of high- $T_c$  materials. See Sect. 3.1 for a more extensive discussion.

oriented particles. The functional form of the axial shift powder pattern is the same as for the first-order quadrupolar satellite pattern (2.1.5), namely,

$$\rho_K(K) = [6K_{ax}(K - K_{iso} + K_{ax}/2)]^{-\frac{1}{2}}, \quad (2.1.10)$$

where  $K$  is the shift variable, which is distributed over the range  $K_{iso} - K_{ax}/2 \leq K \leq K_{iso} + K_{ax}$ . For a crystal with applied field at an angle  $\theta$  with respect to the axis of symmetry, the shift may be written  $K_{iso} + K_{ax}(3\cos^2\theta - 1)/2$ , where  $K_{iso}$  and  $K_{ax}$  are the isotropic and axial components of shift, respectively. If the three principal shift values are all different, then the symmetry is lower than axial and the singularity disappears. The distribution will have *edges* at the maximum and minimum shift values, with a peak at the intermediate principal shift value. It is possible, although it may be somewhat laborious, to extract anisotropic shift as well as quadrupole frequency parameters from powder patterns. For the  $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$  transition the change of these two effects with field are opposite, so that field dependence can be employed to determine their separate values. An example of this is shown in Fig. 2.4 axial shift powder patterns.

### 2.1.5 Definition and Interpretation of NMR parameters: $T_1$

$T_1$  is the time constant which describes the exchange of nuclear spin energy with the surrounding lattice, hence it is known as the *spin-lattice relaxation* time. Referring to the energy levels in Fig. 2.1,  $T_1$  determines the rates at which nuclei make transitions between these levels. Magnetic  $T_1$  processes are generated by fluctuating HF fields. Each magnetic HF interaction<sup>5</sup> has a fluctuation spectrum with an amplitude and an autocorrelation time. The corresponding  $T_1$  process is driven by the fourier component of the latter spectrum at NMR/NQR resonance frequency. The magnetic dipole  $T_1$  processes are divided broadly into those driven by spin and orbital HF fields.

The formulation of the various relaxation processes for metallic systems including superconductors has been a major work in progress since NMR was first discovered. Below we review the interpretation of  $T_1$  effects for simple metals and Type I superconductors (Sect. 2.2) and for d-band metals and Type-II superconductors (Sect. 2.3). The interpretation of  $T_1$  processes for the cuprate superconductors will be discussed extensively in Chaps. 3–6. Particularly important is the role played by electron-electron interactions in  $T_1$  phenomena. Accordingly, we review Moriya's theory of correlated electron effects in the  $T_1$  processes of simple metals in Sect. 2.2.

Rather more rare in occurrence are quadrupolar  $T_1$  processes generated by fluctuating components of EFG. A general theory of such effects caused by the *phonon Raman scattering process* was put forward by Van Kranendonk in the early days of NMR [14]. Such processes are extraordinarily weak, however,

---

<sup>5</sup> See Sect. 2.2 for a comprehensive definition of the magnetic HF interactions.

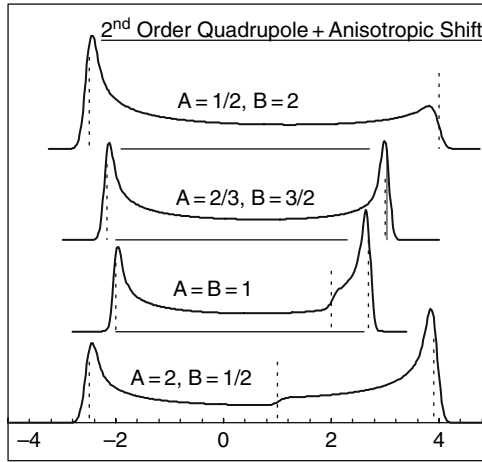


**Fig. 2.4.** Powder patterns are shown for several cases the combined effects of an anisotropic shift and second-order quadrupolar broadening. The total broadening perturbation is  $A \sin^2 \theta (9 \cos^2 \theta - 1) + B (3 \cos^2 \theta - 1)$ . In applied field  $H$ ,  $A \propto 1/H$  and  $B \propto H$ . In reduced units we let  $B = H$ , and the frequency displacement is in units of  $3\nu_Q^2/16\nu_L$  (for  $I = 3/2$ ). The spectra then show a progression of powder patterns as  $H$  is varied from  $1/2$  up to  $2$ . The dashed vertical lines show the positions of the three edges in the absence of broadening. The prominent upper singularity (see Fig. 2.2) converges with the  $\theta = 0$  edge with increasing field and disappears above  $B/A = 8/3$ . However, there is still a visible maximum for the top example, where  $B/A = 4$ . Note that these spectra are actually oriented the way they would appear in a field sweep increasing to the right, and, therefore, the anisotropic shift coefficient is *negative*. With  $B/A < 0$ , the patterns would be quite different. Studies such as are shown here allow the practitioner to extract values of  $A$  and  $B$  from experimental data

and have rarely been identified in metals. Nonetheless quadrupolar relaxation processes for the  $^{63,65}\text{Cu}$  isotopes have occasionally been claimed to exist in solids, using the isotopic ratio of  $T_1$  values as a diagnostic.<sup>6</sup> When quadrupolar  $T_1$  effects occur in metals, it is our conjecture that they are much more likely to be caused by ionic motion (e.g. diffusion) than by phonons.

### *The Magnetic Dipole Relaxation Process*

Nuclear spin transitions generated by the HF interactions in (2.2.1) are known as *magnetic dipole transitions* (as opposed to electric quadrupolar transitions). Here, we analyze the magnetic dipole  $T_1$  process in some detail. We review methods to measure it as well as certain pitfalls to be avoided in conducting

<sup>6</sup> The ratio  $^{63}\text{T}_1/^{65}\text{T}_1$  is a good diagnostic for this purpose, since it is  $(\gamma_{65}/\gamma_{63})^2 = 1.148$  for magnetic relaxation and is  $(Q_{65}/Q_{63})^2 = 0.854$  for electric quadrupolar relaxation.

such measurements. Whether measuring  $T_1$  with high-field NMR or in zero field with NQR, the nuclear spin energy levels  $E_m$  will be labeled with the  $I_z$  quantum number  $m$ . To the extent that  $m$  is a good quantum number, the transition rate between states  $m$  and  $m'$  may be written

$$|\langle m' | I_+ | m \rangle|^2 W = |\langle m | I_- | m' \rangle|^2 W = (I - m)(I + m + 1) W \delta_{m', m+1} \quad (2.1.11)$$

If  $I = \frac{1}{2}$ , then there is only a single rate  $W$  involved. For  $I > \frac{1}{2}$  there are  $I + \frac{1}{2}$  rate constants and  $2I$  relaxation eigenmodes. The formula (2.1.11) will be correct for the cases (a) when  $I = \frac{1}{2}$ , (b) for arbitrary values of  $I$  when  $\eta = 0$  and the field is applied along the principal axis of the EFG tensor, and (c) for NQR when  $\eta = 0$ . It is approximately correct for arbitrary  $\eta$  values when  $\nu_Q \ll \gamma H / 2\pi$  and for NQR when  $\eta$  is small. In other cases  $m$ -state mixing effects become important and it may be necessary to solve the spin Hamiltonian (2.1.1) numerically to obtain accurate matrix elements of  $I_{\pm}$ . In this discussion of  $T_1$  analysis, we shall assume (2.1.11) to be valid, and we shall also neglect nuclear quadrupole relaxation effects. They are, as noted above, quite rare in metallic systems.

### ***Detailed Balance in $T_1$ Processes***

$T_1$  in metals is simplified by the fact that fluctuation spectra for itinerant fermions are constant over the range of typical NMR frequencies.  $T_1$  values are therefore found to be independent of the Zeeman splitting and are the same for NMR and NQR measurements alike.<sup>7</sup> We shall assume, further, that the lattice constitutes an infinite heat reservoir at equilibrium at temperature  $T$ . To illustrate the incorporation of detailed balance into the rate equations, we analyze a two-level system with energies  $E_2 > E_1$ , defining  $\Delta E = E_2 - E_1$ . The populations of these levels are designated  $p_{1,2}$  and will be treated as continuous variables. The rates at which up and down transitions occur are defined to be  $\mathcal{W}_{21}$  (up) and  $\mathcal{W}_{12}$  (down), respectively. At thermal equilibrium the principle of detailed balance gives  $\mathcal{W}_{21} = e^{-\beta \Delta E} \mathcal{W}_{12}$  ([2], Ch.5). The rate equations for populations are then

$$\frac{dp_{1,2}}{dt} = \pm [p_2 \mathcal{W}_{12} - p_1 \mathcal{W}_{21}], \quad (2.1.12)$$

where  $p_1 + p_2 = N$  is the total number of nuclei in the ensemble. When the  $p_{1,2}$  are at equilibrium we have  $dp_{1,2}/dt = 0$ , giving  $p_2/p_1 = \mathcal{W}_{21}/\mathcal{W}_{12} = e^{-\beta \Delta E}$ . Thus, the Boltzmann distribution of spin populations follows from detailed balance.

Writing  $p_{1,2} = \pm \frac{1}{2}(p_2 - p_1) + N/2$ , the (2.1.12) may be combined to give

---

<sup>7</sup> Note, however, that NMR and NQR reflect different relaxation modes, as will be seen below. For example, if  $I = \frac{3}{2}$ , for NMR  $1/T_1 = 2W$ , whereas the single rate measured with NQR is  $6W$ , or one-third the length of the conventionally defined  $T_1$ .

$$d(p_2 - p_1)/dt = (p_2 - p_1)(\mathcal{W}_{12} + \mathcal{W}_{21}) - N(\mathcal{W}_{12} - \mathcal{W}_{21}).$$

From this relation we see that the relaxation rate of  $(p_2 - p_1)$  is  $(\mathcal{W}_{12} + \mathcal{W}_{21})$ . Since this quantity must be independent of  $\Delta E$ , we set  $(\mathcal{W}_{12} + \mathcal{W}_{21}) = 2W$ , where  $W$  is a rate constant which depends only on  $T$ . Detailed balance then leads immediately to

$$\mathcal{W}_{12} = \frac{2W}{(1 + e^{-\beta\Delta E})}; \quad \mathcal{W}_{21} = \frac{2We^{-\beta\Delta E}}{(1 + e^{-\beta\Delta E})}. \quad (2.1.13)$$

Using (2.1.13), (2.1.12) then becomes

$$\frac{dp_{1,2}}{dt} = -2W \left[ p_{1,2} - \frac{Ne^{-\beta E_{1,2}}}{\sum_i e^{-\beta E_i}} \right]. \quad (2.1.14)$$

Even though  $p_1$  and  $p_2$  appear to act independently, they are not, of course, independent. The general solution to (2.1.14) is seen to be

$$p_{1,2}(t) = (p_{1,2}(0) - p_{01,02})e^{-2Wt} + p_{01,02}, \quad (2.1.15)$$

where  $p_{01,02} = N \exp(-\beta E_{1,2}) / \sum_i \exp(-\beta E_i)$  are the equilibrium population values. This result also satisfies  $p_1(t) + p_2(t) = N$  if  $p_1(0) + p_2(0) = N$ , which must be the case.

### ***Relaxation Equations for $I > \frac{1}{2}$***

Generalization of the foregoing result to multi-level nuclear relaxation equations is straightforward. They can always be written in terms of the *difference* variables

$$d_m = p_m - p_{0m}, \quad \text{with } p_{0m} = N \exp(-\beta E_m) / \sum_m \exp(-\beta E_m), \quad (2.1.16)$$

where  $m$  is the quantum number for the energy eigenvalues. We note that the value of  $p_{0m}$  does not depend on the choice of the zero-point of energy. In general, then, one can measure  $T_1$  by creating a non-equilibrium population distribution, then observing the decay toward equilibrium of the population difference of some suitable pair of levels using spin-echo excitation. The latter pair must be chosen to have  $|\Delta m| = 1$  for magnetic excitation, and they must be chosen to reflect a non-equilibrium population difference during the equilibration process.

If the initial non-equilibrium condition is created by applying an *rf* pulse to some pair of levels, note that the recovery can often be observed using spin-echo signals from a *different* pair of levels.<sup>8</sup> This degree of experimental freedom is not often used in NMR. It could be used, for example, to avoid multiple echo effects in a  $T_1$  measurement when  $T_1$  is very short.

---

<sup>8</sup> This requires the ability to be able to apply *rf* pulses to the sample at two separate frequencies, which can be a very useful adjunct to the usual spectrometer setup.

### *Relaxation Eigenmodes for $I > \frac{1}{2}$*

For multi-level nuclear spin Hamiltonians ( $I > \frac{1}{2}$ )<sup>9</sup> there is an eigenmode structure to the relaxation equations with multiple relaxation eigenrates. We illustrate this situation with the simple example of  $I = \frac{3}{2}$ , for which there are four energy levels as shown in Fig. 2.1. The dynamical equations for the differences  $d_m$  are then

$$\frac{dd_{3/2}}{dt} = -3Wd_{3/2} + 3Wd_{1/2} \quad (2.1.17a)$$

$$\frac{dd_{1/2}}{dt} = 3Wd_{3/2} - 7Wd_{1/2} \quad (2.1.17b)$$

$$\frac{dd_{-1/2}}{dt} = 4Wd_{1/2} - 7Wd_{-1/2} + 3Wd_{-3/2} \quad (2.1.17c)$$

$$\frac{dd_{-3/2}}{dt} = 3Wd_{-1/2} - 3Wd_{-3/2} \quad (2.1.17d)$$

We seek solutions of the form  $d_m = c_m \exp(-\lambda Wt)$ . Substitution into (2.1.17) then yields the matrix equation

$$\begin{bmatrix} \lambda - 3 & 3 & 0 & 0 \\ 3 & \lambda - 7 & 4 & 0 \\ 0 & 4 & \lambda - 7 & 3 \\ 0 & 0 & 3 & \lambda - 3 \end{bmatrix} \begin{Bmatrix} c_{3/2} \\ c_{1/2} \\ c_{-1/2} \\ c_{-3/2} \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{Bmatrix}$$

This matrix is solved straightforwardly. The characteristic equation is

$$\lambda^4 - 20\lambda^3 + 108\lambda^2 - 144\lambda = 0, \quad (2.1.18)$$

for which the solutions are  $\lambda = (0, 2, 6, 12)$ . The corresponding decay rates are 0,  $2W = T_1^{-1}$ ,  $6W = 3T_1^{-1}$ , and  $12W = 6T_1^{-1}$ . Ignoring the null mode, the corresponding eigenvectors for  $T_1$ ,  $T_1/3$ , and  $T_1/6$  may be written  $\{3, 1, -1, -3\}$ ,  $\{-1, 1, 1, -1\}$ , and  $\{-1/3, 1, -1, 1/3\}$ , respectively.

The solutions to (2.1.17) may be applied to different techniques for measuring  $T_1$ . We illustrate their use in the simple case of a cubic environment where  $E_m = -\hbar\gamma_n(1 + K)Hm$ . Since  $|E_m| \ll k_B T$ , we may write (2.1.16)  $p_{0m} \approx \frac{N}{2I+1}(1 - \delta m)$ , where  $\delta = \hbar\gamma_n H(1 + K)\beta$ . Then if we apply an *rf* pulse with pulse angle  $\theta$  to the spins, the resulting initial condition is

$$p_m(0) \approx \frac{N}{2I+1}(1 - \delta \cos \theta m).$$

As a result, the initial values are  $d_m(0) \approx \frac{N}{2I+1}(1 - \cos \theta)m$ . The  $d_m(0)$  have the form  $\{3, 1, -1, -3\}$  of the “ $T_1$ ” mode, so that the solution can be written

<sup>9</sup> This discussion only applies to nuclei with odd half-integer spin quantum numbers. Many nuclei of interest answer to this description, and, in fact, there will be no nuclear spins of interest in this volume which have integer values of  $I$ .

$$d_m(t) \approx \frac{Nm\delta}{2I+1}(1 - \cos \theta) e^{-t/T_1}.$$

If  $\theta = \pi$ , then one has a perfect *inversion*, which gives the largest excursion in signal amplitude. The time variation of the spin echo signal for arbitrary  $\theta$  is then proportional to

$$p_m(t) - p_{m+1}(t) = \frac{N\delta}{2I+1}[1 - (1 - \cos \theta) e^{-t/T_1}]. \quad (2.1.19)$$

If  $p_m(0) = p_{m+1}(0)$  for all applicable  $m$ , then we have a condition known as *saturation*, which also yields a single-exponential recovery  $\propto (1 - \exp(-t/T_1))$ , regardless of the distribution of the energies  $E_m$ .

### ***Recovery Mode when only the $(-1/2 \leftrightarrow 1/2)$ Transition is Excited***

If there are quadrupolar splittings, then a single pulse applied to the  $(-1/2 \leftrightarrow 1/2)$  transition results in a  $\{d_m(0)\}$  vector with the form  $a_0\{0, 1, -1, 0\}$ . Writing the decay mode as a superposition of the foregoing eigenmodes, we have

$$\{d_m(t)\} = \frac{1}{10}a_0[\{3, 1, -1, -3\} \exp^{-t/T_1} + 9\{-1/3, 1, -1, 1/3\} \exp^{-6t/T_1}].$$

The spin echo signal for the  $(-1/2 \leftrightarrow 1/2)$  transition will therefore exhibit the well-known decay function

$$E(t) = E_0 (0.9 \exp^{-6t/T_1} + 0.1 \exp^{-t/T_1}). \quad (2.1.20)$$

Such a precise mathematical form occurs only for excitation of a single pair of levels over a time interval which is short compared with  $T_1/6$ . If relaxation begins to take place during the initial excitation phase, then the simple form of the initial condition is lost and the decay will be rather more complicated. In the foregoing example,  $d_{3/2}(t)$  would be proportional to  $(\exp -t/T_1 - \exp -6t/T_1)$ , so that it would deviate very quickly from its initial value of zero. As we noted earlier, the relaxation measurement could be conducted in this fashion, i.e. by monitoring a different transition frequency from the one used for the initial excitation.

### ***The NQR Case***

Continuing our discussion of an  $I = \frac{3}{2}$  nucleus, we consider finally the NQR case, where the  $\pm \frac{1}{2}$  levels and the  $\pm \frac{3}{2}$  levels are degenerate pairs separated by an energy difference of  $h\nu_{NQR} = h\nu_Q(1 + \eta^2/3)^{1/2}$ . A single excitation pulse at the NQR frequency then creates an initial condition given by  $\{d_m\} = a_0\{-1, 1, 1, -1\}$ . This effectively 2-level system relaxes entirely via the *symmetric mode* with a single decay rate  $3/T_1$ . One must be careful to take account of the relaxation mode effects when comparing  $T_1$  data obtained with different methods.

We make a few additional remarks about the decay mode effects described above for the  $I = \frac{3}{2}$  system. First, there are many nominally cubic systems where the observed signal is dominated by the  $(-1/2 \leftrightarrow 1/2)$  transition, because transitions to higher  $m$ -values are broadened by stray first-order quadrupolar splittings. Such splittings are the consequence of impurities and other forms of crystalline disorder. If such broadening is severe, magnetization recovery may take place via (2.1.5) rather than with the expected single-exponential  $T_1$  decay. Since there is a dramatic difference between these two cases, it is very important to be aware of such broadening effects.

A second point we wish to emphasize is that the analysis of  $T_1$  relaxation curves given here for  $I = \frac{3}{2}$  is entirely independent of the nature of the NMR spectrum. The functional behavior depends only on which pair of levels is used to excite a non-equilibrium initial condition, and on the fact that the quantum numbers  $m = \langle I_z \rangle$  are relatively pure in characterizing the energy eigenstates. If the latter condition is not fulfilled, then numerically evaluated eigenfunctions may be needed to generate sufficiently accurate relaxation curves.

### *Measuring $T_1$ in the Presence of Spectral Diffusion*

We consider briefly some well-known problems encountered in  $T_1$  measurements. Two of the most troublesome are the related problems of inhomogeneous broadening and spectral diffusion. These problems occur frequently in d-band metals and intermetallic compounds. The key to accurate  $T_1$  measurements is the experimenter's ability to create a strongly non-equilibrium population difference between a pair of nuclear energy levels as an initial condition. The  $T_1$  recovery will then be accompanied by a spin-echo signal which undergoes a substantial change in amplitude. In cases of severe inhomogeneous broadening such as that shown in Fig. 2.5, a difficulty arises from the fact that a single pulse of rf field will only affect a region of width  $\gamma H_1$ , where  $H_1$  is the amplitude of the rf pulse field. The narrow region saturated by a single pulse is shown as a dotted line in Fig. 2.5(a). If *the broadening is entirely static*, it may be possible to focus the measurement on the polarization behavior at precisely the irradiation frequency, i.e. the center frequency of the population disturbance shown in the figure. As noted in Sect. 1.2.2, this can be done by carefully integrating the entire area under the spin echo, so that the measured recovery curve will accurately reflect what is taking place at  $\omega = \omega_{rf}$ .

However, such broadening may actually have a partially *dynamical* character owing to the presence of spin-spin couplings of the form

$$\mathcal{H}_{ff} = BI_{i\pm}I_{j\mp} \quad (2.1.21)$$

between neighboring nuclei. Under circumstances which occur frequently, the  $\mathcal{H}_{ff}$  interactions lead to *flip-flop* dynamical processes between neighboring spins, which then leads to a rapid smearing of the band of excited spins

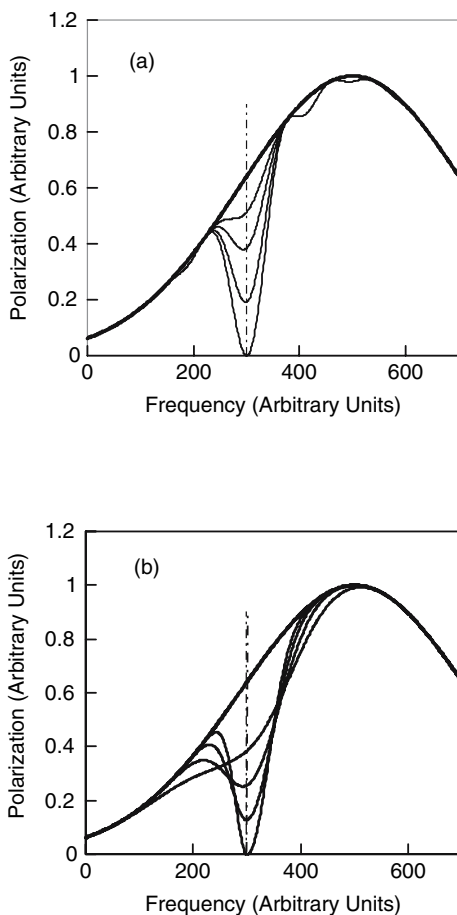


**Fig. 2.5.** (a) The saturation effect of a  $\pi/2$  pulse applied at frequency  $\omega_0$  is shown for an effective pulse field amplitude of 20 in units of the frequency scale. The polarization curve is also shown at several later times as  $T_1$  recovery takes place *without spectral diffusion*. (b) Development with time of the polarization curve is shown at several stages following the same initial saturation pulse as in (a). The curves are a Gaussian model in which there is no  $T_1$  recovery effect, thus the total polarization, plus its first moment  $\int (\omega - \omega_0) P(\omega) d\omega$ , are conserved over the time interval shown. Note the spurious “recovery” of the polarization at frequency  $\omega_0$  as a function of time

over a much wider range of frequencies than those excited directly by the *rf* pulse(s). This process, known as *spectral diffusion*, is illustrated with dashed lines in Fig. 2.5b. There results what appears to be a rapid recovery of the polarization at the excitation frequency. However, such a recovery has nothing to do with the  $T_1$  process, but is easily mistaken for it. Often it is much faster than  $T_1$ , and results in the experimenter’s inability to achieve inversion of the

polarization<sup>10</sup>. This highly undesirable effect has been known in adverse cases to render  $T_1$  measurements unfeasible.

We consider here the circumstances which give rise to spectral diffusion effects and offer a few suggestions on how to deal with this problem. The flip-flop process  $(m, m') \rightarrow (m \pm 1, m' \mp 1)$  between (primarily) nearest-neighbor ( $nn$ ) spins has been recognized since the early days of NMR as essential for spin diffusion, as well as for maintaining thermal equilibrium within the nuclear spin system. Spectral diffusion is, in fact, a process whereby a disturbance in a narrow frequency range is able to diffuse over the entire NMR line so as to create a *uniform spin temperature*. However, since an energy-conserving flip-flop transition can only take place between neighbors with nominally the same Larmor frequency, i.e. the same shift value, it is interesting to consider how polarization can migrate over large frequency intervals such as depicted in Fig. 2.5b. With coupling energy of the form of (2.1.21), it is plausible that a flip-flop transition could take place between neighboring spins with a Zeeman frequency mismatch of the order of  $\Delta\omega \sim B$  and still conserve energy. The difference in Zeeman energies is taken up by the transverse terms and eventually dissipated by other flip-flop processes. Over a large number of such fluctuations, the narrow polarization disturbance created by an *rf* pulse could broaden symmetrically over frequencies well beyond the confines of the initial excitation profile. To have this happen, of course, the inhomogeneous broadening must be local in character and be otherwise configured to facilitate the process.

One method for measuring  $T_1$  under these circumstances is to endeavor to saturate the entire line with a string of pulses known as a *comb* instead of a single pulse. Were this possible, then all polarization variables would relax back to equilibrium with the single time constant  $T_1$ . If pulses at a single frequency do not produce the desired saturation effect, then applying frequency modulation to cover the entire resonance line is known to be effective<sup>11</sup>. At low temperatures, however, long strings of pulses may produce undesirable heating effects. If  $T_1$  is long enough, another more exotic (but widely used) method is to use *field switching* to create a non-equilibrium initial condition for the  $T_1$  measurement. The field at the sample can be switched mechanically or electronically.

The most obdurate cases occur when  $T_1$  is too short, even at low temperatures, for field switching, and pulse combs are also not feasible. One's only option may be to hope that spectral diffusion will run its course in a time less than  $T_1$ , and that the final stage of the polarization recovery process can be analyzed to extract the  $T_1$  rate. Needless to say, such an approach also has limited applicability.

---

<sup>10</sup> Inability to invert polarization can result from fast spectral diffusion, but it is also caused by an inhomogeneous *rf* field  $H_1$  so that the pulse condition varies over the sample volume.

<sup>11</sup> The author is indebted to W.G. Clark for this observation.

## 2.2 NMR Probe of sp-Band Metals and Type I Superconductors

In order to put high- $T_c$  materials into context, this section gives as background material a brief summary of the basic static and dynamic magnetism of “simple” metals as sensed by the NMR probe. These systems give a historical perspective of the subject and provide foundation for the treatment of the more complex d-electron metals. In typical *good* metals we think about electrons as itinerant fermions which occupy Bloch wavefunctions  $u_k(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$ . Such orbitals are often far removed in character from the atomic states they are actually composed of. Calculations of NMR shift, relaxation, and indirect spin-spin couplings in metals were originally formulated in this band-theoretical language. The s-character of band electrons is always present and often plays a major role. In contrast, high- $T_c$  systems are *bad metals*, often with just enough mobile carriers to render the *d*-holes on the  $Cu^{2+}$  sites itinerant. Some properties remain atomic-like in character and can be thought of usefully in terms of localized wavefunctions. Perhaps by accident, there is very little *s*-character in the wavefunctions of most high- $T_c$  ions, allowing the less familiar *p* and *d* orbitals to dominate.

In this section we review the energy-band, k-space picture used to describe the static and dynamic magnetism sensed by the NMR probe in both the *normal* (nonsuperconducting) and *superconducting* (SC) states. We begin the discussion with the idealized Korringa treatment of NMR shifts and relaxation, then discuss important modifications of this picture for actual sp-band metals.

Historically, the first NMR studies of superconductivity were done on this class of materials. We review problems encountered in reconciling both the shift and relaxation behavior with the BCS theory [15] for these systems. It was with the elemental metals Hg, Sn, Pb, and Al that questions such as the role played by spin-orbit coupling in the behavior of the spin susceptibility and corresponding NMR (Knight) shift first came to light. They also gave us our first clear understanding of the BCS coherence peak in the  $T_1$  rate [16].

Since even before the BCS theory of superconductivity [15] was announced, NMR shifts have been employed to investigate the nature of the superconducting state. In the early days the only known metallic NMR shift was the *s-contact Knight* shift. Moreover, the original BCS ground state was an eigenfunction of  $S_z$ , leading to the naive expectation that  $K(T) \propto \chi_{spin}(T)$ . The actual reality was rather more complex. This interesting piece of NMR history will be touched upon in Sect. 2.2. Measurement of such effects has become a standard application for NMR studies. Observation of shift behavior is also very important in the study of high- $T_c$  systems and for any of the latter-day unconventional superconductors.

### 2.2.1 NMR Shifts and Relaxation in Simple Pauli Paramagnets

Following on the discovery of the s-contact NMR shift by Knight [17], one of the first theoretical milestones for the NMR study of metals was the Korringa relation between the latter shift and the product  $T_1 T$ , which was also shown to be independent of temperature [18]. These results were expected to apply to cubic sp-band metals, where it is noteworthy that the p-electrons with their far smaller HF couplings have a nearly negligible effect on both the NMR shift and  $T_1$ . The surprise of substantial deviations from the Korringa relation for simple systems such as the alkali metals were therefore a stimulus for Moriya's treatment of electron-electron interactions in these systems. The result was important modifications to the Korringa relation, which were then verified experimentally. This was an important step in the treatment and understanding of electron interactions in metals. We review these developments in the following subsections.

#### *The Comprehensive HF Coupling Hamiltonian in Solids*

As a preliminary step we introduce here the comprehensive HF Hamiltonian

$$\mathcal{H}_{HF} = 2\gamma\hbar\mu_B\mathbf{I} \cdot \left[ \frac{\mathbf{l}}{r^3} - \frac{\mathbf{s}}{r^3} + \frac{3\mathbf{r}(\mathbf{s} \cdot \mathbf{r})}{r^5} + \frac{8}{3}\pi\mathbf{s}\delta(\mathbf{r}) \right], \quad (2.2.1)$$

where  $\gamma\hbar\mathbf{I}$  is the nuclear moment located at  $\mathbf{r} = 0$  and  $\mathbf{l}$  and  $\mathbf{s}$  are the orbital and spin angular momentum operators, respectively, of an itinerant fermion located at  $\mathbf{r}$  (see [1], Ch. VI). (2.2.1) can be written  $-\gamma\hbar\mathbf{I} \cdot \mathbf{H}_e$ , where  $\mathbf{H}_e$  is an effective HF-field operator which is the ultimate source of all magnetic shift and relaxation effects in the metallic environment. There are three distinct types of interactions, namely the orbital field, the dipolar field, and the s-contact interaction. Although it took a number of years for them to emerge, calculations for the metallic shifts listed above were all ultimately based on (2.2.1). Evaluating the thermally averaged effects of  $\mathbf{H}_e$  in metallic systems is a matter of great subtlety and complexity. In a very real sense, this is the essence of the *high- $T_c$  problem* for the NMR probe.

#### *The Knight Shift: S-contact HF Coupling in an sp-band Metal*

The so-called s-contact HF field and its corresponding NMR shift in copper metal were discovered by W. D. Knight [17]. This shift is simply given by the expectation value of the final term of (2.2.1) when spin polarization from an external field  $H$  is present. There results a temperature-independent NMR shift given by

$$K_s = \alpha_s \chi_{sp}, \quad (2.2.2)$$

where  $\alpha_s = \frac{8\pi}{3} \langle |u_{\mathbf{k}}(0)|^2 \rangle$ ,  $\langle \rangle$  indicating an average over the Fermi surface.  $\chi_{sp} = \frac{1}{2}(g\mu_B)^2 n(E_F)$  is the spin susceptibility of the  $sp$  band, where  $n(E_F)$  is the

Fermi surface density of states per atom for one direction of spin<sup>12</sup>. We also note that the dipolar HF coupling, i.e. the second and third terms of (2.2.1), also yields a palpable NMR shift in many cases. It vanishes at sites having cubic symmetry, and is, in any case, an order of magnitude or so smaller than the contact shift. In high- $T_c$  materials, where contact shifts are often absent, the dipolar terms take on a much greater significance than for cubic metals.

Interestingly for the case of copper metal, it later developed that some 40% of the orbital character of the Fermi surface is d-like [19]. As a result, a significant fraction of the observed Knight shift for copper is attributable to the orbital Van Vleck term discussed in the next subsection [20].

### *The Korringa Calculation of $T_1$*

The idealized viewpoint regarding a simple metal is epitomized by the seminal calculation of NMR shift and relaxation time by Korringa [18]. In this case, noninteracting electrons were assumed, with a density of states at the Fermi surface describable by band theory. HF interactions with the relevant nuclear spins were limited, not unreasonably, to the  $s$ -contact interaction (2.2.1), the  $p$ -electron dipolar coupling being negligibly weak in comparison. Cubic symmetry allowed quadrupolar effects and  $p$ -electron contributions to the NMR shift to be ignored, and any gradient to the density of states deemed too small to alter low-temperature behavior. The shift expression is given above in (2.2.2).

Next, we need to develop an expression for  $T_1$  at the same level of approximation. We use the basic *golden rule* expression from time-dependent perturbation theory, where the perturbing interaction is the  $s$ -contact term from (2.2.1),  $\mathcal{H}_{sc} = -\frac{8\pi}{3}\hbar^2\gamma_n\gamma_e\delta(\mathbf{r})\mathbf{I} \cdot \mathbf{s}$ . If we consider the elemental transition from state  $|\mathbf{k} \uparrow m\rangle$  to state  $|\mathbf{k}' \downarrow m+1\rangle$ , where  $m$  is the initial nuclear spin quantum number, the rate for such a transition may be written [2]

$$\mathcal{W}_{\mathbf{k}' \downarrow m+1, \mathbf{k} \uparrow m} = \frac{2\pi}{\hbar} |\langle \mathbf{k}' \uparrow m+1 | \mathcal{H}_{sc} | \mathbf{k} \downarrow m \rangle|^2 \delta(E_k - E_{k'}). \quad (2.2.3)$$

To complete the calculation this transition rate must be summed over initial electron states  $|\mathbf{k} \uparrow\rangle$  which are occupied and final states  $|\mathbf{k}' \downarrow\rangle$  which are unoccupied. The operative term in  $\mathcal{H}_{sc}$  is the one  $\propto I_+ S_-$ , whereupon the squared matrix element becomes

$$|\langle \mathbf{k} \uparrow m | \mathcal{H}_{sc} | \mathbf{k}' \downarrow m+1 \rangle|^2 = \left[ \frac{4\pi}{3} \gamma_n \gamma_e \hbar^2 |u_k(0) u_{k'}(0)| \right]^2 (I - m)(I + m + 1). \quad (2.2.4)$$

The principal approximation is to assume that all states in the vicinity of the Fermi surface have approximately the same probability density at the

<sup>12</sup> In discussions of experimental susceptibilities, it will be more convenient to use molar units, whereupon the shift coefficient  $\alpha_s$  will be written  $8\pi \langle |u_k(0)|^2 \rangle / 3N_A$ , where  $N_A$  is Avogadro's number.

nucleus. Thus, we may replace the quantity  $|u_k(0)u_{k'}(0)|^2$  with the squared Fermi surface average  $\langle |u_{\mathbf{k}}(0)|^2 \rangle^2$ . Introducing the restricted sums on  $\mathbf{k}$  and  $\mathbf{k}'$  and noting further that  $1/T_1$  is twice the coefficient of  $(I - m)(I + m + 1)$  (see (1.10)<sup>13</sup>), this gives

$$1/T_1 = \frac{4\pi}{\hbar} \left[ \frac{4\pi}{3} \gamma_n \gamma_e \hbar^2 \langle |u_{\mathbf{k}}(0)|^2 \rangle \right]^2 \sum_{\mathbf{k}, \mathbf{k}'}^{(r)} \delta(E_{\mathbf{k}} - E_{\mathbf{k}'}). \quad (2.2.5)$$

The restricted sums  $\sum_{\mathbf{k}, \mathbf{k}'}^{(r)}$  can be replaced with energy integrals where, for example, the sum on  $\mathbf{k}$  of states with energy  $E$  becomes  $\int n(E) dE$ , where  $n(E)$  is the density of states, and the occupation restriction is enforced with the Fermi occupation function  $f(E) = [\exp \beta(E - E_F) + 1]^{-1}$ .

The summation in (2.2.5) then becomes

$$\int dE \int dE' n(E) n(E') f(E) (1 - f(E')) \delta(E - E') = \int n(E)^2 f(E) (1 - f(E)) dE. \quad (2.2.6)$$

The final step is to note that the function  $f(E)(1 - f(E))$  is very sharply peaked at  $E_F$  at the usual experimental temperatures, so that  $n(E)^2$  can be replaced with  $n(E_F)^2$ . Then we note that the area under the peak in  $f(E)(1 - f(E))$  is easily shown to be  $k_B T$ . The relaxation rate becomes

$$1/T_1 = \frac{4\pi k_B T}{\hbar} \left[ \frac{4\pi}{3} \gamma_n \gamma_e \hbar^2 \langle |u_{\mathbf{k}}(0)|^2 \rangle \right]^2 n(E_F)^2. \quad (2.2.7)$$

This expression may be combined with the result in (2.2.2) to give the *Korringa product*, which we write as

$$\frac{1}{T_1 T K_s^2} = \frac{4\pi k_B \gamma_n^2}{\hbar \gamma_e^2}. \quad (2.2.8)$$

Equation (2.2.8) suggests that  $1/T_1 T$  divided by  $K_s^2$  for these kinds of metals should equal an expression made up of physical constants which is independent of the other properties of the metal. As we shall see below, the result of Moriya's theory is to multiply the right-hand side of (2.2.8) by a constant factor  $< 1$ . Setting that aside for the moment, however, let us see how well the Korringa relation is obeyed in simple metals. In Table 2.1 shift and relaxation data from the literature are listed for the alkali metals and the noble metals Cu, Ag, and Au [3].

These elemental metals all have cubic crystal structures, so that dipolar shift effects do not come into play. Using the measured shift values, values of  $T_1 T$  extracted from (2.2.8) are compared with experimental values. It is seen that the latter values are generally smaller than those obtained from

<sup>13</sup> For simplicity, detailed balance considerations are omitted here.

**Table 2.1.** NMR shift and relaxation data are tabulated for alkali metals and for the noble metals, along with values of  $T_1T$  derived from (2.2.8). To test the validity of the Korringa relation, a relative Korringa product defined as  $(T_1TK_s^2)^{-1}$  divided by  $4\pi k_B\gamma_n^2/\hbar\gamma_e^2$  is listed in column five

| Metal and Isotope | $K_s(\%)$ | $T_1T(\text{expt.})$<br>(secK) | $T_1T(\text{Korringa})$<br>(secK) | Relative<br>Korr.Prod. |
|-------------------|-----------|--------------------------------|-----------------------------------|------------------------|
| <sup>7</sup> Li   | 0.0263    | $45.0 \pm 2$                   | 26.0                              | 0.58                   |
| <sup>23</sup> Na  | 0.112     | $4.8 \pm 0.1$                  | 3.1                               | 0.65                   |
| <sup>85</sup> Rb  | 0.650     | $0.81 \pm 0.08$                | 0.63                              | 0.78                   |
| <sup>133</sup> Cs | 1.47      | $0.13 \pm 0.01$                | 0.069                             | 0.53                   |
| <sup>63</sup> Cu  | 0.232     | $0.9 \pm 0.2$                  | 0.7                               | 0.78                   |
| <sup>109</sup> Ag | 0.522     | $9.0 \pm 1.0$                  | 4.5                               | 0.50                   |
| <sup>197</sup> Au | 1.4       | $4.0 \pm 0.5$                  | 4.5                               | 1.13                   |

(2.2.8). Including  $p$ -electron dipolar hyperfine fields in the relaxation calculation would only make this discrepancy larger. Thus, the most serious defect in the Korringa treatment appears to be the neglect of electron-electron exchange enhancement effects, which we shall discuss next.

### 2.2.2 The Moriya Theory of Exchange Enhancement in Simple Metals

There are various corrections one could make to the Korringa treatment of relaxation. The electron-electron interaction potential has the effect of enhancing the spin susceptibility, and thus the NMR shift [21], in close analogy with the enhancement effect of ferromagnetic exchange among localized moments. However, it was pointed out by Moriya [22] that exchange fluctuations would also enhance the  $T_1$  process. Moriya's calculation of this effect in the *random phase approximation* showed this enhancement effect to be substantial, but not as great as that of the shift and susceptibility. This is consistent with the values shown in Table 2.1, where the experimental Korringa product (Relative Korr. Prod.) is consistently smaller than the result in (2.2.8). Thus, the measured Korringa products can be used with the Moriya theory (see below) to estimate the magnitude of these enhancement effects.

We give an outline of the random-phase approximation calculation here, and refer the interested reader to [22] and [3] for a more detailed account. As noted above, the shift has a simple exchange-enhancement factor,  $K_s = K_{s0}/(1 - \alpha) = \alpha_s\chi_{s0}/(1 - \alpha)$ , where  $\alpha = \rho_0\chi_{s0}$ , and  $\rho_0 = 2\pi\zeta/\hbar^2\gamma_e^2$ . Finally,  $\zeta$  is the  $q$ -independent (by assumption) electron-electron interaction potential. The single parameter  $\zeta$  drives the enhancement of both static and dynamic spin susceptibilities in the random phase approximation picture. For  $T_1$  the fluctuation enhancement is  $q$ -dependent. In Sect. 3.5 these magnetic properties will be discussed in terms of  $q$  and  $\omega$ -dependent susceptibilities. Here, we simply state the result for a spherical Fermi surface:

$$\frac{1}{T_1 T K_s^2} = \frac{4\pi k_B \gamma_n^2}{\hbar \gamma_e^2} \mathcal{K}(\alpha), \quad (2.2.9)$$

where  $\mathcal{K}(\alpha) = 2(1 - \alpha)^2 \int_0^1 dx x / [1 - \alpha G(x)]^2$ , and  $G(x)$  is the Lindhard function for free electrons given by  $\frac{1}{2}\{1 + [(1 - x^2)/2x] \ln |(1 + x)/(1 - x)|\}$ , with  $x = q/2k_F$ .  $G(x)$  is integrated over the range of  $\mathbf{q}$  values which span the Fermi surface. We see in (2.2.9) that the Korringa product of (2.2.8) is simply multiplied by the quantity  $\mathcal{K}(\alpha)$ . The enhancement factor for  $K_s$  is that for  $\mathbf{q} = 0$  ( $G(0) = 1$ ), while that for  $1/T_1$  is for  $G(q > 0) < 1$ . Therefore,  $\mathcal{K}(\alpha)$  declines from 1 to 0 as  $\alpha$  varies from 0 to 1<sup>14</sup>.

If other effects which modify the Korringa product are largely absent<sup>15</sup>, the experimental value of  $\mathcal{K}(\alpha)$  can be used to estimate the electron-electron exchange (i.e. the value of  $\alpha$ ) in *sp*-band metals. A few examples are given in Table 2.2, where  $\alpha$  values in the range of  $0.2 \leq \alpha \leq 0.4$  are seen to be typical. Rather surprisingly, susceptibility enhancement effects are present to the degree of 25% to more than 50% in these *nearly free-electron metals*. The Korringa product is often used as a diagnostic tool to examine the nature of the  $T_1$  process.

**Table 2.2.** A tabulation of enhancement parameters  $\alpha$  derived for a selection of s-band metals from experimental data using (2.2.9). For comparison, calculated values given by Pines [21] are listed

| Elemental<br>Metal | $\alpha$ from<br>$\mathcal{K}(\alpha)$ | $\alpha$ calc.<br>(Pines) |
|--------------------|----------------------------------------|---------------------------|
| <sup>7</sup> Li    | 0.36                                   | 0.37                      |
| <sup>23</sup> Na   | 0.30                                   | 0.24                      |
| <sup>85</sup> Rb   | 0.19                                   | 0.15                      |
| <sup>109</sup> Ag  | 0.43                                   | 0.32                      |

<sup>14</sup> A plot showing  $\mathcal{K}(\alpha)$  vs.  $\alpha$  is given in [3].

<sup>15</sup> Experimental values of the Korringa product can deviate sharply from that in (2.2.8) for a number of reasons. We give three examples. First, if the s-character of Fermi surface orbitals is unusually weak, then p-electron contributions which have been neglected here may play a large role. Second, if the degree of s-character is strongly non-uniform over the Fermi surface, then one of the principal assumptions of the calculation breaks down. Third, if there are multiple bands or multiple neighbors (in the case of ligand nuclei), the experimental Korringa product will change drastically. For example, if a ligand nucleus has N independent but equivalent sources of HF field and fluctuations, then the shift and relaxation rate will both be N times that from a single source. It follows that the Korringa product will be the value from a single source divided by N. The latter case is encountered frequently for ligand nuclei in intermetallic compounds.

### 2.2.3 NMR in the Superconducting State of Simple Metals

We present here a brief account of the superconducting properties of sp-band metals. Historically, several fundamental issues were resolved with these systems following initial uncertainties regarding both theory and experiment. A clear and comprehensive review of early work was given by MacLaughlin [5]. Some elemental metals addressed in the early days were Hg(4.15K),  $\beta$ Sn(3.74K), Pb(7.22K), and Al(1.18K), where their respective values of  $T_c$  are given in parentheses. They are all Type I superconductors, which means that their coherence lengths  $\xi(0)$  are long compared with their London penetration depths  $\lambda(0)$ <sup>16</sup>.

With the announcement of BCS theory [15], there were a number of interesting issues to investigate. The principal ones for the NMR probe were (a) the expected collapse of the spin susceptibility at  $T < T_c$  owing to the SC energy gap for quasiparticle excitations and (b) the existence of a singularity, which becomes the *coherence peak*, just below  $T_c$  in a plot of  $1/T_1$  vs.  $T$ . Because of the large superconducting diamagnetism which occurs below  $T_c$ , virtually the only means of measuring the relatively tiny Pauli susceptibility term is through the associated Knight shift  $K_s$  (2.2.2). We shall discuss the superconducting shift measurements first.

#### *The Knight shift for $T < T_c$ : Verifying the Yosida function*

Performing NMR measurements in the SC state of Type I superconductors was a particular experimental challenge, because of the limited magnetic field penetration depth  $\lambda \sim 500\text{\AA}$  for these systems. In order to get a reasonably uniform internal field for NMR studies, experiments were performed on fine particles or thin films with at least one dimension which was small compared with  $\lambda$ . The resulting samples generally exhibited superconductivity with  $T_c$  near the bulk value and NMR lines with relatively little diamagnetic shift or inhomogeneous broadening. Particles with dimension  $d \ll \lambda$  have greatly reduced diamagnetism in the SC state. Other than that, it was generally believed that these samples exhibited *bulk NMR properties*.

However, the peculiar results obtained at first for  $K(T)$  vs.  $T$  for  $T < T_c$  demonstrated that the foregoing statements were not entirely correct. To see this clearly, we must first describe the results that were expected from the shift measurements, then what was actually found, and finally, how to account for the observed data. The BCS theory prescribed an energy gap  $\Delta(T)$  above the superconducting ground state for quasi-particle excitations when  $T < T_c$ . As  $\Delta(T)$  increases below  $T_c$  the spin susceptibility  $\chi_{sp}(T)$  and  $K_s(T) = \alpha_s \chi_{sp}(T)$  were expected to decline and asymptotically approach 0 as  $T \rightarrow 0$ . The theoretical functional form of  $\chi_{sp}(T)$  for  $T < T_c$  is known as the Yosida function [23].

---

<sup>16</sup> A brief discussion defining the coherence length and penetration depth parameters is given in Sect. 2.2.4.

Experimentally, however, large residual  $T \rightarrow 0$  shift values were reported. For the  $^{199}\text{Hg}$  NMR in SC Hg, for example,  $K_s(T \rightarrow 0)/K(T > T_c) \simeq 2/3$  was found [24], with similar results for  $^{119}\text{Sn}$  in  $\beta\text{Sn}$  [25],  $^{207}\text{Pb}$  in  $\text{Pb}$  [26], and  $^{27}\text{Al}$  in  $\text{Al}$  [27]. These results caused great consternation and confusion, and it was a number of years before a satisfactory understanding was reached [28].

### *Spin–Orbit Scattering: The Ferrell–Anderson Picture*

In the end, it was realized that the theoretical preparation was incomplete, and further developments with the  $\text{Al}$  metal samples showed that the earliest results were incorrect. We shall return to the  $\text{Al}$  story below. The problem with the Yosida/BCS calculation was that it had neglected spin-orbit coupling and its role in generating spin-flip scattering processes. The situation was eventually addressed and for the most part resolved in short papers by Ferrell [29] and Anderson [30], as well as in a longer paper by Abrikosov and Gorkov [31].

We consider briefly the physical picture presented in Anderson’s treatment [30]. In the presence of spin-orbit coupling one must bear in mind that  $S_z$  for the electrons is no longer a good quantum number, and that the spin-up and spin-down states are mixed into eigenstates which are no longer have any particular average value of spin. However, a very subtle point is this: In *clean, bulk regions of the pure metal* there is no spin-flip scattering even in the presence of strong spin-orbit coupling. Thus, the spin susceptibility will still vanish as  $T \rightarrow 0$  in the SC state. However, what modifies this ideal result is a spin-flip scattering lifetime  $\tau_{so}$  which is short enough that the quantity  $\hbar/\Delta(0)\tau_{so}$  is no longer small. In other words the smearing of the eigenstate energies from  $\tau_{so}$  becomes comparable with the SC energy gap. Spin-flip scattering occurs only where ordinary potential scattering is strong, e.g. near surfaces and near impurities in the bulk. Ironically, then, this effect will be important near surfaces where *rf* fields penetrate and NMR signals are excited, but not necessarily in bulk regions which cannot be probed.

Anderson treated the spin-orbit scattering problem using his theory of *dirty superconductors* [32]. His result for the  $T \rightarrow 0$  susceptibility ratio is an expression which can be integrated numerically, from which the following limiting cases are given [30]:

$$\frac{\chi_{so}(T \ll T_c)}{\chi_{so}(T > T_c)} \approx \frac{1}{6} \frac{\hbar}{\Delta(0)\tau_{so}}, \quad \Delta(0) \gg \hbar/\tau_{so} \quad (2.2.10a)$$

$$\frac{\chi_{so}(T \ll T_c)}{\chi_{so}(T > T_c)} \approx 1 - 2 \frac{\Delta(0)\tau_{so}}{\hbar}, \quad \Delta(0) \ll \hbar/\tau_{so}. \quad (2.2.10b)$$

Equations(2.2.10) show that when  $\tau_{so}$  is long there is only a small residual value of  $\chi_{sp}(T \ll T_c)$ , but when it is short, i.e. strong spin-orbit scattering near surfaces,  $\chi_{sp}(T \ll T_c)$  is only slightly perturbed from its normal state value. The latter case is often found for heavy metals such as Hg [24] and Pb [26], and was also found for  $\beta\text{Sn}$  [25, 33]. These authors performed various

doping experiments, which were also consistent with (2.2.10). Ferrell obtained a result similar to (2.2.10b) by means of a physical argument [29].

In a metal as light as elemental *Al* one might expect spin-orbit effects to be very small. Since colloids of *Al* are difficult to prepare, shift studies were performed on thin film samples. The first results gave, surprisingly, residual shift values of  $\sim 75\%$  [27]. It appears that orientation of their multi-film samples was quite critical, as subsequent work [34] yielded a very small residual shift. Later measurements by Fine, et al., on a single thin-film sample [35] gave results in good agreement with the Yosida function [23]. These data are displayed in Fig. 2.6, finally giving verification to the BCS theory-based prediction.

### **$T_1$ Behavior Below $T_c$ : The BCS Coherence Factor**

The behavior of  $T_1$  for an sp-band (Type I) superconductor according to the BCS theory was first investigated, theoretically and experimentally, by Hebel and Slichter [16]. We sketch the calculation of  $T_1$  in the SC phase following the derivation in [5]. First, recall from Sect. 1.2.1 that the  $T_1$  process consists of scattering fermions from an initial state  $|\mathbf{k}\sigma\rangle$  to a final state  $|\mathbf{k}' - \sigma\rangle$ , while the nuclear spin goes from  $m$  to  $m \pm 1$  so that angular momentum is conserved. This outline is maintained in the SC state, but other circumstances change drastically. For  $T < T_c$  there is some fraction of fermions which are paired ( $|\mathbf{k}\sigma\rangle$  with  $|\mathbf{k} - \sigma\rangle$ ) into singlet states and do not scatter. The quasiparticles not condensed into the ground state are thermally excited above the energy gap  $\Delta(T)$  and are available to scatter as sketched above. The main differences are that, first, there appears in the summation in 2.2.5 a factor  $C_{\pm}(\mathbf{k}, \mathbf{k}') = \frac{1}{2}[1 \pm (\Delta^2/E_{\mathbf{k}}E_{\mathbf{k}'})]$  known as the *coherence factor*, and second, the normal state density of states factors in the integrals leading to 2.2.7 are replaced by the BCS density of states  $n_{BCS}(E) = n(E_F)E/(E^2 - \Delta^2)^{1/2}$ , where  $\Delta \leq$

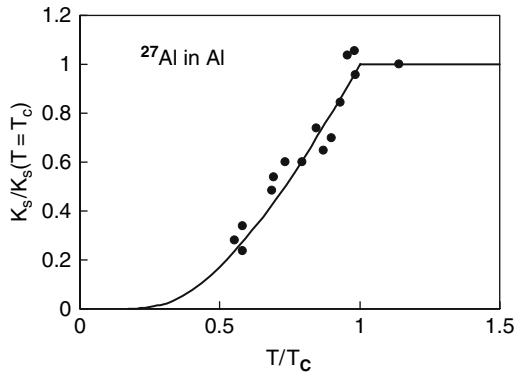


**Fig. 2.6.** Data for the  $^{27}\text{Al}$  Knight shift in Al metal from [35] are shown, plotted in units of the normal state shift as a function of  $T/T_c$ . The solid curve is the Yosida function, i.e. behavior expected on the BCS theory

$E \leq \infty$ . The coherence factor arises because of the pairing of electrons in the condensed phase, and is characteristic of many dynamical properties treated with BCS theory [7]. The choice of sign for  $C_{\pm}(\mathbf{k}, \mathbf{k}')$  depends on whether the scattering perturbation is invariant under time reversal applied to the fermion bath. If it is, as in the case of phonons (e.g. ultrasonic attenuation) then  $C_{-}(\mathbf{k}, \mathbf{k}')$  applies. If it is not invariant, such as for electromagnetic absorption and magnetic dipolar nuclear relaxation, then  $C_{+}(\mathbf{k}, \mathbf{k}')$  applies.

For the superconducting nuclear relaxation rate  $1/T_{1s}$  one finds, in units of the normal state rate  $1/T_{1n}$ ,

$$\frac{T_{1n}}{T_{1s}} = \frac{2}{k_B T} \int_{\Delta}^{\infty} \frac{dE (EE' + \Delta^2) f(E) (1 - f(E'))}{[(E^2 - \Delta^2)(E'^2 - \Delta^2)]^{1/2}}, \quad (2.2.11)$$

where  $E' = E \pm \hbar\gamma_n H$ . Below  $T_c$  the excitation probability is the Fermi function  $f(E_g) = [\exp(\beta E_g) + 1]^{-1}$  of the gapped energy  $E_g = (E^2 + \Delta^2)^{1/2}$ . Since the nuclear Zeeman energy  $\hbar\gamma_n H$  is minuscule on the scale of the quasiparticle energy, there is in fact a logarithmic singularity in 2.2.11 for the case of the coherence factor  $C_{+}(E, E')$ . The most satisfactory explanation for how this singularity is “tamed” is by means of anisotropy of the gap energy  $\Delta(T)$  [5, 36]<sup>17</sup>. The nuclear Zeeman energy will be neglected henceforward.

The behavior of  $T_{1n}/T_{1s}$  in 2.2.11 may be divided into two regions,  $k_B T \ll \Delta(T)$  and  $k_B T > \Delta(T)$ . For  $k_B T \ll \Delta(T)$  the integral is dominated by the peak in  $n_{BCS}(E)$  near the gap, which becomes very nearly constant  $\Delta(T) \approx \Delta(0)$ . In this limit the factor  $f(E)(1 - f(E)) \approx \exp(-\beta\Delta(0))$ , so that  $1/T_{1s}$  decays exponentially at low T. In the other limit  $k_B T > \Delta(T)$  ( $T$  near  $T_c$ ), the factor  $f(E)(1 - f(E))$  will have nearly its normal-state value, and the singularity in 2.2.11 has the potential to elevate  $T_{1n}/T_{1s}$  to values considerably in excess of 1. This is the source of the well-known BCS *coherence peak* in  $1/T_1(T)$  at  $T < T_c$ . This peak was first measured on  $^{27}\text{Al}$  in Al metal and identified by Hebel and Slichter [16], establishing a major milestone in experimental confirmation of the BCS theory.

It is important to note that for measurements such as ultrasonic attenuation the appropriate coherence factor to use is  $C_{-}(\mathbf{k}, \mathbf{k}')$ , whereupon the factor  $(EE' + \Delta^2)$  in the numerator of (2.2.11) is replaced by  $(EE' - \Delta^2)$ . This effectively cancels the singularity at  $E \simeq \Delta$ . As a result, the ultrasonic attenuation coefficient was expected to fall abruptly below  $T_c$ , as had been confirmed experimentally [37]. This striking contrast between results obtained with probes having different symmetry properties was an important confirmation of the correctness of the BCS picture.

Following the Hebel-Slichter results, Masuda and Redfield [36] reported further  $T_1$  measurements on  $^{27}\text{Al}$  in Al metal taken at temperatures ranging

<sup>17</sup> This broadening mechanism was suggested in [36], where it was noted that it gave a good account of the variation of  $T_1$  below  $T_c$ . The uniform energy gap parameter  $\Delta(T)$  in BCS theory is, in fact, an approximation, where the actual gap parameter is properly a function of  $\mathbf{k}$ . See the book by Tinkham [6], Sect. 2–6, for more discussion of this point.

from above to well below  $T_c$ . Their results (Fig. 2.7) offered a full panorama of the BCS-theoretical behavior, with a coherence peak (in  $1/T_1$ ) rising above the normal state Korringa curve by a factor  $\sim 2$ , then descending into the superconducting state in a clearly exponential fashion. These data were obtained with a field-switching technique similar to that used in [16], the main difference being that pumped  $^3\text{He}$  cooling allowed them to extend the measurements to  $0.35\text{K}$ , i.e. far below  $T_c = 1.18\text{K}$  for Al metal.

### Analyzing $T_1$ Data in the Superconducting State

Since the formulation of (2.2.11) has been widely employed to analyze SC-state data on high- $T_c$  materials as well as all manner of unconventional superconductors, we recount here the analytic procedure used to fit the Al data in some detail [5, 36]. These results are referred to in other sections of the book as well.

In order to control the singularity in (2.2.11), Hebel and Slichter [16] postulated a broadening of the electronic energy levels. While such a device enabled them to obtain a reasonable result for the coherence peak, it lacked a clear physical basis. Masuda and Redfield, on the other hand, suggested that the

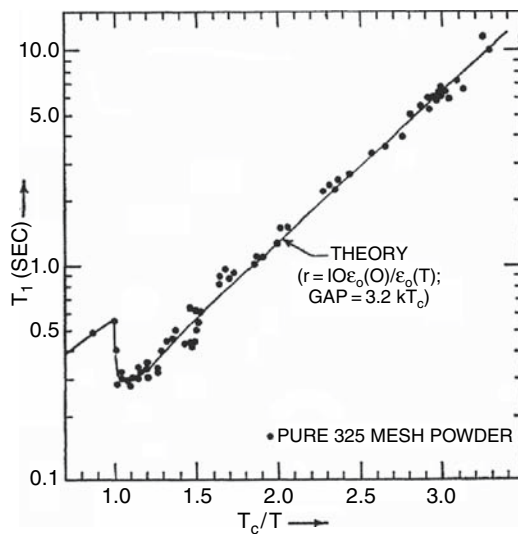


**Fig. 2.7.** A semilog plot of  $T_1$  data for the superconducting state of Al metal vs.  $T_c/T$  (dots) [36]. Also shown is their fit to the BCS theory (solid line), where the coherence peak (i.e.  $T_1$  minimum) amplitude was adjusted using a distribution of energy gap values attributed to anisotropy. The low-temperature energy gap value is adjusted to the slope of the data, yielding  $\Delta_0 = 3.2 k_B T_c$  in reasonable accord with the BCS weak-coupling value of  $3.52 k_B T_c$ . Reprinted figure from Y. Masuda, A. C. Redfield, Phys. Rev. **125**, 159 (1962). Copyright 1962 American Physical Society

observed peak was conditioned by a mild anisotropy of the gap parameter  $\Delta(T)$ . This has a clear physical origin in the BCS equations and gives quite a good fit to the data as well. There, the gap parameter is formally a function of  $\mathbf{k}$ , and the  $\mathbf{k}$ -independent gap parameter is just a convenient approximation used to solve the equations. Ample theoretical evidence has been reported for gap anisotropy effects from van Hove singularities and other causes [38].

To illustrate the  $T_1$  analysis with (2.2.11) we summarize briefly the development in [5] and [36], and refer the reader to these sources for a more detailed discussion. The procedure is to incorporate the gap anisotropy into the BCS density of states factors in (2.2.11) at the point where sums on  $\mathbf{k}$  and  $\mathbf{k}'$  are converted to energy integrals. We therefore back up a step from (2.2.11) and rewrite it as

$$\frac{T_{1n}}{T_{1s}} = \frac{2}{k_B T} \int_0^\infty [N_s(E)^2 + M_s(E)^2] f(E) (1 - f(E)) dE, \quad (2.2.12)$$

where

$$N_s(E) = \text{Re} \int_{a_1}^{a_2} \frac{E P(a) da}{[E^2 - \Delta(T)(1+a)^2]^{1/2}}, \quad (2.2.13a)$$

$$\text{and } M_s(E) = \text{Re} \int_{a_1}^{a_2} \frac{\Delta(T)(1+a) P(a) da}{[E^2 - \Delta^2(1+a)^2]^{1/2}}. \quad (2.2.13b)$$

In (2.2.13) the variation of  $\Delta_{\mathbf{k}}$  over the Fermi surface is represented as a distribution  $P(a)$  extending over  $a_1 \leq a \leq a_2$ , where  $\Delta_{\mathbf{k}} \Rightarrow \Delta(T)(1+a)$  and  $\int a P(a) da = 0$  by definition. As noted in [5], because the averaging over  $a$  is followed by integration over  $E$ , the precise shape of  $P(a)$  is functionally immaterial to the final results. In fitting the  $T_1$  data of Fig. 2.7,  $\langle a^2 \rangle$  determines the depth of the  $T_1$  minimum and  $\Delta(0)$  fixes the slope of the exponential tail. The fit shown corresponds to  $2\Delta(0) = (3.2 \pm 0.2)k_B T_c$  and  $\langle a^2 \rangle^{1/2} \simeq 0.05$ , in reasonable agreement with the BCS weak-coupling theoretical value  $2\Delta(0) = 3.52k_B T_c$ . Comparable gap values are given by other probes [5].

There has also been extensive experimentation with doping effects on the SC  $T_1$  behavior, yielding some interesting effects. For example, it was found that shortening the mean free path  $l$  of the quasi-particles led to even larger coherence peaks in the  $T_1$  data for Al [39] and In-based [40] dilute alloys. This effect can be rationalized in terms of the theory of “dirty superconductors” [32], where potential scattering caused by impurities can become strong enough to cause effective mixing between Bloch functions on different parts of the Fermi surface. The result is a smoothing out of intrinsic gap anisotropy. Data for the Al-based systems was in good agreement with a theory of this effect [41], but for In-based alloys, there was only agreement for  $l > \xi_0$ , where  $\xi_0$  is the coherence length. It was suggested that *gap inhomogeneity* might be suppressing the coherence peak in such a case. However, no further resolution of this point has apparently been reported.

As we shall see in the next subsection, there are a number of d-electron superconductors where  $T_1$  has no coherence peak for reasons which are also not

clear. Moreover, among high- $T_c$  systems, suppression of the coherence peak in  $T_1$  is universal, as is also the case for many *unconventional superconductors*. We defer further discussion of this point to subsections below, where fuller descriptions of the systems concerned are presented.

## 2.3 Static and Dynamic Magnetism in d-band Metals

In this subsection we review the additional complexities which arise when a conductive solid has an open d-shell in addition to its sp-band effects. D-electrons in solids are typically more tightly bound to their host ion, interacting more weakly with neighbors. As a result they have narrower, more highly structured energy bands with substantially higher densities of states at their Fermi surfaces. Moreover, they are subject to a *crystalline electric field* (CEF) which results from bonding and proximity to neighboring ions, which breaks the full rotational potential symmetry enjoyed by a free ion. As a result, the d-electron angular momentum “always” has a zero expectation value in the ground state. On the other hand, the greater densities of states of d-bands, when combined with the electron-electron exchange effects [21] which came to light in the Moriya treatment of enhanced NMR shifts and relaxation [22], lead to strongly enhanced susceptibilities and even to permanently magnetized ground states in a number of pure metals (e.g. Fe, Co, and Ni in the  $3d$  series). Moreover, ions with d-electrons as dilute impurities or dopants frequently possess a localized magnetic moment. However, discussion of d-ion systems possessing full atomic magnetism is beyond the scope of this volume.

### *Special Features of NMR in d-Band Metals and Superconductors*

Keeping superconductivity in mind, we shall restrict our attention to d-electron systems which do not order magnetically. We consider, as an example, the behavior of the  $V_3X$  series of compounds, which are superconductors as well. There is a wealth of interesting NMR phenomena which arise in such systems, including:

- Prominence of the *core-polarization* (CP) d-spin HF field in studies of d-band magnetism. Since d-electrons have no contact interaction, this isotropic, negative HF coupling, which was identified by Heine [42] and by Wood and Pratt [43], takes its place. The core polarization plays a major role, since dipolar interactions are often smaller and are cancelled by cubic symmetry.
- The greatly enhanced importance of orbital effects, both the static (Van Vleck) shift and susceptibility and the robust orbital  $T_1$  mechanism. The d-band orbital susceptibility was first formulated by Kubo and Obata [44]. Its contribution to the NMR shift was identified by Clogston et al., [45] in connection with the  $V_3X$  compounds, where it had important consequences for the interpretation of superconducting shift data.

- The latter authors [46] also pioneered the use of the  $K-\chi$  plot as a means of analyzing NMR shifts and their corresponding susceptibility components in d-band metals. This technique continues to be used very widely and has led to great insight into the magnetic infrastructure of metals and intermetallic compounds. We present their method below.
- When d-electron metals are superconductive, they are nearly always Type-II superconductors. Thus, NMR studies are very often conducted in the *mixed state*, i.e. in the presence of a large magnetic field and a vortex lattice. The field penetrates throughout the sample, dividing itself into as many flux bundles as possible, which occurs when each vortex contains just one fluxon. We shall review results on NMR shifts, lineshapes, and on  $T_1$  studies as well. These effects are directly relevant to superconductive high- $T_c$  NMR studies, since they are often conducted under the same conditions.

### 2.3.1 The d-Electron HF Interactions

In general there are two types of d-electron HF interactions, namely spin and orbital, the latter arising from the first term in (2.2.1), and the former from the second two terms. In d-band metals there are also multiple bands with their own Fermi surface density of states and corresponding HF interaction terms. These terms will make additional contributions to the NMR shift and relaxation rates, rendering the task of analyzing experimental data for these parameters a bit more complex. By and large, however, d-electron bands are somewhat more “lively” than their rather prosaic s and p counterparts, and tend to dominate the nuclear spin properties. In high- $T_c$  materials, depending on your point of view, there is scant evidence for actual sp-bands *per se*, so the d-electron HF effects are, by any measure, the dominant ones.

#### *Anisotropic d-Spin Susceptibility and HF Tensor*

If we allow the d-spin HF coupling to be anisotropic, we then take

$$\mathcal{H}_{ds} = \sum_{\xi=x,y,z} A_{d\xi} I_{\xi} S_{\xi} \quad \text{with} \quad \chi_{d\xi} = \frac{N_A g_{\xi} \mu_B \langle S_{\xi} \rangle}{H}. \quad (2.3.1)$$

The d-spin shift coefficient is then defined as

$$\alpha_{d\xi} = \frac{K_{d\xi}}{\chi_{d\xi}} = \frac{A_{d\xi}}{N_A \gamma \hbar g_{\xi} \mu_B}. \quad (2.3.2)$$

For ordinary 3d metals we shall take  $g_{\xi} \sim 2$ , whereupon  $\alpha_d$  becomes isotropic. However, these definitions will carry over into the cuprate discussion in Chap. 3, where for the cuprates there is evidence for substantial g-shifts. We also note here that the HF coefficient can be quoted as simply  $A_{d\xi}$  in ergs, as  $A_{d\xi}/\hbar$  in units of  $s^{-1}$ , as  $10^{-3} A_{d\xi}/\gamma \hbar$  in kG/spin, as  $10^{-3} A_{d\xi}/\gamma \hbar g_{\xi}$  in units of  $kG/\mu_B$ , or as  $A_{d\xi}/1.60218 \times 10^{-12}$  in eV. Although it may be somewhat

confusing, one finds all of these units in use in the high- $T_c$  literature. The d-spin HF field is also known as the core-polarization HF field (hence  $A_d \rightarrow A_{cp}$ ), which we now discuss.

### *Core-Polarization Hyperfine Coupling: The Mechanism*

Since d-electron wavefunctions vanish at the site of the nucleus, they possess no direct contact HF field from the final term in (2.2.1). However, they do activate the contact HF term indirectly in such a way as to generate an effectively isotropic HF coupling with the nuclear spins. This mechanism came to light with the work of Heine [42] and of Wood and Pratt [43]. Detailed calculations have been given by Freeman and Watson [47]. The mechanism of the *core polarization HF field* is a simple consequence of the Pauli exclusion principle, and works as follows. In d-electron atoms there are two or more filled s-shells which are magnetically inert. Nonetheless, these filled s-shells undergo repulsive coulombic interactions with the Fermi-surface d-electrons which, generally speaking, lie outside of them, i.e. at larger distances from the nucleus. Thus, coulomb repulsion drives the s-shell electron orbitals closer to the nucleus. This repulsive effect is, however, dependent on spin. Consider the majority d-spin moment to point up. The up-moment s-shell electrons are then known to avoid close proximity with the up-moment d-electrons in a Pauli-exclusion effect known as the *Fermi hole*. The down-moment s-electrons have no such effect. With the same wavefunction, then, the down-moment s-electrons will have a higher coulomb repulsion energy. For that reason, the down-moment s-shell orbitals will tend to “shrink” toward smaller radii relative to the up-moment s-shell orbitals, creating a *net down moment of s-electron density at the nucleus*, i.e. a net negative contact HF interaction. The differential orbital distortion effect is small, but the core s-shell HF couplings are enormous, so that there is a substantial net HF coupling. For 3d-electrons the resulting HF field is  $\sim -125kG/\mu_B$ , increasing gradually across the 3d series. For the 4d and 5d shells the effect is generally larger [47]. As an example, we note that the  $5\mu_B$  S-state moment of  $\text{Mn}^{2+}$  in  $\text{MnF}_2$  generates a HF field  $\simeq -127kOe/\mu_B$  at the  $^{55}\text{Mn}$  nucleus. This compound has purely 3d-spin magnetism.

### 2.3.2 Orbital Shift and Susceptibility

The orbital term in (2.2.1) comes into play for both the NMR shift and  $T_1$ . The orbital shift is driven by the Van Vleck orbital susceptibility, which was first formulated for band electrons by Kubo and Obata [44]. The susceptibility was formulated in a tight-binding approximation, yielding the following expression for the  $\alpha$ -axis susceptibility,

$$\chi_{orb} = N_A \Omega \mu_B^2 \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_{nn'} \frac{f(E_{n\mathbf{k}}) - f(E_{n'\mathbf{k}})}{E_{n'\mathbf{k}} - E_{n\mathbf{k}}} \langle n\mathbf{k} | l_\alpha | n'\mathbf{k} \rangle \langle n'\mathbf{k} | l_\alpha | n\mathbf{k} \rangle, \quad (2.3.3)$$

where  $N_A$  is Avogadro's number,  $\Omega$  is the atomic volume, and the summing indices  $n$  and  $n'$  represent the five d-orbital subbands as well as the spin quantum number. The quantity  $f(E_{n\mathbf{k}}) = [\exp(\beta(E_{n\mathbf{k}} - E_F)) + 1]^{-1}$  is the Fermi occupation function.  $\chi_{orb}$  is written here as a molar susceptibility.

Clogston et al., [48] have derived a companion expression to (2.3.3), which gives the induced orbital hyperfine field at the nucleus when the effects of the spin-orbit coupling and certain other terms in the general expression, deemed to be small, are neglected. The simplified expression is

$$H_{orb} = \Omega \mu_B^2 \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_{nn'} \frac{f(E_{n\mathbf{k}}) - f(E_{n'\mathbf{k}})}{E_{n'\mathbf{k}} - E_{n\mathbf{k}}} \langle n\mathbf{k} | 2l_\alpha / r^3 | n'\mathbf{k} \rangle \langle n'\mathbf{k} | H l_\alpha | n\mathbf{k} \rangle, \quad (2.3.4)$$

where the field  $H$  is taken to be directed along the  $\alpha$  axis. If we make the assumption that the radial functions of all the d-orbitals in the band are approximately the same, then we may extract  $\langle 1/r^3 \rangle$  from the latter expression, finding

$$K_{orb} = [2\langle 1/r^3 \rangle / N_A] \chi_{orb}, \quad (2.3.5)$$

where the quantity in brackets is identified as the orbital shift coefficient  $\alpha_{orb}$ . When using calculated ionic values for  $\langle 1/r^3 \rangle$  [47], the foregoing authors suggest that a correction factor  $\xi = \langle 1/r^3 \rangle_{metal} / \langle 1/r^3 \rangle_{ion} \simeq 0.75$  be invoked for realistic estimates of the metallic shift coefficient  $\alpha_{orb}$ .

### ***Analysis of NMR Shift and Susceptibility for d-Band Metals: The $(\mathbf{K}, \chi)$ plot***

With the foregoing additions to our list, we are now in a position to formulate a complete model of the shift and susceptibility of a d-band metal. The following model would apply to a pure metal from the 3d, 4d, or 5d transition series, but is also intended to represent a binary or ternary intermetallic compound as long as its Fermi surface can be modeled with two bands, an sp-band which belongs mostly to the transition metal atoms and a d-band which belongs exclusively to the transition metal atoms. The p-orbitals on the ligands are assumed to be strongly mixed into the d-band, while the s-orbitals are not, i.e. are presumably nearly filled [46]. We then write for the susceptibility,

$$\chi_{tot} = \chi_{dia} + \chi_s + \chi_d(T) + \chi_{orb}, \quad (2.3.6)$$

where  $\chi_s$  and  $\chi_d(T)$  are the spin-paramagnetic terms,  $\chi_{orb}$  is the d-electron orbital term given by (2.3.3), and  $\chi_{dia}$  is the core diamagnetic term. Among these,  $\chi_s$  is quite small, though its associated Knight shift may not be, so that any Landau diamagnetism is very small, indeed. Neither the latter nor  $\chi_{dia}$  has any appreciable NMR shift effect[48]. Molar susceptibilities are used throughout this volume<sup>18</sup>

<sup>18</sup> From the standpoint of the microscopic physics of solids, we regard the susceptibilities per atom  $\chi_{at}$  (or per formula unit  $\chi_{fu}$ ) as fundamental, representing the

The NMR shift for the nucleus of a transition-metal ion, then, has three significant terms [48],

$$K(T) = K_s + K_d(T) + K_{orb} = \alpha_s \chi_s + \alpha_d \chi_d(T) + \alpha_{orb} \chi_{orb}, \quad (2.3.7)$$

in conventional notation for the shift coefficients. Typically, the only temperature dependence originates in  $\chi_d(T)$ . Therefore an experimental plot of  $K(T)$  vs.  $\chi_{tot}(T)$  with  $T$  as the implicit variable should yield a straight line of slope  $\alpha_d$ . An experimental  $K$  vs.  $\chi$  plot is just the beginning of a full  $(K, \chi)$  analysis of the various terms in (2.3.6) and (2.3.7). Such an analysis for the case of Pt metal was presented in [48], with the plotted result shown here in Fig. 2.8. We give a brief account of the analytic procedure.

First, any  $K - \chi$  analysis must begin at the origin, and several parameters need to be estimated in order to proceed. We refer the reader to the original paper for full details. The first step is to plot  $\chi_{dia} \simeq -28 \times 10^{-6} \text{emu/mole}$

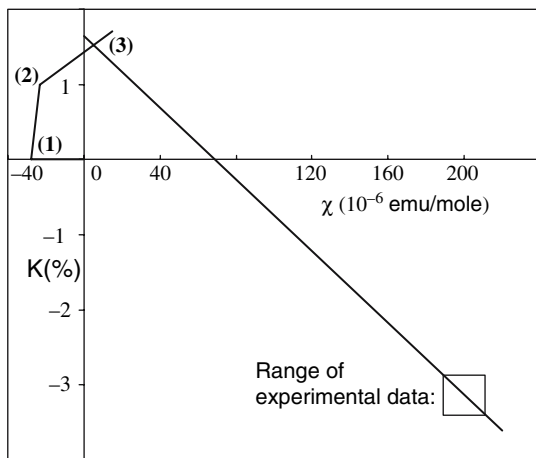


**Fig. 2.8.** A  $K$ - $\chi$  plot is shown for  $^{195}\text{Pt}$  in Pt metal. Plotting of successive contributions to  $(K, \chi)$  carries one from the origin to point 1 ( $\chi_{dia}$ ), then from point 1 to point 2 ( $K_s, \chi_s$ ), and finally from point 2 with an estimated slope  $\alpha_{orb}$ . The intersection at point 3 with the line through the experimental data completes the partition of the susceptibility. A detailed discussion of the analysis is given in the text. Reprinted figure from A. M. Clogston, V. Jaccarino, Y. Yafet: Phys. Rev. **134**, A650 (1964). Copyright 1964 American Physical Society

---

magnetic polarization which occupies one Wigner-Seitz (or unit) cell. Their companion molar susceptibilities are  $\chi_M = N_A \chi_{at}$  and  $\chi_{Mfu} = N_A \chi_{fu}$ . If  $\Omega$  is the atomic (or  $\Omega_c$  the unit cell) volume, then the dimensionless volume susceptibility fundamental to electromagnetic theory is  $\chi_V = \chi_{at}/\Omega$  ( $\chi_{fu}/\Omega_c$ ), and the gram susceptibility is  $\chi_{gm} = \chi_{at}/\Omega\rho$ , where  $\rho$  is the volume density. It is clear that the actual dimensions of  $\chi_M$  are  $\text{cm}^3$  and of the  $\alpha$  shift coefficients are  $\text{cm}^{-3}$ , although these are usually cited as  $\text{emu/mole}$  and  $(\text{emu/mole})^{-1}$ .

at  $K = 0$  (point 1), since there is no appreciable diamagnetic shift [48]. This value of  $\chi_{dia}$  may be taken from the literature [49]. From point 1 we construct a line of slope  $\alpha_s$  to extend over the interval  $\Delta\chi = \chi_s$ . For this step,  $\alpha_s$  was obtained from HF structure parameters derived from optical data, yielding  $\alpha_s \simeq 2.12 \times 10^3 (emu/mole)^{-1}$ .  $\chi_s$  is estimated using a free-electron model, where the number  $n_{s,d}$  of ( $s, d$ ) electrons satisfies  $n_s + n_d = 10$ . With a parabolic model for the 5d-band a value of  $n_s = 10 - n_d = 0.2$  was obtained, giving  $\chi_s \simeq 4.8 \times 10^{-6} (emu/mole)$ . The s-band line in Fig. 2.8 then extends from point 1 to point 2. Next, we construct a line from point 2 with a slope equal to the estimated value of  $\alpha_{orb} = 2\langle 1/r^3 \rangle / N_A$ . The ionic value of  $\langle 1/r^3 \rangle$  has been estimated to be 9.5a.u. from HF spectroscopic data, leading to the value  $\alpha_{orb} \simeq 264 (emu/mole)^{-1}$ , including a relativistic correction [48]. Drawing a line with slope  $\alpha_{orb}$  from point 2, the intersection of that line with the line through the data (point 3) then partitions the remaining susceptibility into orbital and d-spin contributions as shown.

In the case of Pt metal,  $\chi_{tot}$  is dominated by  $\chi_d(T)$ , and  $\chi_{orb}$  is a relatively small fraction ( $\simeq 15\%$ ) of  $\chi_{tot}$ . In cases where  $\chi_{orb}$  is a significant fraction of the total, its temperature dependence may be a big enough effect so that a simple  $(K, \chi)$  plot is no longer reliable [48]. Nonetheless, the  $(K, \chi)$  method has been widely used to analyze NMR shift data with experimental susceptibilities. For example, it was used to determine that substantial  $\chi_{orb}$  terms were present in the  $V_3X$ 's and in V metal [45]. We reproduce in Table 2.3 the table of results from [45].

In this table, values of  $\chi_{orb}$  from  $(K, \chi)$  analyses are subtracted from experimental susceptibilities to estimate  $\chi_d$ , which is given as  $\chi_{expt} - \chi_{orb}$ . The latter values are then to be compared with d-spin susceptibilities estimated from the specific heat coefficient  $\gamma$ , where  $\chi_{sp.ht.} = 3\mu_B^2\gamma/\pi^2k_B^2$ . A simple theory gives electron-phonon enhancement of  $\gamma$  by a factor  $[1 + N(0)\mathcal{V}]$ .  $\mathcal{V}$  is the BCS electron-phonon interaction parameter. Since  $\chi_d$  is not so enhanced

**Table 2.3.** Table of susceptibility components and BCS parameters for  $V_3X$  compounds and V metal. The estimates for  $\chi_{orb}$  were determined using  $(K, \chi)$  plot analyses. The values of  $\chi_d = \chi_{expt} - \chi_{orb}$  so deduced are checked using density-of-states estimates from specific heat data as corrected for electron-phonon enhancement by means of BCS theory. See text for detailed explanation. All susceptibilities are in units of  $10^{-4}$  emu/mole

|         | $R \equiv \chi_d(0) / \chi_d(T_c)$ | $\chi_{expt}$ | $\chi_{orb}$ | $\chi_{sp.ht.}$ | $\chi_{expt} - \chi_{orb}$ | $N(0)\mathcal{V} (Sp.Ht.)$ | $N(0)\mathcal{V} (BCS)$ |
|---------|------------------------------------|---------------|--------------|-----------------|----------------------------|----------------------------|-------------------------|
| $V_3Ga$ | $0 \leq R \leq 0.25$               | 17.9          | 5.2–7.5      | 14.0            | 12.7–10.4                  | 0.13–0.39                  | 0.35                    |
| $V_3Si$ | $0 \leq R \leq 0.25$               | 15.7          | 5.2–7.5      | 10.7            | 10.5–8.2                   | 0.09–0.35                  | 0.35                    |
| V       |                                    | 3.08          | 2.11         | 1.22            | 0.971                      |                            | 0.244                   |

[50], one may estimate  $\mathcal{V}N(0) \simeq \chi_{sp.ht.}/\chi_d - 1$ . In the last two columns of Table 2.3, values of  $N(0)\mathcal{V}$  deduced in that way are compared with those derived from  $T_c$  using the BCS formula  $N(0)\mathcal{V} = [ln(0.855\theta_D/T_c)]^{-1}$ . Considering the difficulty of estimating the relevant parameters, this analysis gives a nicely consistent picture in which it is established that (a)  $\chi_d$  at  $T \ll T_c$  is a small fraction of its normal-state value, and (b), values of  $\chi_d$  consistent with electron-phonon enhancement of  $\gamma$  are obtained. Note that  $\chi_s \simeq 0.3$  (units of Table 2.3) has been ignored and is essentially negligible.

### 2.3.3 Spin-Lattice Relaxation Effects for d-Band Electrons

An open d-band brings added richness - and complications - to the  $T_1$  process as well, contributing a total of three additional terms to the  $T_1$  rate. These are the d-spin core polarization (CP), the d-spin dipolar, and the d-orbital terms. The d-orbital relaxation process was first discussed by Obata [51]; we shall spell out the results of that calculation below. The general treatment of the CP relaxation process, on the other hand, is an enterprise of great complexity. Under a set of straightforward restrictions, Yafet and Jaccarino have presented a very clear discussion of this problem [52], which has been useful under a variety of circumstances. Here we discuss briefly the approximations employed and give the results.

The stated approximations are as follows:

- Spin-orbit coupling is disregarded.
- The unperturbed states (i.e. without HF terms) are taken to be Hartree-Fock solutions of the simplified Hamiltonian.
- Exchange integrals responsible for the CP effect are treated in first order.
- Exchange effects between conduction band orbitals are neglected.
- Conduction band states are self-consistent Bloch states, which are admixtures of s, p, and d orbitals.
- The conduction band d-states are treated in a tight-binding approximation.
- Finally, consideration is limited to the case of a cubic metal. As a result, the cross terms between sp and d-orbital matrix elements can be shown to vanish.

The resulting expressions for the shift and relaxation rate are:

$$K = \frac{4\pi}{3}(\gamma_e\hbar)^2[\langle\phi_s^2(0)\rangle(1 - F_d) - |\phi_{cp}(0)|^2 F_d]n(E_F) \quad (2.3.8)$$

and

$$\begin{aligned} \frac{1}{T_1 T} = & \frac{4\pi k_B}{\hbar} \left[ \frac{4\pi}{3} \gamma_n \gamma_e \hbar^2 \right]^2 [\langle\phi_s^2(0)\rangle(1 - F_d)^2 \\ & + |\phi_{cp}(0)|^4 F_d^2 (\frac{1}{3}f^2 + \frac{1}{2}(1 - f)^2)] n(E_F)^2, \end{aligned} \quad (2.3.9)$$

where  $F_d$  is the fraction of d-character of all the states at the Fermi surface, and  $n(E_F)$  is the total density of states (of all “bands”) at the Fermi surface. Thus, even if there is appreciable s-d mixing in the Bloch functions the contributions to shift and relaxation will occur separately as shown. CP terms are only kept for the d-orbitals, even though they may occur in the calculation for the s and p orbitals. The reason for this is that the contact terms dominate the sp regions of the Fermi surface, and any CP terms are neglected for those states as small corrections.

The parameter  $f$  gives the relative weight of  $\Gamma_5$  character for d-orbitals at the Fermi surface, while  $1 - f$  gives the proportion of  $\Gamma_3$  character<sup>19</sup>. It is seen that the sp-contact and d-CP portions of the formulas for  $K$  and  $1/T_1T$  obey separate Korringa-like relations (see 2.2.8), where the Korringa relation for the CP terms has a reduction factor  $q(f) = \frac{1}{3}f^2 + \frac{1}{2}(1 - f)^2$ , i.e.

$$\frac{1}{T_{1cp}T} = \frac{4\pi k_B}{\hbar} \left[ \frac{4\pi}{3} \gamma_n \gamma_e \hbar^2 |\phi_{cp}(0)|^2 \right]^2 n_d(E_F)^2 q(f) = \frac{4\pi k_B \gamma_n^2}{\hbar \gamma_e^2} K_{cp}^2 q(f), \quad (2.3.10)$$

where the second equality shows the modified Korringa relation.  $q(f)$  is essentially a degeneracy factor, having a value 1/2 for the two  $\Gamma_5$  orbitals ( $f = 1$ ), 1/3 for the three  $\Gamma_3$  orbitals ( $f = 0$ ), and 1/5 when all five d-orbitals are equally weighted ( $f = 0.6$ ). Thus the five d-orbitals contribute independently to  $1/T_{1CP}$ , very much like the fluctuations of separate magnetically-active neighbors contribute to the  $T_1$  process of a ligand nucleus. The difficulty in utilizing (2.3.10) is that the parameter  $f$  for d-band metals is generally unknown.

The orbital  $T_1$  process was first discussed in detail by Obata [51], treating both orbital and dipolar relaxation rates in the same calculation. As with the CP calculation above, spin-orbit coupling is neglected, the d-orbitals are treated in a tight-binding approximation, and the system considered is a cubic metal. There are no cross terms between orbital and spin-scattering relaxation processes. It was noted in [52] that the dipolar process has interference with the contact and CP processes, but if the states at the Fermi surface can be separated into a d-band and an sp-band, then the interference terms vanish. For a cubic metal, both the orbital and dipolar relaxation rates are isotropic, but both depend on the symmetry parameter  $f$ , according to

$$\frac{1}{T_{1orb}T}, \left[ \frac{1}{T_{1dip}T} \right] = \frac{4\pi k_B}{\hbar} [\gamma_n \hbar H_{orb}]^2 n_d(E_F)^2 p(f), [d(f)], \quad (2.3.11)$$

where  $H_{orb} = 2\mu_B \langle 1/r^3 \rangle$ ,  $p(f) = \frac{2}{3}f[2 - \frac{5}{3}f]$ , and  $d(f) = \frac{5}{49}[\frac{1}{3}f^2 + \frac{2}{5}(1 - f)]$ .

Comparison of the dependences of  $q(f)$ ,  $p(f)$  and  $d(f)$  on  $f$  is shown in Fig. 2.9. The orbital relaxation rate ( $p(f)$ ) is seen to vary from zero, when the  $\Gamma_5$  orbitals alone are occupied at the Fermi surface, to a maximum when all

<sup>19</sup> In the present notation of d-functions in the cubic space group,  $\Gamma_3$  refers to the d functions  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$ , while  $\Gamma_5$  refers to  $d_{x^2-y^2}$  and  $d_{3z^2-r^2}$ .

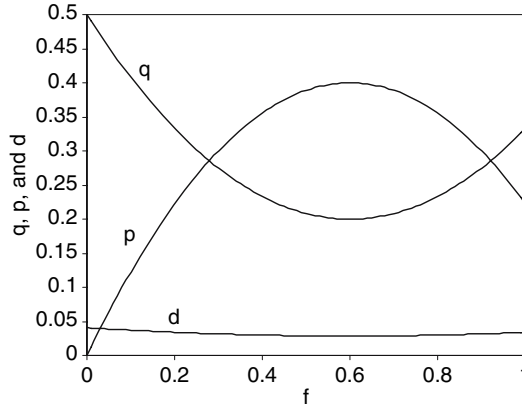


**Fig. 2.9.** The symmetry factors  $q(f)$ ,  $p(f)$ , and  $d(f)$  pertaining to CP, orbital, and dipolar relaxation rates discussed in the text [52], respectively, are plotted as a function of the fraction  $f$  of  $\Gamma_5$  character in the relevant d-band orbitals at the Fermi surface. The point  $f = 0.6$  represents equal weight of all five d-orbitals and is the maximum and minimum point of  $p(f)$  and  $q(f)$ , respectively. In many cases the dipolar rate is negligible, as it is only  $\sim 9\%$  of the average value of the closely related orbital rate. Reprinted figure from Y. Yafet, V. Jaccarino: Phys. Rev. **133**, A1630 (1964). Copyright 1964 American Physical Society

five orbitals are equally occupied, since the orbital matrix elements between the two symmetries are the largest ones. The dipolar relaxation rate ( $d(f)$ ) varies only slightly across the full range of  $f$ , but it is only about 10% of the average value of  $p(f)$ . Thus, the dipolar relaxation is only significant when  $p(f)$  is near zero.

The complete list of magnetic relaxation processes for d-band metals is then

$$1/T_1 = 1/T_{1s} + 1/T_{1cp} + 1/T_{1orb} + 1/T_{1dip}. \quad (2.3.12)$$

We illustrate the analysis of experimental  $T_1$  rates into these different contributions with calculations given in [52] for d-band metals V and Nb. In stating these results we define  $H_s = (8/3)\pi\mu_B\langle\phi_s^2(0)\rangle$  and  $H_{cp} = (8/3)\pi\mu_B|\phi_{cp}(0)|^2$ , whereupon (2.3.9) becomes

$$\frac{1}{T_{1s,cp}T} = \frac{4\pi k_B}{\hbar} [\gamma_n \hbar H_{s,cp}]^2 n_{s,d}^2 [1, q(f)] \quad (2.3.13)$$

for the s-band and CP contributions. The parameters  $H_{s,cp}$  are the HF fields per unit of spin from these sources. The  $T_1$  contributions from the three main sources have been estimated [52] for V and Nb metals as listed in Table 2.4. For this purpose,  $H_s$  has been estimated using data from the literature [52], and  $H_{cp}$  and  $H_{orb}$  have been derived from Hartree-Fock calculations given by Freeman and Watson [53]. The total densities of states for these elements are taken from specific heat measurements, where the s-band components are

**Table 2.4.** Table of HF parameters and specific heat densities of states leading to estimates of  $(T_1T)^{-1}$  for elemental  $V$  and  $Nb$  using the formulas given in the text. The total relaxation rates are stated for  $f = 0.6$ , but would not change significantly for other values of  $f$ . The theoretical estimate undoubtedly exceeds the experimental numbers because of the electron-phonon enhancement of the specific heat density of states, which does not affect nuclear relaxation rates. See text for data sources and additional discussion. HF fields are given in units of  $10^6 Oe$ , densities of states in states/eV-atom, and relaxation rates in  $(sK)^{-1}$

|    | $H_s$ | $H_{cp}$ | $H_{orb}$ | $n_s(E_F)$ | $n_d(E_F)$ | $R_s$ | $R_{cp}$ | $R_{1orb}$ | $(T_{1calc}kT)^{-1}$ | $(T_{1exp}T)^{-1}$ |
|----|-------|----------|-----------|------------|------------|-------|----------|------------|----------------------|--------------------|
| V  | 1.12  | -0.117   | 0.19      | 0.12       | 1.84       | 0.642 | 1.65     | 4.35       | 2.86                 | 1.27               |
| Nb | 2.48  | -0.21    | 0.285     | 0.14       | 1.66       | 3.76  | 3.74     | 6.9        | 7.55                 | 2.8                |

estimated assuming for simplicity one s-electron per atom. The quantities  $R_s$ ,  $R_{cp}$ ,  $R_{orb}$  are defined to be the expressions given above for  $1/T_1T$  from these sources *without the symmetry factors*  $[1, q(f), p(f)]$ . The experimental values of  $(T_{1exp}T)^{-1}$  are data reported by Butterworth [54].

This table illustrates the importance of the CP and orbital relaxation mechanisms in d-band metals. For the lighter metals, where the s-band contribution is smaller, these d-electron terms may even be the dominant ones. On the other hand, we see that the specific heat density of states clearly overestimates the relaxation rates, pointing to a substantial electron-phonon enhancement effect for V and Nb metals (which are also superconductors). In [5] a quantitative discussion of the latter effect is given, finding reasonable agreement between the nuclear relaxation data and estimates from other measurements, somewhat like the comparisons in Table 2.3. As the details go beyond the intended scope of this discussion, the reader is referred to [5] and references therein for details.

This completes our discussion of normal-state NMR shift and relaxation effects in transition metals. The mechanisms in (2.3.2) and (2.3.12) are the foundation of effects to be found in high- $T_c$  materials, though the details remain to be worked out. We next consider the effects of Type II superconductivity in the d-band metals.

### 2.3.4 NMR Studies of 3d Metals as Type-II Superconductors

The type-II superconductivity of d-band metals and intermetallic compounds presents a rather different set of problems from those of the type-I systems discussed in Sect. 1.2.2. First, type-II systems exhibit great complexity of behavior in a magnetic field, showing three phases as a function of the magnitude of the applied field for  $T < T_c$  and exhibiting two critical fields,  $H_{c1}$  and  $H_{c2}$ . Below  $H_{c1}$  there is the typical Meissner exclusion of all magnetic flux except for the usual penetration depth  $\lambda$ .

Between  $H_{c1}$  and  $H_{c2}$  there is a state of essentially complete, but inhomogeneous field penetration in the form of superconducting current vortices

which allow a single fluxon of field to exist in a region of normal (i.e. non-superconducting) metal with a diameter  $\sim \xi_0$ , the Pippard coherence length. Of course, the magnetic field of a fluxon penetrates the surrounding material to a depth of  $\sim \lambda$ . Each fluxon comprises one flux quantum  $\Phi_0 = hc/2e = 2.07 \times 10^{-7} G cm^2$ .

Because of the accommodation of type-II superconductivity to applied fields through the penetration of vortices, the superconducting state can persist up to fields much higher than the thermodynamic critical field  $H_c$ . One can make a rough estimate of  $H_{c2}$  using a picture of vortices with normal cores of approximate radius  $\xi_0$ . In the mixed state with field  $H$  ( $T \ll T_c$ ) the density of vortices is  $H/\Phi_0$ . The fraction of normal sample material is then  $\sim \pi \xi_0^2 H/\Phi_0$ . Setting this expression equal to 1 gives an estimate  $H_{c2} \sim \Phi_0/\pi \xi_0^2$ . This is only slightly larger than the expression deduced from Ginzburg-Landau (GL) theory,

$$H_{c2} = \frac{\Phi_0}{2\pi \xi_0^2}. \quad (2.3.14)$$

As was first demonstrated by Abrikosov [55], the normal-superconducting boundary wall has positive energy for  $\lambda < \sqrt{2}\xi$ . On the other hand, if the GL parameter  $\kappa = \lambda/\xi > \sqrt{2}$ , then the boundary wall has negative energy, so that the system will lower its free energy by making the boundary area as large as possible. Thus, the field arranges itself into individual fluxons, each surrounded by a normal-superconducting wall. Abrikosov predicted the existence of such a *mixed state*, in which the vortices arrange themselves (in reasonably clean material) into an ordered lattice [55]. The lowest energy state of such a lattice was shown to be minimized by a triangular arrangement of vortices by Kleiner et al., [56]. Below, we describe NMR spectra which are consistent with this theoretical conclusion.

It is interesting to look at simple expressions for  $\xi$  and  $\lambda$  to see why there is a general tendency for d-electron superconductors to exhibit type-II superconductivity. The expressions

$$\lambda_0 = \left[ \frac{m c^2}{4\pi n_s e^2} \right] \quad \text{and} \quad \xi_0 = a \frac{\hbar v_F}{k_B T_c}, \quad (2.3.15)$$

where  $a$  is a constant of order unity, come from the London equations and from Pippard's uncertainty principle argument, respectively. Since d-bands tend to have large effective masses and high- $T_c$  materials in particular have low carrier densities  $n_s$ , we expect  $\lambda_0$  values to be larger than for sp-band superconductors. Furthermore, small values of  $E_F$  (and thus of  $v_F$ ) as well as higher values of  $T_c$  will make for short  $\xi_0$ 's. Thus, it is generally expected that  $\lambda > \sqrt{2}\xi_0$ . As an example, we mention  $V_3Si$ , a superconductor at  $\sim 17K$  which we shall discuss further below. Here, we only note that Greytak and Wernick [57] reported a measurement of  $\lambda_0 = 1500 \text{\AA}$  and a related estimate of  $\xi_0 = 25 \text{\AA}$ . Thus,  $\kappa \simeq 60$  and from (2.3.14) we estimate  $H_{c2} \simeq 530 kG$ . A second estimate can be made from the thermodynamic critical field  $H_c = 6370 G$  [58]

and the measured value of  $\lambda_0$  using (4-62) from [6],  $H_{c2} = 4\pi\lambda_0^2/\Phi_0$ . This yields  $H_{c2} = 550kG$ , which is in surprisingly good accord with the previous number. In any case,  $V_3Si$  is a very “hard” superconductor, indeed.

### *Internal Field Distributions in the Mixed State from NMR Studies*

NMR studies of type-II superconductors are typically done in the mixed state, i.e. for  $H_{c1} < H < H_{c2}$ . There is substantial NMR line broadening from spatially-dependent shielding supercurrents in the mixed state. We shall first review studies conducted to map the distribution of such currents, after which we will look at shift and relaxation studies. A number of internal field studies have been reported for V and Nb metals [59, 60, 61]. We review briefly the results given by Redfield [60], who conducted the following field-switching NMR experiment on  $^{51}V$  in V metal. The sample was polarized in  $\simeq 10kG$ , after which the field was switched to a value below  $H_{c2} \sim 3,000G$  for a time of  $0.1s$ , during which an  $rf$  field was applied transverse to the steady field. The field was then switched back to  $10kG$  where the nuclear polarization was recorded. By scanning the frequency of the  $rf$ , the spectrum of internal fields could be mapped out. Results from this study are shown in Fig. 2.10a for two field values. These data have been fitted to calculated internal field distributions based on the GL equations in the Abrikosov limit, assuming both square and triangular lattices [60]. The raw calculated distributions are shown in Fig. 2.10b. Fits are carried out by convoluting the latter distributions with a Gaussian of adjustable width, then adjusting the width and total area for best fit.

The triangular lattice unit cell is shown as an inset to Fig. 2.10b, where the points V, C, and S are seen to correspond to the maximum field, minimum field, and the singularity in the distribution, respectively. The singularity appears much closer to C for triangular lattice than for the square lattice. Results for the lower field value ( $\simeq 0.73H_{c2}$ ) are seen to be in good accord with the triangular lattice. The higher field value is rather closer to  $H_{c2}$ , where a kind of gapless superconducting state sets in and there are many corrections to the simple field-distribution calculation. Thus, it is not surprising that the simple triangular lattice calculation is no longer accurate [60]. Studies of effects near  $H_{c2}$  are reviewed in [5]. We shall, however, restrict our attention here to the region  $H_{c1} \ll H \ll H_{c2}$ .

It is interesting to compare the field distribution results from [60] with theoretical predictions. For example, the results from Kleiner, et al., [56] predict that  $H_V - H_S = 1.35(H - B)$ . From [60] we find for the conditions of Fig. 2.10 the experimental value  $H_V - H_S = 285G$ , while  $1.35(H - B)$  under the same conditions  $\simeq 165G$ , a considerable underestimate. On the other hand,  $1.35(H - B)$  according to the Abrikosov solution [5, 55] equals  $1.35(H_{c2} - H)/\beta_a(2\kappa^2 - 1)$ , which we find to be  $520G$ , which is a considerable overestimate. For this purpose we take  $\beta_a = 1.16$  for the triangular

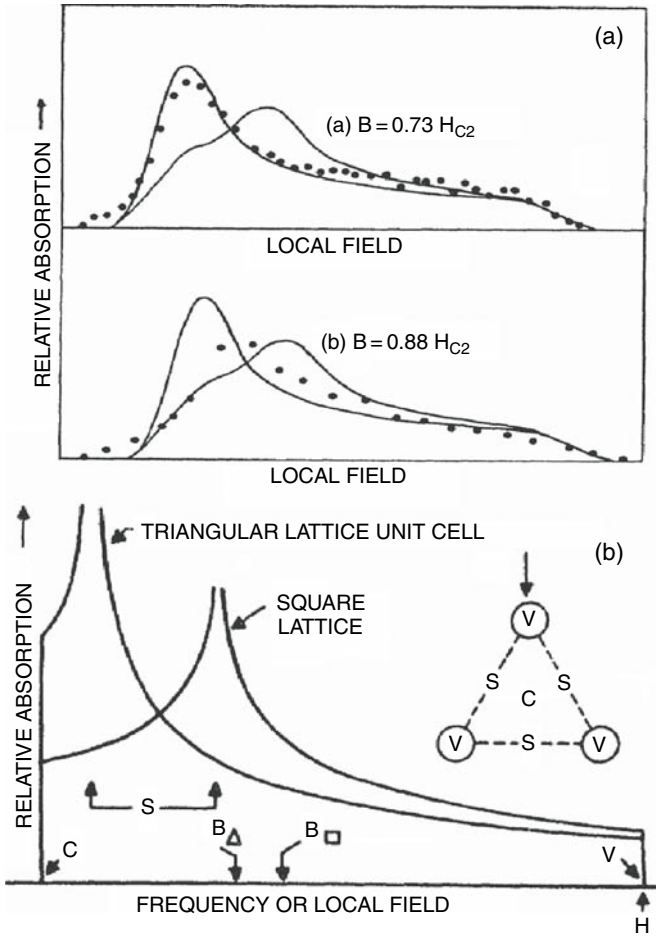


**Fig. 2.10.** (a) Distributions of diamagnetic shielding fields measured using *rf* saturation of the  $^{51}\text{V}$  NMR in superconducting V metal, and (b) simulations of internal field distributions under similar circumstances for both square and triangular vortex lattices. In (a) results are given for  $T \simeq 1.4\text{ K}$  and for fields of  $0.73 H_{c2}$  and  $0.88 H_{c2}$  as shown, where  $H_{c2} = 2720\text{ G}$ . For (b) the field simulations were done on the basis of solutions of the Ginzburg-Landau equations in the Abrikosov limit. The inset shows the triangular lattice unit cell, with points there and on the distribution labelled V, S, and C corresponding to a vortex (V), a saddle point (S) showing a divergence, and the minimum field (C). Reprinted figure from A. G. Redfield: *Phys. Rev.* **162**, 367 (1967). Copyright 1967 American Physical Society

lattice from [56] and employ (2.3.14) to obtain  $\xi_0 = [\Phi_0/2\pi H_{c2}]^{1/2} = 348\text{ \AA}$ . The estimate  $\lambda = 400\text{ \AA}$  [62] then leads to  $\kappa = 1.15$ . Substantial corrections to these simple theoretical results have been given by Eilenberger [63].

### *The NMR Shift in Type-II Superconductors*

In the foregoing study of elemental vanadium, the precision with which the vortex lattice could be characterized was not great enough to resolve changes in the d-spin shift  $K_d(T)$  below  $T_c$  [60]. However, in a truly *hard* type-II system where  $\kappa \gg 1$ , it is possible to resolve small shift changes at field values such that  $H_{c1} \ll H \ll H_{c2}$ . The reason for this is that the NMR lineshape is then strongly dominated by the singularity from the saddle regions S (Fig. 2.10b), which is therefore shifted only slightly away from the applied field. Moreover, the NMR linewidth from diamagnetic shielding is typically only modestly greater than one might find in the normal state.

We illustrate these points with data and discussion of the closely related cases of  $V_3Si$  and  $V_3Ga$ , where  $V_3Si$  was touted earlier as a truly hard superconductor. Interestingly, somewhat before the nature of the type-II diamagnetic shielding was investigated in detail in the 1960's, The NMR shifts in these compounds of both  $^{51}V$  and  $^{71}Ga$  were reported by Clogston et al., [45]. We reproduce their  $(K, \chi)$  plot in Fig. 2.11. The interesting point here is that all NMR shift values here are consistent with the interpretation that, at  $T = 1.8 K$ , the corresponding d-band susceptibility is diminished to  $\sim 25\%$  of its value at  $20 K$ . Further, its low temperature value is smaller than that at room temperature. Since these NMR shifts were measured in the mixed state at a field of  $14 kOe$ , where they found "negligible diamagnetic *rf* susceptibility" [45], one can only conclude that spurious frequency shift effects from the diamagnetic shielding are negligibly small in comparison. Note that the total range of  $^{51}V$  shift values in Fig. 2.10 is only  $\sim 0.1\%$ .

It is interesting to consider the nature of the internal field distribution in  $V_3Si$  given the values of its parameters  $\xi_0$  and  $\lambda_0$  ( $25\text{\AA}$  and  $1500\text{\AA}$ , respectively) stated above. First, the second moment of this distribution has been calculated by Pincus et al., [58], yielding the expression

$$\langle \Delta H^2 \rangle_{av}^{1/2} \simeq \frac{\Phi_0}{4\pi^{3/2}\lambda^2} \quad (2.3.16)$$

under conditions where not only  $H_{c1} \ll H \ll H_{c2}$  holds, but also  $\lambda/d \gg 1$ , where  $d$  is the separation of vortices in the mixed state. At  $H = 14 kOe$  (i.e. for the data of Fig. 2.11), we find  $d = [2\Phi_0/\sqrt{3}H]^{1/2} = 413\text{\AA}$  for the triangular lattice, giving  $\lambda/d = 3.6$ . For these conditions (2.3.16) gives  $\langle \Delta H^2 \rangle_{av}^{1/2} = 41 Oe$  for a square lattice. This may be a slight overestimate, but is of the right order, since the measured peak-to-peak derivative linewidth is  $39 \pm 5 Oe$  [58]. It is interesting to note in this case, where  $\kappa \gg 1$ , the Abrikosov relation [5, 55] yields  $H_V - H_S = 86 G$ , barely twice the second moment estimate.

We therefore find for the hard type-II superconductors that it is quite feasible to measure shift values with weak temperature dependences in the mixed state of superconductivity. This is a very important result for high- $T_c$  NMR studies.

### 2.3.5 $T_1$ Phenomenology for Type-II Superconductors

In this final subsection of Chap. 2 we review  $T_1$  behavior at  $T < T_c$  for type-II d-band superconductors. Because of the complications which attend the measurement and interpretation of  $T_1$  in the *mixed state* of these systems, our discussion of this topic will be limited to a few simple cases. A clear and thorough discussion of these effects, in terms of both theory and experiment, is given in [5]. The hallmarks of type-I system  $T_1$  behavior are the coherence peak (in  $T_1^{-1}$ ) just below  $T_c$  and the exponential decay  $T_1^{-1} \propto \exp(-\Delta_0/k_B T)$

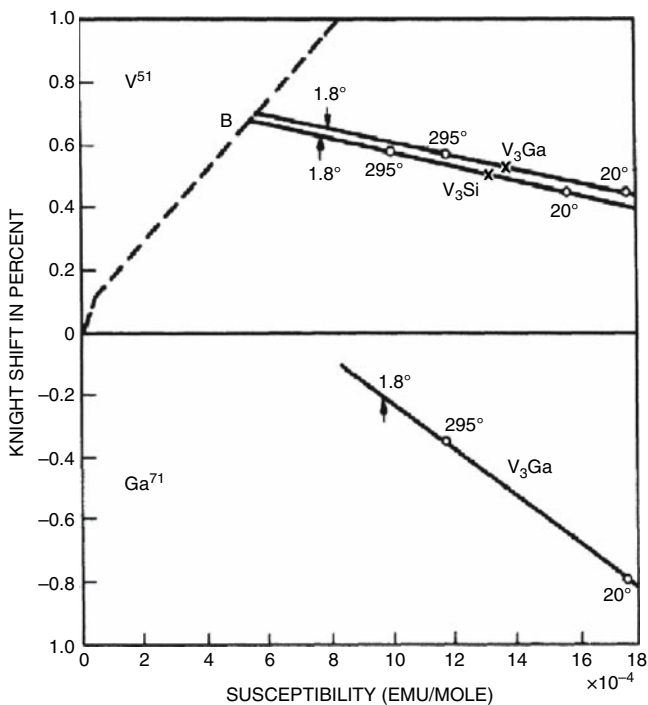


**Fig. 2.11.** Measured Knight shifts are plotted vs. molar susceptibilities for  $^{51}V$  in both  $V_3Si$  and  $V_3Ga$  and for  $^{71}Ga$  in  $V_3Ga$  [45]. For the  $^{51}V$  shifts a  $(K, \chi)$  construction is shown, including the s-band contribution (point A) and the orbital contribution (points A-B), which intersects with lines through the data points. For the  $^{71}Ga$  the results clearly show a transferred shift which is driven by the temperature-dependent d-band susceptibility. In both cases the location of the shift values measured at 1.8 K are shown, indicating that the negative CP shift is diminished to  $\sim 75\%$  of its value at 20 K, and that the values of  $|K_d(T)|$  in both cases are smaller than the values found at room temperature. Reprinted figure from A. M. Clogston, A. C. Gossard, V. Jaccarino, Y. Yafet: Phys. Rev. Lett. **9**, 262 (1962). Copyright 1962 American Physical Society

for  $T \ll T_c$ . For type-II systems these behaviors carry over in a modified way or not at all. The differences found between type-I and type-II behavior appear to be caused by the field penetration in the mixed state and the consequent spatial inhomogeneities.

### *The Coherence Peak Region, $T \leq T_c(H)$*

Caroli et al., have shown that in the vicinity of a vortex core the excited state energies are diminished to  $\Delta E \sim \Delta_0^2/E_F \ll \Delta_0$  [64]. Thus, for points near the  $(H, T)$  phase boundary, i.e. for  $H$  near  $H_{c2}(T)$ , there is a gapless region which has received a detailed theoretical examination [65, 66, 67]. The fluctuation (i.e.  $T_1$ ) properties in this region are different from a type-I system and appear to depend on whether the carriers have a long mean-free path  $l \gg \xi_0$  (“clean”) or whether it is short  $l < \xi_0$  (“dirty”). In the simpler dirty limit case the electronic properties are local in character, and Cyrot [68] has derived the relation

$$\frac{T_{1n}}{T_{1s}} = 1 + \frac{ec}{\sigma k_B T_c} (H_{c2} - H) g(t), \quad (2.3.17)$$

where  $t = T/T_c$ ,  $\sigma$  is the normal state conductivity and  $H_{c2} = H_{c2}(T)$ . This relation is only valid for  $(H_{c2} - H) \ll H_{c2}$ , so that it only gives the slope  $T_{1n} d(T_{1s}^{-1})/dH$  near  $H_{c2}$ . The function  $g(t) > 0$  for  $t > 0.6$ , while  $g(t) < 0$  below that point. One must be very careful in using (2.3.17) to interpret actual data, since  $T_1$  is usually measured by scanning temperature rather than field.

Masuda and Okubo have obtained  $T_1$  data on  $^{51}\text{V}$  in  $\text{V}_3\text{Sn}$ , a superconductor with  $T_c \simeq 3.6\text{ K}$  (their sample) and  $H_{c2}(0) = 16\text{ kG}$  [69, 70]. Their data are shown for three values of applied field in Fig. 2.12. These authors used (2.3.17) to show that

$$d(T_{1n}/T_{1s})/dT \propto g(t) \quad (T \leq T_c(H)), \quad (2.3.18)$$

as well, and have evaluated the constant of proportionality. We note that for  $H = (4470, 8940, 13410)\text{ G}$ ,  $T_c(H) = (3.2, 2.6, 1.8)\text{ K}$  and thus  $t(H_{c2}) = (0.89, 0.72, 0.50)$  for the three data curves in Fig. 2.12. Thus, the slopes of the data plots at  $T \leq T_c$  are nicely consistent with these parameters, since  $d(T_{1n}/T_{1s})/dT$  is positive for the first two, then turns negative for the third, where  $t(H_{c2})$  falls below 0.6. It seems, then, that measurements at low (or zero) field on  $\text{V}_3\text{Sn}$  yield a conventional BCS coherence peak, but that it is gradually quenched out by fluxoids at higher field values.

We mention three other cases of type-II  $T_1$  studies at  $T \leq T_c$ . Each is somewhat anomalous in its own way. The first is the case of elemental V metal [71], where no convincing coherence peak was observed. The authors considered a number of possible explanations, finally suggesting that the  $T_1$  peak may be suppressed by trapped flux. However, sometime after these results were published, a theory of  $T_1$  in the clean limit emerged [65], and this interpretation was applied to the case of vanadium by Pesch [67]. The result

was a good fit to the data for both samples [71], with no sign of a coherence peak. It seems, then, that coherence peaks will appear at low fields in the dirty limit, but not in clean samples.

No coherence peaks were observed in any of the  $V_3X$  compounds, where  $X = \text{Ga, Si, Ge, and Pt}$ , in the study conducted by Silbernagel et al., [72, 73]. The ostensible reason for this is disorder caused by the “Martensitic” structural transformation which was reported at temperatures just above  $T_c$  in these compounds [74, 75]. The authors offer no further discussion of the point [73].

The third and most anomalous case to be reported was that of niobium [76]. The relaxation of  $^{93}\text{Nb}$  nuclear spins was studied in the SC state at field values varying from  $2.40\text{ kG}$  up to  $6.80\text{ kG}$  corresponding to  $T_c$  values which vary from  $6.8\text{ K}$  down to  $3.0\text{ K}$ . Using (2.3.14),  $H_{c2}$  corresponds to  $\xi_0 \sim 200\text{ \AA}$ , so that the given mean-free path  $l \simeq 140\text{ \AA}$  is on the borderline between the clean and dirty cases. In any case, the  $T_1$  data were found to fit the gapless theory [66, 67] for the higher field values. For the lower two field values, however, the  $T_1$  data were found to execute a deep minimum just below  $T_c(H)$ , contrary to the gapless theoretical fits. Such behavior is clearly reminiscent of the  $V_3\text{Sn}$  data in Fig. 2.12, and one might inquire as to whether the calculation of  $d(T_{1n}/T_{1s})/dT$  given in [70] based on (2.3.17) could be applied in this case. The authors did such a calculation and found that the coefficient of  $g(t)$  for Nb is smaller by a factor 150–200, so that

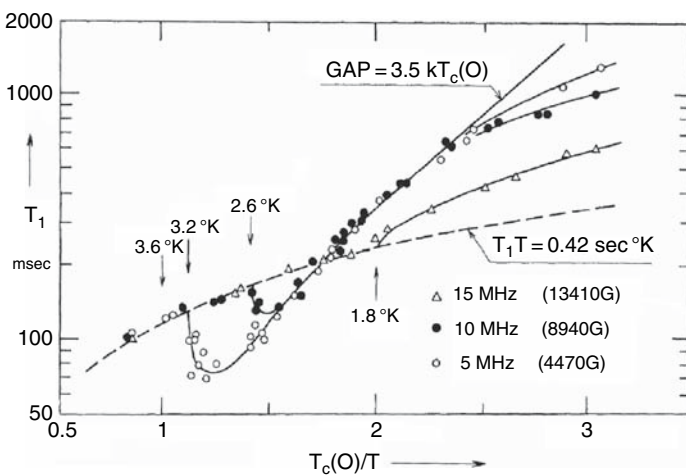


**Fig. 2.12.** A semilog plot of data for  $T_1$  of  $^{51}\text{V}$  in  $V_3\text{Sn}$  vs.  $T_c(0)/T$  in the superconducting state for three values of applied field [69]. The data shown exhibit coherence peaks for  $1341\text{ G}$  and  $8940\text{ G}$ , but not for  $13410\text{ G}$ . All three plots show deviations from the exponential BCS behavior at the lowest temperatures, an effect attributable to spin diffusion to the normal cores. See text for discussion. Reprinted figure from N. Okuda, Y. Masuda: Phys. Rev. Lett. **20**, 1475 (1968). Copyright 1968 American Physical Society

similar behavior cannot be expected on that basis. There seems to be no straightforward explanation for this anomalous result.

### **Type-II $T_1$ Behavior for $T \ll T_c$**

For values of  $T$  well below  $T_c$ , an exponential decay  $T_{1s}^{-1} \propto \exp(-\Delta_0/k_B T)$  has generally been found to appear. However, as this intrinsic BCS rate weakens, another contribution attributable to the fluxoids is often seen. Since the energy gap near the fluxoids is very small [64],  $T_{1s}$  for a region of area  $\sim \xi_0^2$  is essentially that of the normal state. When the BCS  $T_1$  process in the bulk of the SC material becomes very slow, then a process whereby the nuclear polarization diffuses to the normal cores becomes predominant. This process was found to be present in three of the four examples given above [69, 71, 72] but was studied most systematically in the case of  $V_3Si$  [72].

$^{51}V$   $T_{1s}$  data for  $V_3Si$  [72] are plotted semilogarithmically in Fig. 2.13 as a function of  $T_c/T$ , where  $T_c = 15.35 K$ . Results are given for four

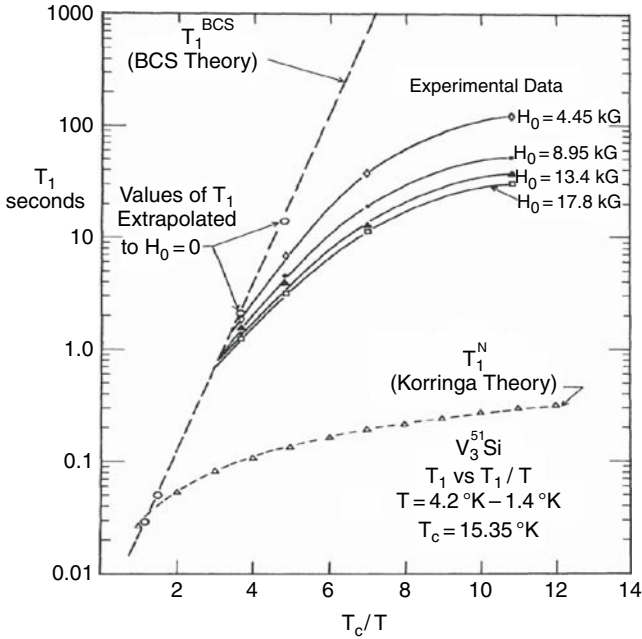


**Fig. 2.13.** A semilog plot of data for  $T_1$  of  $^{51}V$  in  $V_3Si$  vs.  $T_c/T$  in the superconducting state for four values of applied field as shown [72]. The data shown exhibit no coherence peaks, but follow exponential BCS-theory behavior up to  $T_c/T \sim 4$ . Beyond that point the mechanism of spin diffusion to the normal fluxoid cores takes over, giving a relaxation rate which is proportional to the applied field (i.e., to the fluxoid density), as expected. See text for further discussion. Reprinted figure from B. G. Silbernagel, M. Weger, J. H. Wernick: Phys. Rev. Lett. **17**, 384, (1966). Copyright 1966 American Physical Society

different field values at temperatures in the SC state which extend down below  $T_c/10$ . At higher temperatures the data points asymptotically approach the dashed line which represents BCS behavior, i.e.  $T_{1s} \propto \exp \Delta_0/k_B T$ , where  $\Delta_0 = 1.76 k_B T_c$ .  $T_{1s}$  veers away from the BCS curve at  $T_c/T \geq 4$ , then ranges up to values more than three orders of magnitude longer than its value at  $T_c$ . The flattening of these curves is suggested to be caused by spin diffusion to the normal cores, which then becomes the only effective  $T_1$  mechanism at the lowest temperatures. If the spin diffusion time, estimated below, is not an impediment, then at the lowest temperature we should have

$$\frac{T_{1n}}{T_{1s}} = \frac{p\xi_0^2 H}{\Phi_0}. \quad (2.3.19)$$

where  $p$  is a numerical factor of order unity. Equation (2.3.19) simply states that the normal  $T_1$  should be diluted by the ratio of  $p\xi_0^2$  to the area per fluxoid  $\Phi_0/H$ . First, we note that  $1/T_{1s}$  should be linear in  $H$ , as is clearly the case in Fig. 2.13. With the estimate  $\xi_0 \simeq 25\text{\AA}$  for  $V_3Si$  given above, we find  $p = 1.9$ , so that the effective area of normal-state relaxation is a circle of radius slightly smaller than  $\xi_0$  for each fluxoid. The corresponding spin diffusion times for the results in Fig. 2.13 can be estimated with

$$t_{diff} \sim \frac{d^2}{4D_{sp}}, \quad (2.3.20)$$

where  $d$  is the distance between fluxoids and  $D_{sp}$  is the spin diffusion constant. Taking  $d = [2\Phi_0/\sqrt{3H}]^{1/2}$  and  $D_{sp} \sim 10^{-12} \text{cm}^2 \text{s}$  [77], we find  $t_{diff} \sim 13 \text{s}$  at  $H = 4450 \text{ G}$ . This is an order of magnitude less than  $T_1$  itself, lending credence to the use of (2.3.19).

While the foregoing scenario gives an appealingly straightforward interpretation of the  $V_3Si$  data for  $T_{1s}$ , there did arise in the literature a rather knotty problem in connection with this interpretation. Genack and Redfield suggested some time later [78] that the spin diffusion relaxation mechanism in type-II superconductors would not work, because it did not conserve energy. We give the essence of their argument here, then cite further work which provided something of an antidote to this objection.

If spin diffusion takes place along a field gradient, then the simple flip-flop events between neighboring nuclei no longer conserve energy. The difference in Zeeman (field) energies has to be taken up by the spin-spin (usually dipolar) interactions. Viewing this process thermodynamically, the dipolar reservoir then quickly becomes overheated and must, itself, relax to the lattice. The total relaxation process by spin diffusion is thus formulated as a dual process, with Zeeman (magnetization) and dipolar energies both diffusing to the normal cores in the mixed superconducting state. These processes were analyzed in [78] and found to be too slow to provide the observed  $T_1$  processes in V metal [71]. It was concluded that these clearly observed diffusion-like  $T_1$  processes must originate in some other way [78].

The problem is, of course, that no other ideas to explain type-II relaxation have been forthcoming. However, more recently, this problem has been revisited in terms of basically the same ideas, but using more sophisticated mathematical methods (see [79] and references cited therein). These authors have analyzed in detail the relaxation curves of  $^{51}\text{V}$  in V metal at  $T \ll T_c$  taken from [71] in terms of spatially varying Zeeman and dipolar spin temperatures. They find a good fit to the vanadium data, where the dipolar relaxation time constants are relatively short, thus not obstructing the longer diffusion-mediated Zeeman  $T_1$ 's.

It seems, then, that the phenomenology of (2.3.19) is basically correct, so that low-temperature type-II  $T_1$  behavior is clearly understood. This is very important for the interpretation of  $T_1$  data for high- $T_c$  systems as well. However, as we shall see, the fundamental behavior of  $T_1$  in high- $T_c$  compounds involves SC gap symmetries which usually have line nodes, giving power-law behavior at low temperatures [80]. Thus, the issues regarding  $T_1$  data analysis differ somewhat from those of d-band SC metals discussed here. Nonetheless, the spin-diffusion-to-normal-cores  $T_1$  mechanism in the mixed state has been found to play a significant role in the phenomenology of cuprate superconducting  $T_1$  effects. The understanding of this effect gained with ordinary 3d metals will be an important resource in the chapters to follow.

## References

1. A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1983) 13, 14, 15, 19, 22, 33
2. C.P. Slichter, *Principles of Magnetic Resonance*, 3rd edn. (Springer-Verlag, New York, 1992) 13, 14, 15, 21, 25, 34
3. A. Narath, *Hyperfine Interactions*, ed. by A.J. Freeman and R.B. Frankel (Academic Press, New York, 1967), p.287 13, 35, 36, 37
4. J. Winter, *Magnetic Resonance in Metals*, (Clarendon Press, Oxford, 1971) 13
5. D.E. MacLaughlin, "Magnetic Resonance in the Superconducting State", in *Solid State Physics*, vol. 31, ed. by H. Ehrenreich, F. Seitz, D. Turnbull (Academic Press, New York, 1976), p. 1 13, 38, 40, 41, 42, 43, 53, 55, 57, 58
6. M. Tinkham, *Introduction to Superconductivity*, (McGraw-Hill, New York, 1975) 13, 41, 55
7. J.R. Schrieffer, *Theory of Superconductivity*, (Westview Press, Boulder, 1999) 13, 41
8. R.E. Walstedt, "The two-pulse spin echo revisited", in *Pulsed Magnetic Resonance: NMR, ESR and Optics*, ed. by D. M.S. Bagguley (Clarendon Press, Oxford, 1992), p. 242 18
9. E.L. Hahn, *Phys. Rev.* **80**, 580 (1950) 18
10. N. Bloembergen, T.J. Rowland, *Phys. Rev.* **97**, 1679 (1955) 19
11. M.A. Ruderman, C. Kittel, *Phys. Rev.* **96**, 99 (1954); T. Kasuya, *Prog. Theoret. Phys.* **16**; K. Yosida, *Phys. Rev.* **106**, 893 (1957) 19
12. C.H. Pennington, C.P. Slichter, *Phys. Rev. Lett.* **66**, 381 (1991) 19
13. R.E. Walstedt, *Phys. Rev. Lett.* **19**, 146 (1967); **19**, 816 (1967) 21

14. J. Van Kranendonk, *Physica* **20**, 781 (1954) 23
15. J. Bardeen, L.N. Cooper, J.R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957) 32, 38
16. L.C. Hebel, C.P. Slichter, *Phys. Rev.* **113**, 1504 (1957) 32, 40, 41, 42
17. W.D. Knight, *Phys. Rev.* **76**, 1259 (1949); C.H. Townes, C. Herring, W.D. Knight, *Phys. Rev.* **77**, 852 (1950) 33
18. J. Korringa, *Physica* **16**, 601 (1950) 33, 34
19. D.L. Randles, *Proc. Roy. Soc. London, Ser. A* **331**, 85 (1972) 34
20. R.E. Walstedt, Y. Yafet, A.I.P. Conference Proceedings **24**, 522 (1974) 34
21. D. Pines, in *Solid State Physics*, vol. I, ed. by F. Seitz, D. Turnbull (Academic Press, New York, 1954), p. 1 36, 37, 44
22. T. Moriya, *J. Phys. Soc. Japan* **18**, 516 (1963) 36, 44
23. K. Yosida, *Phys. Rev.* **110**, 769 (1958) 38, 40
24. F. Reif, *Phys. Rev.* **102**, 1417 (1956); **106**, 208 (1957) 39
25. G.M. Androes, W.D. Knight, *Phys. Rev.* **121**, 779 (1961) 39
26. W.A. Hines, W.D. Knight, *Phys. Rev. Lett.* **18**, 341 (1967); *Phys. Rev. B* **4**, 893 (1971) 39
27. R.H. Hammond, G.M. Kelly, *Rev. Mod. Phys.* **36**, 185 (1964) 39, 40
28. See Ref.5 for a more detailed account of these developments 39
29. R.A. Ferrell, *Phys. Rev. Lett.* **3**, 262 (1959) 39, 40
30. P.W. Anderson, *Phys. Ref. Lett.* **3**, 325 (1959) 39
31. A.A. Abrikosov, L.P. Gorkov, *Zh. Eksp. Teor. Fiz.* **42**, 1088 (1962); [*Sov. Phys.-JETP* **15**, 752 (1962)] 39
32. P.W. Anderson, *J. Phys. Chem. Solids* **11**, 26 (1959) 39, 43
33. F. Wright, W.A. Hines, W.D. Knight, *Phys. Rev. Lett.* **18**, 115 (1967) 39
34. R.H. Hammond, G.M. Kelly, *Phys. Rev. Lett.* **18**, 156 (1967) 40
35. H.L. Fine, M. Lipsicas, M. Strongin, *Phys. Lett.* **29A**, 366 (1969) 40
36. Y. Masuda, A.C. Redfield, *Phys. Rev.* **125**, 159 (1962) 41, 42, 43
37. H. Bommel, *Phys. Rev.* **96**, 220 (1954) 41
38. C.R. Leavens, J.P. Carbotte, *Solid State Commun.* **9**, 75 (1971); *Ann. Phys. (N. Y.)* **70**, 338 (1972) 43
39. Y. Masuda, *Phys. Rev.* **126**, 1271 (1962) 43
40. J.D. Williamson, D.A. MacLaughlin, *Phys. Rev. B* **8**, 125 (1973) 43
41. J.R. Clem, *Phys. Rev.* **148**, 392 (1966) 43
42. V. Heine, *Phys. Rev.* **107**, 1002 (1957) 44, 46
43. J.H. Wood, G.W. Pratt Jr., *Phys. Rev.* **107**, 995 (1957) 44, 46
44. R. Kubo, Y. Obata, *J. Phys. Soc. Japan* **11**, 547 (1956) 44, 46
45. A.M. Clogston, A.C. Gossard, V. Jaccarino, Y. Yafet, *Phys. Rev. Lett.* **9**, 262 (1962) 44, 49, 57, 58
46. A.M. Clogston, V. Jaccarino, *Phys. Rev.* **121**, 1357 (1961) 45, 47
47. R.E. Watson, A.J. Freeman, *Hyperfine Interactions*, ed. by A. J. Freeman, R.B. Frankel (Academic Press, New York, 1967), p. 53 46, 47
48. A.M. Clogston, V. Jaccarino, Y. Yafet, *Phys. Rev.* **134**, A650 (1964) 47, 48, 49
49. F.E. Hoare, J.C. Matthews, *Proc. Roy. Soc. (London)* **A212**, 137 (1952); D.W. Budworth et al., *ibid.* **A257**, 250 (1960) 49
50. L.P. Kadanoff, *Phys. Rev.* **132**, 2073 (1963) 50
51. Y. Obata, *J. Phys. Soc. Japan* **18**, 1020 (1963) 50, 51
52. Y. Yafet, V. Jaccarino, *Phys. Rev.* **133**, A1630 (1964) 50, 51, 52
53. R.E. Watson, A.J. Freeman, *Phys. Rev.* **123**, 2027 (1961) 52
54. J. Butterworth, *Phys. Rev. Lett.* **5**, 305 (1960); J. Butterworth, *Proc. Phys. Soc. London* **85**, 735 (1965) 53

55. A.A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **32**,1442 (1957) [English transl.: Soviet Phys.- JETP **5**, 1174 (1957) 54, 55, 57
56. W.H. Kleiner, L.M. Roth, S.H. Autler, Phys. Rev. **133**, A1226 (1964) 54, 55, 56
57. T.J. Greytak, J.H. Wernick, J. Phys. Chem. Solids **25**, 535 (1964) 54
58. P. Pincus, A.C. Gossard, V. Jaccarino, J.H. Wernick, Phys. Lett. **13**, 21 (1964) 54, 57
59. J.-M. Delrieu, J.-M. Winter, Solid State Commun. **4**, 545 (1966) 55
60. A.G. Redfield, Phys. Rev. **162**, 367 (1967) 55, 57
61. D. Rossier, D.E. MacLaughlin, Phys. Kondens. Mater. **11**, 66 (1970) 55
62. P.R. Radebaugh, P. Keesom, Phys. Rev. **149**, 209 (1966); **149**, 217 (1966) 56
63. G. Eilenberger, Phys. Rev. **153** 584 (1967) 56
64. C. Caroli, P.G. deGennes, J. Matricon, Phys. Lett. **9**, 307 (1964) 59, 61
65. U. Brandt, W. Pesch, L. Tewordt, Z. Physik **201**, 209 (1967) 59
66. U. Brandt, Phys. Letters **27A**, 645 (1968) 59, 60
67. W. Pesch, Phys. Letters **28A**, 71 (1968) 59, 60
68. M. Cyrot, J. Phys. (Paris) **27**, 283 (1966) 59
69. N. Okuda, Y. Masuda, Phys. Rev. Lett. **20**, 1475 (1968) 59, 60, 61
70. Y. Masuda, N. Okuda, J. Phys. Soc. Japan **26**, 309 (1969) 59, 60
71. W. Fite, A.G. Redfield, Phys. Rev. **162**, 358 (1967) 59, 60, 61, 62, 63
72. B.G. Silbernagel, M. Weger, J.H. Wernick, Phys. Rev. Lett. **17**, 384, (1966) 60, 61
73. B.G. Silbernagel, M. Weger, W.G. Clark, J.H. Wernick, Phys. Rev. **153**, 535 (1967) 60
74. B.W. Batterman, C.S. Barrett, Phys. Rev. Lett. **13**, 390 (1964) 60
75. A.C. Gossard, Phys. Rev. **149**, 246 (1966) 60
76. D. Rossier, D.E. MacLaughlin, Phys. Rev. Lett. **22**, 1300 (1969) 60
77. A.G. Redfield, W.N. Yu Phys. Rev. **169**, 443 (1968); **177**, 1018 (1969) 62
78. A.Z. Genack, A.G. Redfield, Phys. Rev. Lett. **31**, 1204 (1973) 62
79. G.B. Furman, S.D. Goren, Phys. Rev. B**68**, 064402 (2003) 63
80. H. Monien, D. Pines, Phys. Rev. B **41**, 6297 (1990); N. Bulut, D. Scalapino, Phys. Rev. B**45**, 2371 (1992) 63

*This page intentionally blank*

## The Superconducting Cuprates: Preliminary Steps in their Investigation via NMR

The purpose of this chapter is twofold. First, it is partly historical, to recount the somewhat uncertain beginnings and explain how ideas developed the way they did, and secondly, to review the early milestones which laid the foundations for the many years of study which were to follow. These agendas will unfold simultaneously in an essentially chronological recounting of the important first steps in constructing the edifice of high- $T_c$  NMR phenomenology which exists today.

Although the cuprates form a large family of compounds<sup>1</sup>, in recounting the major accomplishments in the field of NMR studies, one's attention is drawn to three compounds, namely  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (LSCO:x),  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO7-x), and  $\text{YBa}_2\text{Cu}_4\text{O}_8$  (Y248). These three have played a major role, both in terms of experimental results and theoretical interpretation. There are other interesting compounds with higher  $T_c$ 's (e.g.  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ ) and with quantum chemistry just as clean ( $\text{Hg}_2\text{Ba}_2\text{Cu}_2\text{O}_4$ ). It seems that it was just an historical accident that the three listed above became prominent. Accordingly, they will become our main focus.

In Sect. 3.1 we review the structures, phase diagram, and some of the early theoretical models regarding transport and quasiparticle dynamics. Of course with a research topic as completely new and unfamiliar as the cuprates, one spends a great deal of time and effort at the outset simply establishing the basic experimental features of the system under investigation. Some of this activity is reviewed in Sect. 3.2, where we shall see that the anomalous nature of the spin dynamics (i.e.  $T_1$ ) emerged from the earliest papers to appear.

A major milestone in understanding all HF effects in the cuprates came with the Mila-Rice-Shastry picture of predominant transferred HF couplings with their quantum-chemical foundations [2, 3]. This work, presented and discussed in Sect. 3.3 for  $^{63,65}\text{Cu}$ , established a model HF Hamiltonian for the principal nuclei which has been an important touchstone ever since. The

---

<sup>1</sup> See, for example, the wide variety of cuprate structures reviewed by Hazen [1].

application of this picture to the NMR studies of planar  $^{17}\text{O}$  and the  $^{89}\text{Y}$  in the YBCO structure is the subject of Sect. 3.4.

The relationship between nuclear spin-lattice relaxation ( $T_1$ ) and the dynamical susceptibility  $\chi(\mathbf{q}, \omega)$  via the fluctuation-dissipation theorem has been well known for many years [4]. With the cuprates, however, this quantity quickly became the basis for the expression of static and dynamic NMR, for inelastic neutron scattering (INS) results, as well as for theoretical modeling. In Sect. 3.5 we review the derivation of the basic results and give standard expressions for  $T_1$  at various nuclear sites in cuprates for reference throughout the book.

Finally, in Sect. 3.6 the early and highly significant d-wave interpretation of  $T_1$  in the superconducting state by Monien and Pines [5] is reviewed in some detail. This was based on an RPA model of the dynamical susceptibility which formed a basis for future modeling of normal-state dynamics as well [6, 7]. As we shall see throughout the volume, fundamentally d-wave behaviors for  $T_1$  and for the transverse decay constant  $T_{2g}$  were firmly established several years in advance of the Josephson junction phase-boundary results which finally turned the tide on the d-wave vs. s-wave question.

### 3.1 Cuprate Structures and Doping Effects: LSCO and YBCO

The first high- $T_c$  materials to be announced [8] left some degree of uncertainty about the actual crystal structures of the superconducting phases. In the weeks that followed, among the first structural refinements to be announced were those of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (LSCO) [9] and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) [10]. For that reason as well as the fact of their ease of synthesis into high-quality specimens and of subsequent characterization, these two compounds and closely related materials have been a strong focus of NMR/NQR studies from the inception down to the present era. In this section we present a brief discussion of the structures, doping, and quasiparticle dynamics in these typical cuprates. Discussions of NMR studies on the LSCO family of compounds will be given in Chaps. 4 and 6.

#### 3.1.1 LSCO: A superconductor with $T_c(\text{max}) \simeq 40\text{ K}$

LSCO has the  $K_2\text{NiF}_4$  crystal structure shown in Fig. 3.1(a) [11]. The key structural element in all of the cuprate superconductors is the  $\text{CuO}_2$  quadratic array (Cu-O1 in Fig. 3.1(a)), which has been identified as the region where the hole current is carried in these systems. Note that the O1 ions also form a quadratic array rotated  $45^\circ$  from that of the Cu, and having a lattice constant of  $a/\sqrt{2}$ . Cu ions in adjacent planes are staggered, so that AFM couplings between layers are extremely weak. The physics of these structures is strongly two dimensional.

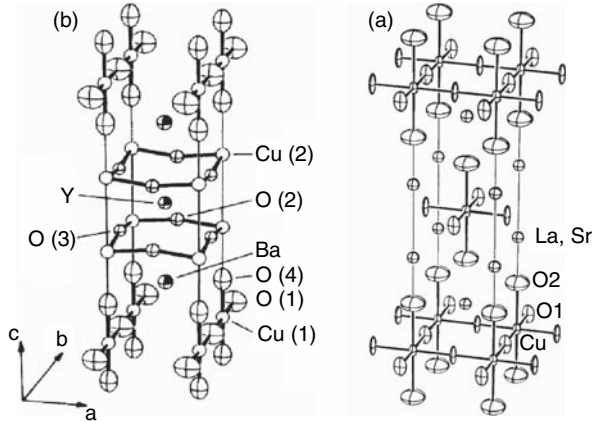


**Fig. 3.1.** (a) The  $(K_2NiF_4)$  structure of  $La_{2-x}Sr_xCuO_4$ , showing the locus of the  $CuO_2$  conducting plane. The  $Sr^{2+}$  dopant ions go substitutionally into the  $La^{3+}$  sites, leading to a set of mobile holes which run on the square lattice of planar  $O^{2-}$  ions [11]. The structure shown has tetragonal symmetry. However, below a few hundred  $K$  an orthorhombic distortion sets in, where the  $CuO_6$  octahedra tilt through small angles in the  $[110]$  planes. Reprinted figure from J.D. Jorgensen, H.-B. Schüttler, et al., Phys. Rev. Lett. **58**, 1024, (1987). Copyright 1987 American Physical Society. (b) The  $YBa_2Cu_3O_{7-x}$  structure is shown with the chain layers ( $Cu(1)$ ) on the top and bottom and a pair of  $Cu(2)O(2,3)_2$  layers in the middle [12]. Note that there is no bonding between adjacent  $Cu(2)$  layers except via rather inert  $Y^{3+}$  ion cores. The  $O1$  sites are shown filled, forming chains along the  $b$  axis. The structural symmetry is orthorhombic. Reprinted figure from J.D. Jorgensen, B.W. Veal, W.K. Kwok, et al., Phys. Rev. B **36**, 5731 (1987). Copyright 1987 American Physical Society

The physics of transport is dramatically different in the cuprates from what it is in an ordinary d-band metal. For LSCO we consider first the case of  $x = 0$ , i.e.  $La_2CuO_4$ . With the expected valence ( $La^{3+}$ ,  $Cu^{2+}$ , and  $O^{2-}$ ), the conduction plane consists of  $Cu^{2+}$  ions, i.e. with a single hole in the d shell ( $d_{x^2-y^2}$ ) plus  $O^{2-}$  closed-shell ion cores. The 3d holes are strongly hybridized with the  $O^{2-}$  2p orbitals, such that over 30% of the localized d-hole density resides on the planar oxygens [13, 14]. In the conventional picture of weakly-interacting fermions, this would simply be a half-filled band like an alkali metal.

On the contrary, however, the hopping process which might lead to hole conduction is strongly inhibited by coulomb repulsion ( $U \sim 10 eV$ ) on the  $Cu^{+2}$  ion complexes in what is known as a “Mott insulator” [15]. Instead, immobile  $S = 1/2$  local moments on the  $Cu^{+2}$  ions condense to an insulating, antiferromagnetic ground state with  $T_N \simeq 325 K$ . In order to generate conductivity in the  $CuO_2$  planes, it is necessary to dope additional holes into the system. This may be done by replacing some of the  $La^{+3}$  ions with  $Sr^{+2}$  ions

as in LSCO. For each such substitution a hole must appear in or near the  $\text{CuO}_2$  plane. Above a small threshold concentration these holes become mobile. In the Zhang-Rice singlet picture, they combine with  $\text{Cu}^{2+}$  holes to form a singlet quasiparticle. After considerable investigation and debate, such singlets have finally been concluded to have negligible HF interactions on their own. It has been suggested that they serve the function of rendering the  $\text{Cu}^{2+}$  holes itinerant [16].

### *The LSCO Phase Diagram*

The phase diagram of Fig. 1.1 illustrates the resulting behavior as a function of the hole-doping parameter  $\delta \sim x$ . First, the antiferromagnetism collapses very quickly with hole doping. At  $x \sim 0.02$  there is an insulator-to-metal transition, though conductivity is still rather poor. In this region, spin-glass-behavior is thought to occur. At  $x \simeq 0.05$  the superconducting phase appears, although the normal-state conductivity is still that of a very bad metal. With an optimum concentration of  $x = 0.15$ ,  $T_c$  then peaks at  $\sim 40\text{ K}$ . Beyond that point is the *overdoped region*, where the system becomes more and more like a normal metal.  $T_c$  then declines to zero at  $x \sim 0.35$ . The pattern seen with LSCO is repeated with essentially every cuprate superconductor, except that in many cases it is not possible to vary the carrier content all the way from the antiferromagnetic phase through superconductivity and into the overdoped phase.

The line in Fig. 1.1 running from the top of the superconducting dome upward to the left (“S”) is the locus of maxima in the spin susceptibility, and also an approximate boundary between the tetragonal (above) and orthorhombic (below) phases in LSCO. However, there is a “crossover” line in approximately that position in various theories of magnetic behavior [17, 18], for which there is growing experimental evidence in other cuprate compounds. In the Barzykin-Pines model this is a boundary between mean-field behavior for the dynamical exponent ( $z = 2$ ) on the high-temperature side and quantum-critical ( $z = 1$ ) behavior on the low-temperature side. NMR evidence supporting this picture will be presented and discussed in Chap. 6.

### **3.1.2 The 92 K Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO)**

Many cuprates have multiple  $\text{CuO}_2$  planes neighboring each other with a single layer of cations between them.  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO7-x) has two such neighboring planes separated by a single layer of  $\text{Y}^{3+}$  ions, as shown in Fig. 3.1(b) [12]. This structure also features a “chain” layer, known as the Cu(1) sites, which is a quadratic array of copper ions, but where half of the ligand  $\text{O}^{2-}$  ions seen in the Cu(2) layers are absent, leaving 1D Cu-O chains running along the  $b$  axis of the crystal. The chain sites are a complication in understanding the behavior of YBCO, because as we shall see below, the Cu(1) and Cu(2) sites behave rather differently.

On the other hand, regarding the level of mobile carriers, the YBCO7-x system is *self-doping*. The minimum doping level is effectively zero when  $x = 1$ , giving six oxygens per formula unit. With the expected valencies ( $Y^{3+}$ ,  $Ba^{2+}$ ,  $Cu(1)^+$ ,  $Cu(2)^{2+}$ , and  $O^{2-}$ ),  $YBa_2Cu_3O_6$  is in a *vacuum state* for conductivity similar to  $La_2CuO_4$ . In this structure there are no oxygens at all in the Cu(1) planes, and their corresponding valence state is  $Cu^{1+}$ . The maximum doping occurs when  $x = 0$ , whereupon the Cu(1) chains are fully oxygenated, and one has an average valence of 2.33 per Cu ion. This is considered to be slightly overdoped, where the maximum  $T_c \simeq 92\text{ K}$  occurs for  $x \simeq 0.1$ . It is noteworthy, however, that YBCO7 is *stoichiometric* and therefore has minimal disorder, i.e. far less disorder than optimally doped LSCO.

### 3.1.3 Physical Models of Itinerant Quasiparticles in Cuprates

At optimum doping levels, then, the cuprate conduction planes then appear to contain a small concentration of mobile holes moving in a sea of  $S = 1/2$ , exchange-coupled local moments. Because of the coulomb repulsion, these holes are thought to be restricted to the oxygen sites. The description of this mixture as a superconducting quantum fluid is therefore dramatically different from a simple 3d-band of partially-occupied Bloch functions. It has posed a stiff theoretical challenge from the beginning, and even now there is not a clear consensus about it. One thing we understand is that it is not a set of exchange-coupled local moments simply coexisting with a hole band of itinerant fermions. For example, at  $T \ll T_c$  all spin magnetism decays to a small fraction of its normal-state level, as we know from NMR shift and relaxation measurements (Sect. 3.2.5). Upon a (low, but) sufficient level of doping, then, all  $Cu^{2+}$  holes become effectively itinerant and part of a superconducting quantum fluid at  $T < T_c$ .

#### *The t-J Model*

How this takes place has been the topic of many theoretical papers. We mention here the “t-J” model [19, 20], which is an approximation to the one-band Hubbard model. A number of theory papers have shown that the t-J model Hamiltonian (here simplified)

$$\mathcal{H}_{t-J} = J \sum_{i,j(nn)} \mathbf{S}_i \cdot \mathbf{S}_j + t \sum_{i,j(nn)} [c_i^* c_j + c_i c_j^*] \quad (3.1.1)$$

results in a band of itinerant quasiparticles of width  $\sim J \sim 0.15\text{ eV}$  [21].

#### *Zhang-Rice Singlets*

A detailed model for the structure of the quasiparticles themselves, known as the “Zhang-Rice singlet model”, appeared very early on and is still considered an interesting conceptual picture [16]. In this model the mobile holes form

a singlet complex with neighboring  $\text{Cu}^{2+}$  “localized” holes, rendering them itinerant. In spite of their small numbers, the mobile holes are said to render all of the  $\text{Cu}^{2+}$  moments effectively itinerant and part of a quantum liquid which condenses into a superconducting spin-paired ground state. That this actually occurs is concluded from decay of the  $\text{Cu}(2)$  Knight shift and relaxation rate, and thus the spin paramagnetism of YBCO7, to a value small compared with its normal-state value for  $T \ll T_c$  (see Sect.3.2).

### *The “Oxygen Hole Band” Issue*

Contrary to the Zhang-Rice singlet picture, many early papers considered that the doped holes in cuprates would result in a separate hole band residing on the oxygen lattice with its own independent HF effects. This idea was often advanced when it seemed that the fluctuating  $S = \frac{1}{2}$  moments which occupy the  $\text{Cu}^{2+}$  sites would not give an adequate explanation of NMR shift and relaxation effects at all sites studied. Often the papers concerned made important contributions in spite of maintaining this point of view. Eventually, as will become clear in Chap. 4 and 5, it was realized that there was simply no need for oxygen hole bands with independent HF effects and no evidence for them either. This issue will be mentioned as appropriate in reviewing the relevant literature.

## **3.2 Early NMR/NQR Studies: The Early Predominance of YBCO**

It was, of course, realized immediately that NMR studies of the  $^{63,65}\text{Cu}$ ,  $^{17}\text{O}$ , and in the case of YBCO,  $^{89}\text{Y}$  nuclear spins could yield a great deal of detailed information about static and dynamic fermion behavior in these systems. Perhaps because of its very high  $T_c$  value, there was an intense focus on YBCO at the outset, which was facilitated by the ease with which samples could be synthesized. Accordingly, there were a great many NMR papers on YBCO, mainly fully doped (YbCO7) during the first year or two. Our focus in this section will be these early studies of YBCO and the issues they raised. LSCO eventually received its share of attention, and will be addressed both in the next chapter and in Chap. 6.

In this section we examine the developments which took place during 1987-88 following the discovery of high- $T_c$  superconductors. It was a time of intensive activity, but at the same time, sample preparation was still in a rather primitive state. There was a definite focus on YBCO7, the 90 – 92 K superconductor, because of its spectacularly high  $T_c$  value and because it is a stoichiometric compound. Even so, almost all of the samples studied during this period were either random powders or milligram-scale crystals which gave narrow resonance lines, but very small signals. The random powders gave  $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$  transition spectra  $\sim 5T$  wide in a typical laboratory (7–8 T) field,

and it took a great deal of noise averaging to obtain a single spectrum. Only with NQR was it possible to do a  $T_1$  measurement.

Even so, many basic issues concerning the NMR/NQR study of the cuprates were addressed during this time period, and impressive progress was made toward their resolution. At the end of the two-year period we are focusing on, there were two events which marked the beginning of a more settled period, namely the appearance of the Mila-Rice-Shastry papers to clarify the quantum chemistry and transferred HF interaction picture [2, 3], and secondly, the advent of the *oriented powder* sample preparation method, which dramatically improved the prospects for precise determination of nearly all experimental NMR parameters. The Mila-Rice-Shastry picture for HF couplings in YBCO is presented in Sect. 3.3.

### 3.2.1 NMR Shift and Relaxation of the $^{89}\text{Y}$ in YBCO7

Not surprisingly, the first papers on cuprate nuclear spin dynamics to appear featured studies of  $^{89}\text{Y}$   $T_1$  behavior in both the normal and superconducting states [22, 23]. The  $^{89}\text{Y}$  nuclei have very small,  $I = 1/2$  nuclear spin moments, but are 100% abundant. They are very weakly hybridized with the Cu(2) 3d moments, giving them a long  $T_1$ , but a relatively isotropic NMR shift, so that they are easy to study in a random powder sample. The quick appearance of these  $^{89}\text{Y}$  studies was a harbinger of a great many fruitful  $^{89}\text{Y}$  NMR studies to follow.

The  $T_1$  data from [22], shown in Fig. 3.2, immediately revealed two striking behaviors. First,  $T_1$  follows a Korringa-like, inverse- $T$  law in the normal state, giving actually a misleading impression of the behavior at its neighboring Cu(2) site to be unveiled soon after. The normal-state data of [23] were in agreement with this finding, and both papers found a normal-state shift  $K \simeq 0.02\%$  as well. As for  $T_1$ , there is no hint of any coherence peak below  $T_c$ ; moreover, the decline of  $1/T_1$  below  $T_c$  is remarkably abrupt. It behaves in a roughly exponential fashion when plotted vs.  $T/T_c$ , and has a slope much larger than the expected asymptotic BCS slope (plotted). If the BCS curve reflects a gap  $2\Delta_{BCS} \simeq 3.5k_B T_c$ , the  $^{89}\text{Y}$   $T_1$  curve shows a gap value  $2\Delta_Y \simeq 11.2k_B T_c$ . While such a characterization is somewhat superficial at this stage, it shows at least that the superconducting  $T_1$  behavior is dramatically different from that of any ordinary d-band metal. (See Sect. 3.6 for further elucidation of  $T_1$  behavior below  $T_c$ .)

#### *NMR/NQR Studies of $^{63,65}\text{Cu}(1,2)$ : The Quadrupolar Tensor and $\mathbf{T}_1(\mathbf{T})$*

Next, many papers appeared in which the four-line NQR spectrum (or part thereof) was reported ( $^{63,65}\text{Cu}(1)$  and  $^{63,65}\text{Cu}(2)$ ) in YBCO7 [23, 24, 25, 26]. Of course, for the  $I = 3/2$ ,  $^{63,65}\text{Cu}$  nuclei the value of  $\eta$  cannot be derived from NQR frequencies alone. The full quadrupolar frequency tensor has been

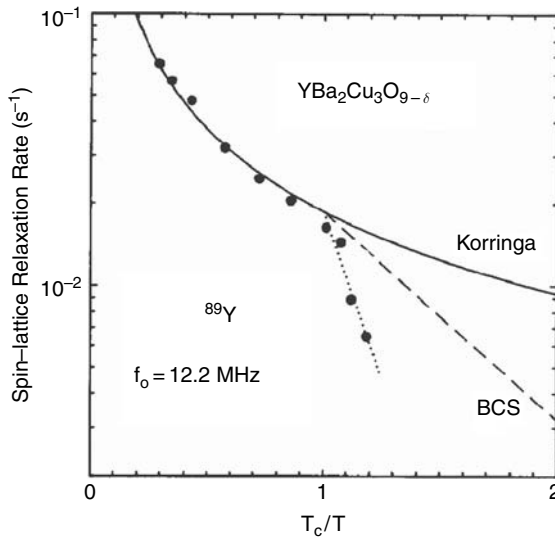


**Fig. 3.2.**  $1/T_1$  of  $^{89}\text{Y}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$  is plotted vs.  $T_c/T$  in a semilog plot, where  $\delta \simeq 2.1$  [22]. In the normal state the data are within error limits of a Korringa curve (solid line,  $1/T_1 \propto T$ ). Below  $T_c$  the measured relaxation rate drops much faster than the BCS energy gap would allow (dashed curve - BCS). See text for discussion. Figure reprinted from J.T. Markert, T.W. Noh, S.E. Russek, R.M. Cotts: Sol. St. Comm. **63**, 847 (1987). Copyright 1987 Elsevier Ltd.

deduced from NMR studies of small single crystals of YBCO7-x, with  $x \simeq 0$  [27, 28], yielding essentially equivalent results. After some refinement, these tensors may be given (in MHz) as  $\nu_{\alpha\alpha} = (-19.03(7), 19.17(7), -0.16(3))$  for Cu(1) and  $(15.94(5), 15.56(5), -31.50(5))$  for Cu(2) at 100 K [29], where the numbers in parentheses are the uncertainties in the last digit quoted. This quadrupolar tensor has been analyzed by Frank Adrian [30].

### *NQR Studies of Cu(1,2) $T_1$ in YBCO7*

NQR was used to measure  $T_1$  for both the  $^{63}\text{Cu}(1)$  and  $^{63}\text{Cu}(2)$  lines at 22 MHz and 31.5 MHz, respectively, giving the first glimpse of  $T_1$  behavior for the copper sites in the cuprates [24, 23]. The  $T_1$  data from [24] are displayed in Fig. 3.3, where markedly different behavior is seen to occur for the two copper sites, both above and below  $T_c$ . In the normal state, the Cu(1) site  $T_1$  behavior is rather Korringa-like, similar to the  $^{89}\text{Y}$ , whereas the Cu(2) site  $1/T_1$  behaves initially like  $a + bT$ , but then flattens off near room temperature. The normal state data from [23] behave in a similar fashion to that in Fig. 3.3, except that  $T_1$  values appear to be about 15% longer than from [24]. The value quoted in [31] is also slightly longer, but well within error limits of the data in Fig. 3.3. The reader may note that different references cited here give  $T_1$  values which are defined variously, none of which agree with the discussion

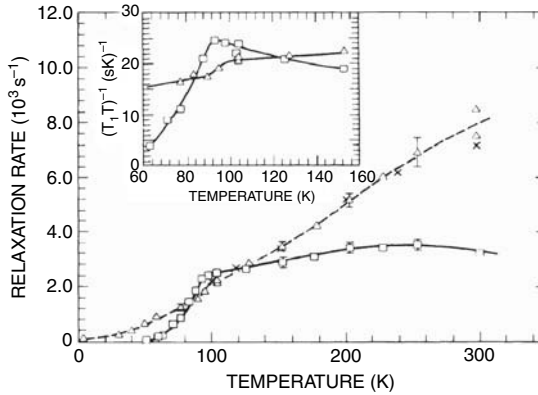


**Fig. 3.3.** The  $^{63}\text{Cu}$  relaxation rate  $1/T_1$  is shown plotted vs.  $T$  for Cu(1) and Cu(2) in a YBCO7 sample ( $T_c \simeq 92\text{ K}$ ) [24]. The NQR rate is shown, which is 3 times the formally defined rate  $1/T_1$ . Reprinted figure from W.W. Warren, Jr., R.E. Walstedt et al: Phys. Rev. Lett. **59**, 1860 (1987). Copyright 1987 American Physical Society

of  $T_1$  in Sect. 1.1.5. Recall that the NQR value of relaxation time measured for  $I = 3/2$  is  $1/3$  of the formally defined  $T_1$  (see Sect. 1.1.5). Finally, regarding the data shown in Fig. 3.3, we shall not consider the temperature dependence of  $T_1$  in depth until Chap. 5. We comment briefly on the general features of these data.

Below  $T_c$  the Cu(2) relaxation rate declines very steeply, rather like the  $^{89}\text{Y}$  data in Fig. 3.2. The data from [23] for  $T < T_c$  are also similar, the main difference being that the Cu(2) curve is extended to somewhat lower temperatures, where it is found to level off markedly. Such behavior is very likely sample dependent. Fitting the Cu(2) rate below  $T_c$  (Fig. 3.3) to a BCS-style exponential decay, a reasonable fit gives  $2\Delta_Y \simeq 8.3 k_B T_c$  with  $T_c = 92\text{ K}$  [24]. This is a qualitatively similar result to the slope found above for the  $^{89}\text{Y}$ , but since the latter studies were done in a field of  $50\text{ kG}$  and the present data were taken in zero field, a quantitative comparison may not be warranted. As we shall see in Sect. 3.6, this low-temperature behavior is characteristic of d-wave pairing.

### 3.2.2 Establishing the Site Assignment for the Cu(1) and Cu(2) NQR Spectra

Following the publication of [24] (and [32]) there was a brief period of controversy, caused by the fact that the identification of the NQR frequencies with the Cu(1) and Cu(2) sites in these papers was reversed from the correct assignment stated above. The  $T_1$  results are valid when attributed to the correct sites, but a large portion of the discussion, based on the incorrect identification, would need to be revised [24, 32]. Since a number of discussion points have also been rendered moot by later insights and improved understanding,

we shall attempt no such revision here. The incorrect assignment was made on the basis of (i) similarity of normal-state  $T_1$  curves between the  $^{63}\text{Cu}(1)$  (Fig. 3.3) and the  $^{89}\text{Y}$  (Fig. 3.2) and (ii) on the relative intensities of the 21 MHz and 31.5 MHz NQR lines in [24] as well as in other papers [25, 26]. These intensities were essentially reversed from the 2:1 ratio expected from the Cu(2):Cu(1) site count, showing the general unreliability of NQR intensities recorded at different frequencies.

Following these papers, other papers appeared whose main purpose was to document the correct site assignment. References [27, 28] argued the correct assignment on the basis of data for the EFG tensor. After all, the Cu(2) site has very nearly axial symmetry, while Cu(1) does not, features which are expressed very strikingly in the EFG tensor. Meanwhile, [33] argued the case on the basis of  $^{63}\text{Cu}$  relaxation studies conducted on a sample of  $\text{GdBa}_2\text{Cu}_3\text{O}_7$ . The  $\text{Gd}^{3+}$  ions each possess a localized moment of nearly  $7\mu_B$ , which fluctuates as a consequence of exchange couplings with the other  $\text{Gd}^{3+}$  moments. The nearby Cu(2) nuclei are strongly relaxed by fluctuating dipolar fields from these moments, whereas, the Cu(1) are largely unaffected. These observations confirm the correct assignment.

### *The $(-\frac{1}{2}, \frac{1}{2})$ Quadrupolar Powder Pattern for Cu(2) in YBCO7*

The authors of [24, 32] also conducted NMR intensity studies for the purpose of site verification, partitioning the  $(-1/2, 1/2)$  NMR line intensity for YBCO7 into Cu(2) and Cu(1) contributions [34] (see also [27]). The intensity of the NMR spectrum was calibrated by comparison with spectra from a known quantity of  $\text{Cu}_2\text{O}$ , yielding an absolute intensity of  $2.7 \pm 0.3$  Copper ions per unit cell of the YBCO7. The Cu(2):Cu(1) intensity ratio was found to be 2 within experimental error. A by-product of the latter exercise was a very precise fit to the  $\eta = 0$ , second-order quadrupolar powder pattern for the  $(-1/2, 1/2)$  (central) transition at  $T = 105\text{ K}$  [34], using the same procedures which gave sample powder patterns in Figs. 2.2 and 2.4. This fit is shown in Fig. 3.4, both as spin echo intensity data recorded at pulse separation  $\tau = 20\mu\text{s}$  and as the extrapolated,  $\tau = 0$  curve with its fit to a quadrupolar powder pattern form (see Fig. 2.2) with Gaussian broadening shown as a dashed line. The residual area above the dashed line fit curve is identified as the Cu(1) site intensity. See [34] for a detailed discussion. Shift values for the Cu(2) are also deduced from this fit (see below).

### **3.2.3 Variation of the $^{89}\text{Y}$ shift $K_{89}(x)$ with $x$ for YBCO6+x**

A study of the doping dependence of the  $^{89}\text{Y}$  NMR shift  $K_{89}(x)$  in YBCO6+x by Alloul and coworkers [35] uncovered some very interesting behavior regarding the Pauli paramagnetism of this system. For  $x \geq 0.4$  they found an essentially linear increase  $K_{89}(x) \propto (x - 0.4)$ , below which  $K_{89}$  levelled off to a value which remained constant throughout the insulating phase. It was

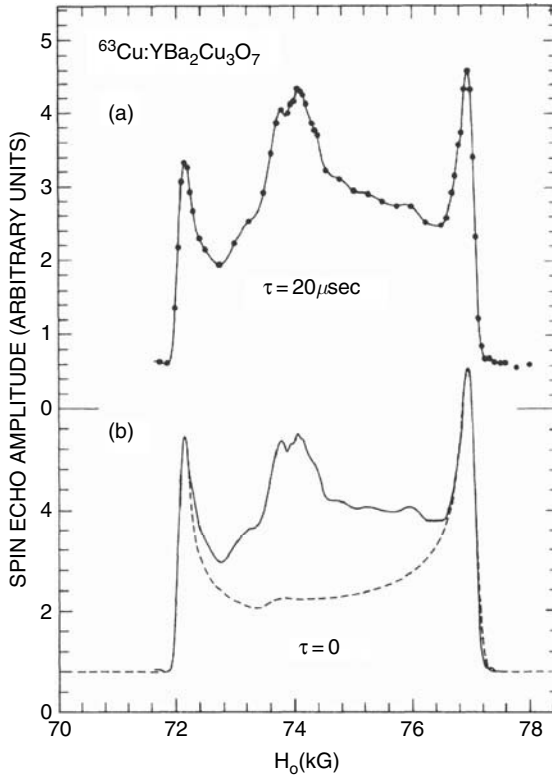


**Fig. 3.4.** NMR field-sweep spectrum of  $^{63}\text{Cu}$  in YBCO7 at  $T = 105\text{ K}$  and an NMR frequency of  $84.07\text{ MHz}$ . Part (a) is uncorrected data taken with a spin-echo pulse separation of  $20\text{ }\mu\text{s}$ . In part (b) the signal has been extrapolated back to  $\tau = 0$  using measured values of  $T_2$  at various points in the spectrum. The outer singularity peaks are characteristic of an  $\eta = 0$   $(-1/2, 1/2)$  quadrupolar powder pattern. Such a powder pattern has been fitted to these peaks (dashed line), and serves to distinguish the Cu(2)-site intensity from that of the Cu(1) sites, which lies above the dashed line. There is a spurious peak to the left of center thought to be caused by accidental powder orientation in this otherwise random sample. The calculated Cu(1) intensity with this scheme is  $\simeq 54\%$  of that assigned to the Cu(2) sites. Reprinted figure from R.E. Walstedt, W.W. Warren, Jr., et al., Phys. Rev. B **38**, 9299 (1988). Copyright 1988 American Physical Society

concluded that the latter value of shift  $K_{89} \simeq 2.25 \times 10^{-5}$  relative to the shift of  $\text{YCl}_3$  is actually *the zero of  $K_{89}$  in this system*. The discrepancy with the  $\text{YCl}_3$  was attributed to a difference in the chemical shifts of the two systems. However, similar results by Balakrishnan et al. [36] included a study of chemical shifts suggesting that the actual chemical shift in  $\text{YBCO}_{6+x}$  at low values of  $x$  is somewhere above  $200\text{ ppm}$  relative to  $\text{YCl}_3$ , contrary to the foregoing

conclusion. Eventually, the latter value gained acceptance as the correct zero for the  $^{89}\text{Y}$  spin paramagnetic shift in YBCO.

The behavior of  $K_{89}(x)$  with doping is shown in Fig. 3.5. The change in  $K_{89}$  above  $x = 0.4$  is seen to be *negative* and is attributed to the core polarization of the  $\text{Y}^{3+}$  4d orbitals hybridized into the conduction band in the  $\text{CuO}_2$  planes of  $\text{YBCO}_{6+x}$ . The Pauli paramagnetism varies in a similar fashion to  $K_{89}$ , so that in a plot of  $K_{89}(x)$  vs.  $\chi_m(x)$  the behavior for  $x > 0.4$  is linear with a slope  $dK_{89}/d\chi_m = -4.6 (\text{emu/mole})^{-1}$ . This is much smaller than would correspond to the full core polarization HF field, showing that the 4d admixture is very slight. The authors comment that this behavior seems contrary to the proposed separation of spin and charge behavior of the RVB model [19, 20].

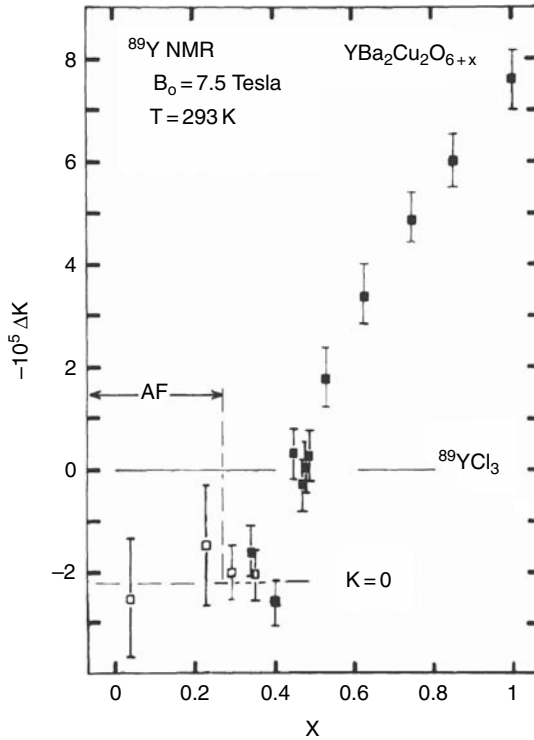


**Fig. 3.5.** The room temperature  $^{89}\text{Y}$  NMR shift in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  is plotted for a series of  $x$  value ranging from nearly zero to one. The is interpreted (see text) to mean that the Pauli paramagnetism vanishes below  $X = 0.4$  and the shift value below that point is simply the difference in chemical shifts between YBCO6 and  $\text{YCl}_3$ . Figure reprinted from H. Alloul, P. Mendels, et al., Phys. Rev. Lett. **61**, 746 (1988). Copyright 1988 American Physical Society

### 3.2.4 Physical Models for the Relaxation of $^{63}\text{Cu}(2)$ in YBCO7

One of the major challenges to the NMR community and to the theorists as well has been the interpretation of the copper-site  $T_1$  data, which is to say the magnitude of  $T_1$ , its *anisotropy*, and its temperature dependence. We discuss the temperature dependence of  $T_1$  (for all sites) in Chap. 5, and as of this writing, it is still an unsettled issue. The magnitude and anisotropy of  $T_1$ , however, came to light early and were the main influences which brought about the Mila-Rice discussion and formulation of the problem. We review here two background developments which highlighted the situation, namely the model treatments of  $T_1$  in experimental papers by Walstedt et al. [37] and by Pennington et al. [29].

Reference [37] reported the first data on the anisotropy of the  $^{63}\text{Cu}(2)$   $T_1$ , finding  $T_{1c}/T_{1ab} \simeq 3.5$ . This was done with a random powder sample, using NQR ( $\theta = 0$ ), and the up-field and down-field singularities of the  $(-1/2, 1/2)$  powder pattern ( $\theta \simeq 43^\circ$  and  $\theta = 90^\circ$ , respectively). The data were not first-rate, but the result for  $T_{1c}/T_{1ab}$  held up in later studies with oriented powders [38]. The paper goes on to discuss the feasibility of explaining the foregoing  $T_1$  data using the typical formulation of spin-lattice relaxation in 3d metals given by Yafet and Jaccarino [39] and discussed in detail in Sect. 2.3. The hyperfine constants are well-known for the  $\text{Cu}^{2+}$ , and the density of states is derived from the susceptibility, where the orbital component is estimated and subtracted off. The result is, if anything, an overestimate for  $n(E_F)$ . The normally dominant orbital relaxation mechanism is vitiated in YBCO by the nearly pure  $d_{x^2-y^2}$  ground state, which has negligible matrix elements for the orbital HF process. As a result, the estimated relaxation rate with this scheme falls far short of the magnitude of the observed rates, and the peak anisotropy available falls well short of the measured ratio. The standard d-band relaxation model was concluded to be incapable of accounting for the cuprate  $T_1$  data.

### 3.2.5 Introduction of the *Spin Hamiltonian* Model for the $\text{Cu}^{2+}$

A different tack was taken by Pennington, Durand, et al. [29]. The  $\text{Cu}(2)$  relaxation tensor was measured using NMR on single crystal samples, finding similar numbers, but an anisotropy of 4.2, rather larger than the 3.5 reported in [37]. This discrepancy is most likely a difference in samples. In any case it has never been resolved. For the analysis of  $T_1$  these authors adopt a model of fluctuating  $\text{Cu}^{2+}$  local moments, adopting a *spin Hamiltonian* form for the spin HF tensor [40] and simply deducing the anisotropy of the spin HF field from the corresponding anisotropy of  $T_1$  for  $\text{Cu}(2)$  given above. Simultaneously, however, Takigawa, Hammel et al. announced their result that the c axis NMR shift changed very little below  $T_c$ , while other components underwent substantial changes [33, 41]. They concluded that the spin paramagnetism declined effectively to zero for  $T \ll T_c$ . It followed that the net c axis

spin HF component for Cu(2) is nearly zero! From this observation sprang the Mila-Rice model for Cu(1,2) HF couplings, presented in Sect. 3.3. Both papers introduced a local moment-based calculation of the orbital susceptibilities on the  $Cu^{2+}$  sites, which, along with the spin and orbital HF tensors, constitutes the *spin Hamiltonian* picture for the detailed physics of the  $Cu^{2+}$  ions [42]. We shall discuss this point of view in detail in Sect. 3.3.

In the meantime, it is interesting to consider the vanishing of the cuprate spin susceptibility  $\chi_s(T)$  at temperatures  $T \ll T_c$ , postulated above, in the context of all of the difficulties over this point which occurred vis-a-vis the *simpler* superconductors discussed in Sect. 2.2.2. We recall that vanishing of  $\chi_s(T)$  required that the inverse lifetime from spin-orbit scattering must be small compared with the energy gap [43] (see (2.2.8)). That this must be so for YBCO7 results from that combined facts that (i) Cu is a very light element with relatively small spin-orbit coupling and (ii) energy gaps in the cuprates are roughly an order of magnitude larger than those found for sp-band superconductors. It is reasonable to suppose, then, that  $\hbar/\Delta(0)\tau_{so} \ll 1$  (1.2.8a), *even in the mixed state*, from which it follows that  $\chi_s(T \ll T_c)/\chi_s(T > T_c) \ll 1$ .

### 3.2.6 Experimental Breakthrough: Oriented Powder Samples

Late in 1987 a paper appeared which reported the technique of creating powdered samples of YBCO in which each crystallite is oriented with its c axis parallel to an applied magnetic field [44]. This scheme relies upon the anisotropy of the (orbital) susceptibility to provide the torque necessary to align each particle with the field. The other necessary condition has to do with the morphology of the polycrystalline material to be oriented. It is assumed that upon reducing sample material synthesized in polycrystalline form to fine powder, each particle of such a powder will be a single crystal, and thus, free to orient with its c axis along the applied field. Any particle consisting of two or more crystallites will not align properly.

The success of this technique is therefore dependent on the particular cuprate under study. YBCO is generally a good candidate for this effect, where one can generally expect the Cu(2)  $(-\frac{1}{2}, \frac{1}{2})$  NMR line to assume a width of 100 Oe or less [38]. Following the original announcement, many NMR studies have appeared using oriented samples [28, 38]. Powder orientation results in an enormous improvement in the NMR signal strength, where signals requiring accumulation of  $\sim 10^5$  echo traces for adequate noise resolution [32] become visible on a single oscilloscope trace. The Cu(1) NMR signal is also greatly improved, where the quadrupole splitting along the c axis corresponds to an extraordinarily small component of the quadrupolar tensor, resulting in a weakly split line [38]. The real significance of this method is that one can now measure the anisotropy of  $T_1$  with a conveniently large signal [38], although remarkably good results were obtained with milligram-scale single crystals [29]. To measure oriented samples in a transverse field, one customarily sets the oriented particles in epoxy. Field oriented samples yield a 2D powder

pattern in a transverse field, which is also important for studies of the  $^{17}\text{O}$  and  $^{89}\text{Y}$  NMR parameters.

### 3.3 The Mila-Rice-Shastry Model: A Universal HF Tensor for the Cuprates

The Mila-Rice-Shastry model [2, 3] for HF coupling with itinerant  $\text{Cu}^{2+}$  holes in a superconducting cuprate clarified a number of murky points regarding NMR shift and  $T_1$  behavior. Important features were (i) transferred HF couplings, (ii) the ability to account for observed behavior with a single “band” of excitations, and (iii) the quantum chemistry framework for the HF Hamiltonian which emerged. Looking back, this was an important turning point in our understanding of HF interactions and of their dynamics. Previous workers had tried to formulate the NMR shift and relaxation in terms of  $\text{Cu}^{2+}$  local moment dynamics driving purely on-site HF couplings, but found peculiar results when trying to fit the extraordinarily large  $T_1$  anisotropy at the Cu(2) site [29]. The demise of the local HF coupling picture was sealed by the observation that the Cu(2)  $c$ -axis shift term attributable to 3d-spin moments was vanishingly small [33, 41], while, in contrast,  $c$ -axis HF fluctuations dominated the  $T_1$  process [29, 37, 38]. It was clear that there were two or more independent contributions to the  $c$ -axis HF coupling which vanished when superimposed to form the net shift, but produced fluctuations which did not cancel and were in fact very large.

#### *The Cu(2)-Cu(2) Transferred HF Coupling*

The resolution of the vanishing  $c$ -axis spin shift question was concluded to be a highly unusual transferred HF coupling between a Cu-site nuclear spin and the four  $nn$  Cu spin moments, which is a great deal larger than previously identified interactions of this sort [45]. The putative isotropic transferred  $nn$  coupling may be written

$$\mathcal{H}_{Tr} = B \sum_{i(nn)} \mathbf{I} \cdot \mathbf{S}_i, \quad (3.3.1)$$

where the sum is over the four nearest-neighbor Cu(2) sites to the site in question.

Nonetheless, it was argued that the only alternative to this was HF coupling with mobile holes on the planar oxygen lattice. Any such hole state would need to hybridize with the Cu(2) 4s state, in order to explain the large, isotropic HF coupling. Suitable oxygen hole states for this purpose were argued to be energetically unfavorable [2]. It was also argued by Mila and Rice that doped holes would be in singlet states which have negligible HF coupling with nuclear moments [46]. Whether this is correct or not is unresolved. To

our knowledge, however, no unidentified HF effect, static or dynamic, has ever been reported to contradict this conclusion.

The result is a quantum fluid of  $\text{Cu}^{2+}$  holes which is expected to be the sole source of HF effects in the normal state and to form spin pairs in the superconducting ground state. Hybridization with the  $\text{O}^{2-}$  neighbors has been proposed as the source of spin HF effects for the  $^{17}\text{O}(2,3)$  sites by Shastry [3], and hybridization with the  $\text{Y}^{3+}$  4d orbitals has been demonstrated by Alloul et al. [35]. That this is a correct picture is evidenced by the vanishing of  $1/T_1$  at  $T \ll T_c$  for the  $^{63,65}\text{Cu}$ ,  $^{17}\text{O}$ , and  $^{89}\text{Y}$  NMR lines for which data have been reported, as well as of the spin-paramagnetic NMR shifts.

### 3.3.1 General Definition of the HF Tensors

Before entering into the details of extracting the HF tensors from shift and susceptibility data, we set down a general framework for the structure of all HF couplings to be discussed from this point forward. The YBCO HF tensor components are defined by

$$\begin{aligned} \mathcal{H}_{HF} = & \sum_{i,\alpha} I_{i\alpha}^{(1)} \left[ A_{\alpha}^{(1)} S_{i\alpha} + B^{(1)} \sum_{j(nn)} S_{j\alpha} \right] \\ & + \sum_{i,\alpha} I_{i\alpha}^{(2)} \left[ A_{\alpha}^{(2)} S_{i\alpha} + B^{(2)} \sum_{j(nn)} S_{j\alpha} \right] \\ & + \sum_{i,\alpha} {}^{17}I_{i\alpha} \sum_{j(nn)} C_{\alpha} S_{j\alpha} + \sum_{i,\alpha} {}^{89}I_{i\alpha} \sum_{j(nn)} D_{\alpha} S_{j\alpha}. \end{aligned} \quad (3.3.2)$$

The four terms in (3.3.2) refer, respectively, to nuclei on the Cu(1), Cu(2), O(2,3), and Y sites. In the first two terms the  $nn$  couplings  $B^{(1,2)}$  are introduced as defined in the foregoing paragraph. The coefficients  $A_{\alpha}^{(1,2)}$  are composites of the on-site Cu(1,2) HF couplings which are derived from the spin Hamiltonian model below. For the O(2,3) and Y, the sums on  $j$  cover two and eight  $nn$  Cu(2) sites, respectively. Omitted are oxygen sites O(1) and O(4) for the sake of simplicity. Their shift and relaxation behavior have been recorded, but are not essential to our understanding of the  $\text{CuO}_2$  planes where the superconductivity resides. The  $^{63,65}\text{Cu}(1,2)$  nuclear spins are labelled  $\mathbf{I}_i^{(1)}$  and  $\mathbf{I}_i^{(2)}$  in an obvious notation. The  $^{17}\text{O}(2,3)$  spins are labelled  $^{17}\mathbf{I}_i$  and the  $^{89}\text{Y}$  spins are labelled  $^{89}\mathbf{I}_i$ .

Note that all HF effects are assumed to be driven by the  $\text{Cu}^{2+}$  spin operators  $\mathbf{S}_j$ , which are rendered itinerant by the hole doping as in the Zhang-Rice model [16]. Our viewpoint regarding hole doping is that there are no HF effects which stem directly from the doped holes [46]. Such effects have been discussed extensively in the literature, and we shall review these discussions where appropriate. It is not felt, however, that convincing evidence for oxygen hole-band HF effects has ever been developed for the cuprates.

### *Evaluation of the HF Coefficients*

The clearest and simplest way to evaluate HF coefficients (e.g.  $A_\alpha^{(1)}$ ,  $A_\alpha^{(2)}$ ,  $C_\alpha$ , and  $D_\alpha$  in (3.3.2)) is by means of analysis of the NMR shifts and the measured susceptibility. In the case of YBCO7- $x$  which we are concerned with here, there is the complication of partitioning the measured susceptibility between the Cu(1,2) sites and neighbors, principally because modeling the behavior of the Cu(1) sites involves a certain amount of guesswork. The spin-Hamiltonian model is used to estimate the orbital terms. In the end, MR simply partitioned  $\chi_s(T)$  equally between the three copper sites. Efforts in the literature to improve on this have only been partially successful [47].

To proceed, then, we first estimate the orbital (Van Vleck) susceptibilities and NMR shifts by means of the spin Hamiltonian model [42]. The core diamagnetic term can be estimated from tables. Subtracting these terms from the measured total then yields the spin susceptibility  $\chi_s(T)$ . Provisions to be described below will be made for its anisotropy, which for the Cu(2) sites will be  $\propto g_\alpha^2$ ,  $\alpha = \text{ab, c}$ , according to the spin Hamiltonian.

HF tensor components will then be derived as follows. We take the  $^{17}\text{O}(2,3)$  sites as a typical example, where  $\mathcal{H}_{HF17} = \sum_i {}^{17}I_{i\alpha} C_\alpha \sum_j S_{j\alpha}$  is the O(2,3) nuclear spin Hamiltonian term from (3.3.2). Taking the expectation value of this term in the presence of a field H along the  $\xi$  axis and equating this result to a nuclear shift Zeeman term  $-\gamma_{17}\hbar H \sum_i I_{i\xi} K_\xi$ , we find

$$K_\xi(T) = \frac{2C_\xi}{\gamma_{17}\hbar g_\xi \mu_B N_A} \chi_{s\xi}(T) = \alpha_{17\xi} \chi_{s\xi}(T), \quad (3.3.3)$$

where  $\alpha_{17\xi}$  is the shift coefficient and  $\chi_{s\xi}(T) = -g_\xi \mu_B N_A \langle S_{j\xi} \rangle / H$  is the molar susceptibility ( $\langle S_{j\xi} \rangle < 0$  is independent of  $j$ ) of a Cu(2) site.

In practice the shift coefficient is determined experimentally by dividing a measured spin-paramagnetic shift by a “best estimate” of the corresponding molar susceptibility. The tensor  $C_\beta$  has the units of energy, so what we will tabulate is the quantity

$$C'_\xi = N_A \mu_B \alpha_{17\xi} / 2 = C_\xi / \hbar \gamma_{17} g_\xi, \quad (3.3.4)$$

in units of “kOe/ $\mu_B$ ”, since this is the HF field which would be found if there were a magnetization of one  $\mu_B$  on each Cu(2) site. It is divided by 2, because each O(2,3) has two Cu(2) neighbors. Appropriate definitions of the HF constant for each case discussed will be given as they come up.

We finally want to emphasize one point, which is that the scale of the HF constants will depend on the value of the  $\chi_s(T)$  tensor adopted. It is given in Table 3.4, and corresponds to  $T = 100\text{K}$ . No other standard will be used for HF coefficients for YBCO7- $x$ , including for the deoxygenated phases. As we shall see, the shift values for YBCO7 are fairly well established, and if more accurate values for the  $\chi_{s\xi}(100\text{K})$  are determined, it is a simple matter to scale all of the HF coefficients uniformly. We proceed, then, with the determination of the HF coefficients.

### 3.3.2 Extracting the Cu(1,2) HF tensors for YBCO7 from Shift and Susceptibility Data Using the Spin Hamiltonian Model

As a preamble to their quantum chemical calculation of hybridized wavefunctions for the Cu(1,2) sites, Mila and Rice [2] analyzed the measured shifts and susceptibility for YBCO7 with the aid of a spin Hamiltonian model, yielding both spin and orbital HF tensors for the Cu(1,2) sites, as well as crystal-field splittings for the Cu(2) site. Although the spin Hamiltonian model is most appropriate for insulators, it appears to provide an accurate description of HF effects in the narrow-bandwidth doped cuprate superconductors.

Since late 1988 when this was first proposed, a good deal of additional data for all the experimental quantities has been reported. Although the original data used served a very important purpose, newer data were published with smaller error bars, and we believe that they lead to a picture with better internal consistency. Accordingly, we discuss here the original  $K$  and  $\chi$  analysis, but re-work the numbers at the same time. The changes are small, but appear to be significant.

#### *The Spin and Orbital NMR Shift Tensors for Cu(1) in YBCO7*

We shall use the notation  $K_t^{(1,2)}(a, b, c) = K_{orb}^{(1,2)}(a, b, c) + K_s^{(1,2)}(a, b, c)$  to represent the total, orbital, and spin shifts along the  $a, b, c$  axes for Cu(1,2). In Table 3.1 we list the original Cu(1)-site shifts [33, 41] and other data which were published a bit later. The total shift values listed were measured at  $T = 100\text{ K}$ , and the orbital shifts, which are assumed to be temperature independent, were measured at  $4.2\text{ K}$ , where it is assumed that  $K_s^{(1,2)}(a, b, c) = 0$ . The spin components listed then correspond to  $100\text{ K}$ . Note that the differences between these two sets of data are not large, but are outside of the stated error bars in a number of cases.

#### *Spin and Orbital NMR Shift Tensors for Cu(2) in YBCO7*

For the Cu(2) NMR shift data in Table 3.2 there are additional data sources listed, and we also include susceptibility data. Since it is not feasible to resolve

**Table 3.1.** Table comparing Cu(1)-site shift values from the original Mila-Rice data [33, 41] and other data which appeared later. The data from [48] are used in the analysis discussed in the text. The spin components are obtained by subtraction:  $K_s = K_t - K_{orb}$ . Shift values are in (%). The numbers in parentheses are uncertainties in the last digit quoted

| Source   | $K_t^{(1)}(a)$ | $K_t^{(1)}(b)$ | $K_t^{(1)}(c)$ | $K_{orb}^{(1)}(a)$ | $K_{orb}^{(1)}(b)$ | $K_{orb}^{(1)}(c)$ | $K_s^{(1)}(a)$ | $K_s^{(1)}(b)$ | $K_s^{(1)}(c)$ |
|----------|----------------|----------------|----------------|--------------------|--------------------|--------------------|----------------|----------------|----------------|
| [33, 41] | 1.34(2)        | 0.61(2)        | 0.60(8)        | 1.18(2)            | 0.43(2)            | 0.31(8)            | 0.16(2)        | 0.18(2)        | 0.29 (8)       |
| [29]     | 1.38(7)        | 0.55(7)        | 0.60(4)        |                    |                    |                    |                |                |                |
| [48]     | 1.32(2)        | 0.56(2)        | 0.59(1)        | 1.08(4)            | 0.27(4)            | 0.25(1)            | 0.25(4)        | 0.29(4)        | 0.33(1)        |

**Table 3.2.** Table comparing Cu(2)-site shift values for YBCO7 from the original Mila-Rice data [33, 41] with other sets of data which have subsequently been reported. Data from the bottom line are employed for the analysis discussed here [48]. No distinction is made between the  $a$  and  $b$  planar axes. The susceptibility components given for [34] are derived by the procedure stated in the text. We note that the spin components are obtained by subtraction:  $K_s = K_t - K_{orb}$ . Shift values are in (%) and susceptibilities in units of ( $10^{-6}$  emu/mole f.u.). The numbers in parentheses are uncertainties in the last digit quoted

| Source   | $K_t^{(2)}(ab)$ | $K_t^{(2)}(c)$ | $K_{orb}^{(2)}(ab)$ | $K_{orb}^{(2)}(c)$ | $K_s^{(2)}(ab)$ | $K_s^{(2)}(c)$ | $\chi_t(ab)$ | $\chi_t(c)$ |
|----------|-----------------|----------------|---------------------|--------------------|-----------------|----------------|--------------|-------------|
| [33, 41] | 0.61(2)         | 1.27(8)        | 0.24(2)             | 1.35(8)            | 0.37(2)         | -0.08(8)       | 250          | 339         |
| [29]     | 0.59(4)         | 1.267(1)       |                     |                    |                 |                |              |             |
| [34]     | 0.55(5)         | 1.30(3)        |                     |                    |                 |                | 224(10)      | 361(10)     |
| [50]     |                 |                | 0.25(2)             | 1.28(2)            |                 |                |              |             |
| [48]     | 0.58(2)         | 1.27(1)        | 0.28(1)             | 1.28(2)            | 0.30(1)         | -0.01(1)       |              |             |

$a$  and  $b$  axis data for the Cu(2) shift, nor for the susceptibility, the in-plane data are labelled “ab”. Again, the original Mila-Rice data are given on the top line, and other sources of data are listed below. There is reasonably good consistency between the last two sources listed. We shall use the bottom line numbers for analysis here. The susceptibility components attributed to [34] were obtained in the following way. The actual data in [34] are measurements on a random powder sample. The 100K susceptibility from these data ( $2.70 \times 10^{-4}$  (emu/mole f.u.)) has been partitioned between  $\chi_t(c)$  and  $\chi_t(ab)$  assuming the ratio  $\chi_t(c)/\chi_t(ab) = 1.61$ , as reported in [49]. This is, to our knowledge, the largest anisotropy ratio which has been reported for an oriented powder sample, and therefore corresponds to an unusually high degree of crystalline alignment. The resulting values for  $\chi_t(ab)$  and  $\chi_t(c)$  are given in the table and are used in the analysis discussed in the text.

### *Determination of the Orbital Susceptibility Tensors*

Our next step is to use the Cu(1,2) shift tensors from the bottom lines of Tables 3.1 and 3.2 to determine the orbital susceptibilities, using the relation

$$\chi_{orb}(a, b, c) = K_{orb}(a, b, c)/\alpha_{orb}, \quad (3.3.5)$$

where  $\alpha_{orb} = 2\langle r^{-3} \rangle/N_A$ . Equation (3.3.5) may be employed for either Cu site. We take  $\langle r^{-3} \rangle = 6.3$  a.u. from [2], yielding  $\alpha_{orb} = 141$  (emu/mole) $^{-1}$ . The resulting orbital susceptibility values for the Cu(1,2) sites are listed in Table 3.3. Note that the  $a$  and  $b$  axis values are identical for Cu(2). Also tabulated are susceptibility values labelled “s+orb”, which are obtained with the following equation:

$$\chi_{s+orb}^{tot} = \chi_s^{tot} + \chi_{orb}^{tot} = \chi_t - \chi_{dia} \quad (3.3.6)$$

**Table 3.3.** Table listing orbital susceptibility components derived from the orbital shifts from the bottom lines of Tables 3.1 and 3.2 using (3.3.5). Also, total susceptibilities from second line of Table 3.2 are listed here after correction for atomic core diamagnetism (see text). Susceptibilities are given in units of ( $10^{-6} \text{ emu/mole}$ ) for individual sites and ( $10^{-6} \text{ emu/mole f.u.}$ ) for  $\chi_{s+orb}^{tot}$

| $\chi_{orb}^{(1)}(a)$ | $\chi_{orb}^{(1)}(b)$ | $\chi_{orb}^{(1)}(c)$ | $\chi_{orb}^{(2)}(ab)$ | $\chi_{orb}^{(2)}(c)$ | $\chi_{s+orb}^{tot}(ab)$ | $\chi_{s+orb}^{tot}(c)$ |
|-----------------------|-----------------------|-----------------------|------------------------|-----------------------|--------------------------|-------------------------|
| 76.5                  | 19.1                  | 17.7                  | 19.8                   | 90.7                  | 399                      | 536                     |

where  $\chi_t$  is the experimental value, and where we use the (isotropic)  $\chi_{dia} = -1.75 \times 10^{-6}(\text{emu/mole})$  from [2]. The measured susceptibilities cannot distinguish between the  $a$  and  $b$  axes.

### *Determination of the Spin Hamiltonian Parameters*

Using the spin Hamiltonian expressions [42]  $\chi_{orb}(c) = 0.70(8\mu_B^2/\Delta_0)$  and  $\chi_{orb}(ab) = 0.70(2\mu_B^2/\Delta_1)$ , we may now use the numbers in Table 3.3 to estimate the crystal field energies  $\Delta_{0,1}$ . The numerical factors 0.70 in these formulas are reduction factors based on measurements [13] and calculations [14] of covalency in the  $\text{CuO}_2$  planes.

Inserting the values of  $\chi_{orb}^{(2)}(ab, c)$  from Table 3.3 then leads to  $\Delta_0 = 2.00$  eV and  $\Delta_1 = 2.29$  eV, in accord with calculations by McMahan et al. [51] which suggest that the  $\Delta_{0,1}$  lie in the vicinity of 2.0 eV and differ by  $\sim 10\%$ . We can now evaluate the g-factor expressions  $g_{\perp} = 2 - 2\lambda/\Delta_1$  and  $g_{\parallel} = 2 - 8\lambda/\Delta_0$ , where  $\lambda$  is the spin-orbit coupling parameter. The free ion value of  $\lambda \simeq -830 \text{ cm}^{-1}$  ([42], Table 7.6). Mila and Rice adopted the value  $\lambda = -710 \text{ cm}^{-1} = -0.088 \text{ eV}$ . We suggest that a slightly greater reduction factor is appropriate here, such as the value 0.75 given by Owen and Thornley for  $\text{Ni}^{2+}$  in  $\text{MgO}$  [52]. This yields  $\lambda = -0.077 \text{ eV}$ , which we employ henceforward. With this value we find

$$g_{\perp} = 2.067; \quad g_{\parallel} = 2.308. \quad (3.3.7)$$

The expected value for the anisotropy  $A_s$  of the spin susceptibility, is  $A_s = \chi_{s\parallel}/\chi_{s\perp} = g_{\parallel}^2/g_{\perp}^2 = 1.247$ . We note that g-factor anisotropies in metals are not unusual, as may be seen in data reported for Cu and other noble metals [53].

Our next task is to partition the measured susceptibility between the Cu(1) and Cu(2) sites. Where Mila and Rice assumed the same isotropic spin susceptibilities for Cu(1) and Cu(2), we shall use the same *axial susceptibility tensors* for both sites. As discussed in [2] this is an oversimplified viewpoint for the Cu(1) site, for which the error incurred is hopefully not too large.

We equate the “s+orb” values in Table 3.3 to expressions using the same axial spin susceptibility tensor components for the Cu(1) site ( $a$  axis) and the

Cu(2) sites ( $c$  axis). For this purpose we introduce the variable  $\chi_{s\perp}$  for a single-site transverse component and  $\chi_{s\parallel} = A\chi_{s\perp}$  for the longitudinal component, where  $A$  and  $\chi_{s\perp}$  are to be determined. This leads to the following equations for  $A$  and  $\chi_{s\perp}$ :

$$\chi_{s+orb}^{tot}(c) = 2\chi_{orb}^{(2)}(c) + \chi_{orb}^{(1)}(c) + (2A + 1)\chi_{s\perp} \quad (3.3.8a)$$

$$2\chi_{s+orb}^{tot}(ab) = 4\chi_{orb}^{(2)}(ab) + \chi_{orb}^{(1)}(a) + \chi_{orb}^{(1)}(b) + (A + 5)\chi_{s\perp}. \quad (3.3.8b)$$

Inserting the numbers from Table 3.3 we solve (3.3.8), finding  $A = 1.166$  and  $\chi_{s\perp} = 1.01 \times 10^{-4}(\text{emu}/\text{mole})$ . This "experimental" value for  $A$  is somewhat smaller than the spin Hamiltonian  $g$ -factor-based estimate of 1.247 calculated in the previous paragraph. The spin susceptibility tensor components deduced here are then 1.01 and  $1.18 \times 10^{-4}(\text{emu}/\text{mole})$  for  $\chi_{s\perp}$  and  $\chi_{s\parallel}$ , respectively, as compared with the isotropic Mila-Rice value of  $1.08 \times 10^{-4}(\text{emu}/\text{mole})$ .

It is interesting to inquire what the possible source might be for the foregoing discrepancy in values for  $A$ . First, it seems likely that the correct value would agree with the spin Hamiltonian model, since other aspects of the model are quite successful. Next, it seems unlikely that approximate treatment of the Cu(1) site behavior is the source of the discrepancy. For example, assuming the Cu(1) site susceptibility to be isotropic would only increase the deduced anisotropy for the Cu(2) site by  $\sim 1\%$ . On the other hand, the deduced anisotropy  $A$  is quite sensitive to the experimental anisotropy value, which was taken to be  $\chi_t(c)/\chi_t(ab) = 1.61$  [49] in the foregoing analysis. If this were increased by less than 4% to 1.67, (3.3.8) would yield the the spin Hamiltonian value  $\chi_{s\parallel}/\chi_{s\perp} = 1.247$ . This result suggests that the correct value for the susceptibility anisotropy may be a few percent larger than the largest value which has been reported.

### 3.3.3 Quantum Chemistry of YBCO7 and the Hyperfine Tensor

While it is to be expected that there is strong covalency between the  $\text{Cu}^{2+}$  moments and the oxygen ligands in the cuprate conducting planes, it seems quite surprising that there is a substantial admixture of the  $4s$  wavefunctions of the nearest-neighbor  $\text{Cu}^{2+}$  ions, as posited in (3.3.1). Yet this is precisely what the quantum-chemical calculations show [2, 54]. We outline the calculation here and refer the reader to the original papers for the details. The tight-binding quantum-chemical calculations for Cu(2) are based on the diagram shown in Fig. 3.6, where the relevant orbitals are shown at each ionic site. The  $d_{x^2-y^2}$  orbital is shown at the central (planar)  $\text{Cu}^{2+}$  ion, the  $p_\sigma$  orbitals on the oxygen ligands, and the  $4s$  orbitals on the four  $nn$   $\text{Cu}^{2+}$  ions. With the sign conventions given in the figure, the  $p$  and  $s$ -orbital admixtures which couple to the central  $d_{x^2-y^2}$  orbital are  $p = (p_{1x} - p_{2y} - p_{3x} + p_{4y})/2$  and  $s = (s_1 - s_2 + s_3 - s_4)/2$ . The energies are as follows: The 3d-orbital energy is taken as the origin,  $\epsilon_d = 0$ . The ligand on-site energies are taken to be  $\epsilon_p = 4\text{eV}$  and  $\epsilon_s \sim -6\text{eV}$ . The hopping energies shown in Fig. 3.6 are  $t_1$

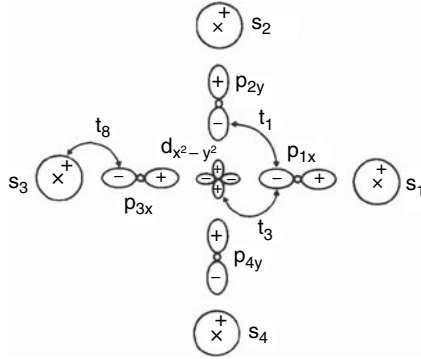


**Fig. 3.6.** A schematic representation of the  $d_{x^2-y^2}$  orbital at a Cu(2) site and the  $p_{\sigma}$  orbitals of the  $O^{2-}$  ligands, as well as the  $4s$  orbitals on the four  $nn$  Cu(2) sites, which are admixed to form the total wavefunction of the Cu(2)  $3d$ -holes for the Mila-Rice quantum chemistry calculation (see text). The  $t_{\alpha}$ 's show hopping matrix elements, and the signs give phase conventions for admixed orbitals. Figure reprinted from F. Mila, T.M. Rice, *Physica C* **157**, 561 (1989). Copyright 1989 Physica C

$= 0.33 \text{ eV}$ ,  $t_3 = 1.38 \text{ eV}$ , and  $t_8 = 3.9 \text{ eV}$ . The Hamiltonian is then solved in conjunction with the somewhat more complex Cu(1)-site Hamiltonian.

### *The Wannier Wavefunction for Cu(2)*

The Cu(2) tight-binding (Wannier) wavefunction is written

$$|\psi(2)\rangle = \alpha_d |d_{x^2-y^2}\rangle + \alpha_p |p\rangle + \alpha_s |s\rangle, \quad (3.3.9)$$

where the solution presented gives  $\alpha_d = 0.9$ ,  $\alpha_p = -0.34$ , and  $\alpha_s = -0.26$ . In addition there is a coupling via the oxygen ligand to the nearest Cu(1) site and to the  $4s$  state on that site. This coupling has some effect on the Cu(2) shift, but an essentially negligible effect on the Cu(2)  $T_1$ . For simplicity we shall omit these terms. The transferred isotropic HF coupling (3.3.1) from the  $nn$  Cu(2) sites may be estimated as follows. The  $4s$  contact HF coupling from EPR data for atomic Cu [55] is

$$\frac{16\pi}{3} |\psi_{4s}(0)|^2 = 0.45 \times 10^{27} \text{ cm}^{-3}. \quad (3.3.10)$$

Referring to (1.2.2) and (1.2.7), the corresponding  $4s$  contact HF coupling is  $2,080 \text{ kOe}/\mu_B$ . The total transferred coupling is then estimated to be  $\alpha_s^2 \times 2080 = 141 \text{ kOe}/\mu_B$ , as compared with  $\sim 160 \text{ kOe}/\mu_B$  required to give the nearly vanishing  $c$  axis spin-paramagnetic shift. Mila and Rice note that the value stated is for atomic Cu, whereas  $\text{Cu}^{2+}$  will have an enhanced value of  $|\psi_{4s}(0)|^2$  because of the ionic plus charge. There seems little doubt that the  $nn$   $4s$  admixture effect is the correct answer to the  $c$  axis HF anomaly.

### *The Composite Cu(2) Spin Hyperfine Tensor*

Let us now state the remainder of the HF coupling terms for Cu(2) and then formulate the Mila-Rice  $T_1$  relaxation tensor. The full HF tensor may be written [42],

$$\mathcal{H}_{HF}^{(2)} = \sum_{\alpha} A_{\alpha}^{(2)} I_{\alpha} S_{0\alpha} + B(2) \sum_{i(nn)} \mathbf{I} \cdot \mathbf{S}_i, \quad (3.3.11)$$

with

$$A_{\alpha}^{(2)} = A_{cp}^{(2)} + A_{dip,\alpha}^{(2)} + A_{so,\alpha}^{(2)}, \quad (3.3.12)$$

where the three terms shown are the isotropic core polarization term, the dipolar term, and the *spin-orbit* term, and where  $\alpha = (ab, c)$  for the axially symmetric Cu(2) site. The spin-orbit terms, being a second-order perturbation effect to higher crystal field states driven by the spin-orbit coupling, are a special feature of the spin Hamiltonian picture. They are actually an orbital field admixed into the spin HF terms.

The core-polarization term is sometimes given as proportional to  $\langle r^{-3} \rangle$ , which is a holdover from EPR studies where the origin of this term had not been identified<sup>2</sup>. Here we shall simply appeal to systematic studies, which give  $A_{cp}/2\hbar\gamma_n \simeq -127 \text{ kOe}/\mu_B$ . The dipolar and spin-orbit terms may be written (in energy units)

$$A_{dip,ab} = 2\gamma_n \hbar \mu_B \frac{2}{7} \langle r^{-3} \rangle, \quad (3.3.13a)$$

$$A_{dip,c} = -2\gamma_n \hbar \mu_B \frac{4}{7} \langle r^{-3} \rangle, \quad (3.3.13b)$$

$$A_{so,ab} = 2\gamma_n \hbar \mu_B \langle r^{-3} \rangle \left[ -\frac{11\lambda}{7\Delta_1} \right], \quad (3.3.13c)$$

$$A_{so,c} = 2\gamma_n \hbar \mu_B \langle r^{-3} \rangle \left[ -\frac{6\lambda}{7\Delta_1} - \frac{8\lambda}{\Delta_0} \right]. \quad (3.3.13d)$$

We use the same parameters used earlier to evaluate the Van Vleck orbital susceptibilities and in (3.3.7) for the anisotropic g-factor to calculate the spin HF tensor. These are  $\lambda = -0.077 \text{ eV}$ ,  $\Delta_0 = 2.00 \text{ eV}$ ,  $\Delta_1 = 2.29 \text{ eV}$ , and  $\langle r^{-3} \rangle = 6.3 \text{ a.u.}$  The resulting values for the Cu(2) spin HF tensor (3.3.11) are listed in Table 3.4 in units of  $\text{kOe}/\mu_B$  (see Sect. 2.3.1). We also employ a reduction factor of 0.70 derived from determinations of covalency [13, 14] for these parameters, as well as the core polarization HF field, in the second line of Table 3.4. The value of  $B^{(2)}$  shown is adjusted to give minimum error for the Cu(2) spin-paramagnetic shift values  $K_s^{(2)}(ab)$  and  $K_s^{(2)}(c)$  (bottom line of Table 3.2). The estimated values  $K_{sE}^{(2)}(ab)$  and  $K_{sE}^{(2)}(c)$ , given by

---

<sup>2</sup> The work of Heine [56] later revealed that it had no connection with  $\langle r^{-3} \rangle$ .

**Table 3.4.** Listing of values of spin HF tensor components for the Cu(2) sites, as derived in the foregoing paragraph. On the second line the free-ion component values have been corrected with a reduction factor 0.70 to account for covalency as mentioned above. A value of  $B^{(2)}$  is stated (see (3.3.11)) which minimizes the errors in the spin-paramagnetic shift components given in the bottom line of Table 3.2. This value of  $B^{(2)}$  is in reasonable accord with the estimate derived from quantum chemistry [2]. The spin susceptibility tensor associated with each Cu(1,2) site deduced earlier is shown, along with the Cu(2) site spin-paramagnetic shift tensor corresponding to the HF parameters given. Finally, the composite on-site HF tensor components given by (3.3.12) are listed. All HF tensor components are in units of  $kOe/\mu_B$ , with susceptibilities in  $10^{-6}(emu/mole)$

|          | $A_{cp}^{(2)}$ | $A_{dip,ab}^{(2)}$ | $A_{dip,c}^{(2)}$ | $A_{so,ab}^{(2)}$ | $A_{so,c}^{(2)}$ | $B^{(2)}$ | $\chi_{s\perp}$ | $\chi_{s\parallel}$ | $K_{sE}^{(2)}(ab)$ | $K_{sE}^{(2)}(c)$ | $A_{ab}^{(2)}$ | $A_c^{(2)}$ |
|----------|----------------|--------------------|-------------------|-------------------|------------------|-----------|-----------------|---------------------|--------------------|-------------------|----------------|-------------|
| (3.3.13) | -127           | 113                | -225              | 21                | 131              | 55        |                 |                     |                    |                   |                |             |
| Corr.    | -89            | 79                 | -158              | 15                | 92               | 38        | 101             | 118                 | 0.28%              | -0.01%            | 5              | -155        |

$$K_{sE}^{(2)}(ab, c) = \left( \frac{A_{ab,c}^{(2)}}{N_A \mu_B} \right) \chi_{s\perp, \parallel}, \quad (3.3.14)$$

where  $A_{\xi}^{(2)} = A_{cp}^{(2)} + A_{dip,\xi}^{(2)} + A_{so,\xi}^{(2)} + 4B^{(2)}$ , are also listed in the table. A good fit is seen to be achieved. To the far right are listed the components of the composite on-site HF tensor  $A_{\alpha}^{(2)}$  defined by (3.3.12).

### 3.3.4 $T_1$ Ratios and Electron Spin Correlation Effects

Mila and Rice introduced the concept of electronic spin-spin correlation factors in their  $T_1$  calculation, but did not use them in their discussion of  $T_1$  anisotropy. Subsequent discussions of the  $T_1$  problem in cuprates have made extensive use of this idea. Here, we find it necessary to consider the effect of spin-spin correlations to obtain agreement with experimental data. All HF constants are given in  $(kG/\mu_B)$ . The primed notation for this option introduced with (3.3.4) is suppressed in this subsection for simplicity.

Using expressions similar to MR, we now present results for the Cu(2) relaxation tensor. The  $1/T_{1ab,c}$  have the form  $H_{HF}^2(ab, c)\chi_s''(\omega_0)$ , where the squared HF field parameters are

$$H_{HF}^2(c) = 2[A_{ab}^{(2)2} + 4B^{(2)2} + 8A_{ab}^{(2)}B^{(2)}\mathcal{K}_{01} + 4B^{(2)2}(2\mathcal{K}_{12} + \mathcal{K}_{13})] \quad (3.3.15)$$

and

$$H_{HF}^2(ab) = [A_{ab}^{(2)2} + A_c^{(2)2} + 8B^{(2)2} + 8(A_{ab}^{(2)} + A_c^{(2)})B^{(2)}\mathcal{K}_{01} + 8B^{(2)2}(2\mathcal{K}_{12} + \mathcal{K}_{13})], \quad (3.3.16)$$

where  $\mathcal{K}_{ij} = \frac{4}{3}\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$  is the normalized spin-spin correlation between sites labeled i and j (see Fig. 3.6). The quantity  $\chi_s''(\omega_0)$  has the dimensions of a correlation time, but also has in it the density of states and temperature factors

that arise out of some specific model of quasiparticle dynamics appropriate to the cuprates. If the system were a Fermi liquid one would have  $\chi_s''(\omega_0) \propto T$ . Without such modeling this theory cannot give absolute values for  $T_1$ , but it can predict the anisotropy of  $T_1$  at the Cu(2) site using the HF tensor data from Table 3.4. Having minimized the error in the spin paramagnetic shift tensor to estimate the value of  $B^{(2)}$  given in the table, we insert the parameter values into the ratio of (3.3.16) to (3.3.15) to determine the expression,

$$\frac{T_{1c}}{T_{1ab}} = 2.64 \frac{[1 - 1.69 \mathcal{K}_{01} + 0.38 (2 \mathcal{K}_{12} + \mathcal{K}_{13})]}{[1 + 0.29 \mathcal{K}_{01} + 0.99 (2 \mathcal{K}_{12} + \mathcal{K}_{13})]}. \quad (3.3.17)$$

Equation (3.3.17) is to be compared with experimental data giving values of  $T_{1c}/T_{1ab}$  of  $\sim 4.5$  [29],  $\sim 3.6$  [38], or the later value  $\sim 3.4$  [57].<sup>3</sup> In any case, it is clear that the spin-spin correlation factors in (3.3.17) are going to have to play a role in order to achieve quantitative consistency with experiment. Regarding (3.3.17), since  $\mathcal{K}_{01}$  is a nearest-neighbor correlation it must be negative, while  $\mathcal{K}_{12}$  and  $\mathcal{K}_{13}$  are correlations between neighbors on the same “sublattice”, so to speak, so they will be positive and undoubtedly smaller in magnitude than  $\mathcal{K}_{01}$ . Thus,  $\mathcal{K}_{01}$  will have a clear effect of increasing the ratio if its value is negative and appreciable. For example, if we neglect the  $\mathcal{K}_{12,13}$  terms for the moment, then a value of  $\mathcal{K}_{01} = -0.07$  would yield a  $T_1$  ratio of 4. With only a modest amount of correlation we can obtain a realistic value for  $T_{1c}/T_{1ab}$ .

### *Temperature-Dependent Spin-Spin Correlations*

It is not clear from the Mila-Rice presentation, either, whether they intended the correlations to be used as temperature-dependent parameters or not, but a number of subsequent developments have employed them in just that role. For example, temperature-varying correlations give a straightforward explanation for the variation found for the  $T_1$  anisotropy in YBCO7 between 100 K and 300 K [38]. These data are shown in Fig. 3.7, where it is seen that  $T_{1c}/T_{1ab}$  diminishes by barely 10% over that temperature interval, and is only barely outside of the error bars. Nonetheless, the trend persists over a series of data points and is clearly established.<sup>4</sup>

As we shall see in Chap. 5, extensive use has been made of the  $\mathcal{K}_{ij}$ ’s as temperature-dependent parameters to describe the behavior of  $T_1$ . In the Uldry-Meier  $T_1$  analysis, for example, the temperature dependence of all  $T_1$ ’s is described in terms of the spin-spin correlations and an effective correlation time [58]. The theoretical basis for this approach is derived in Sect. 3.5.

<sup>3</sup> The difference between these two measurements is outside of error estimates, and can only be attributed to a difference in samples. The lower numbers agree with earlier measurements made on a random powder [37].

<sup>4</sup> It would have been desirable to have this effect confirmed by another experimental group. To our knowledge, no such confirmation has been reported.

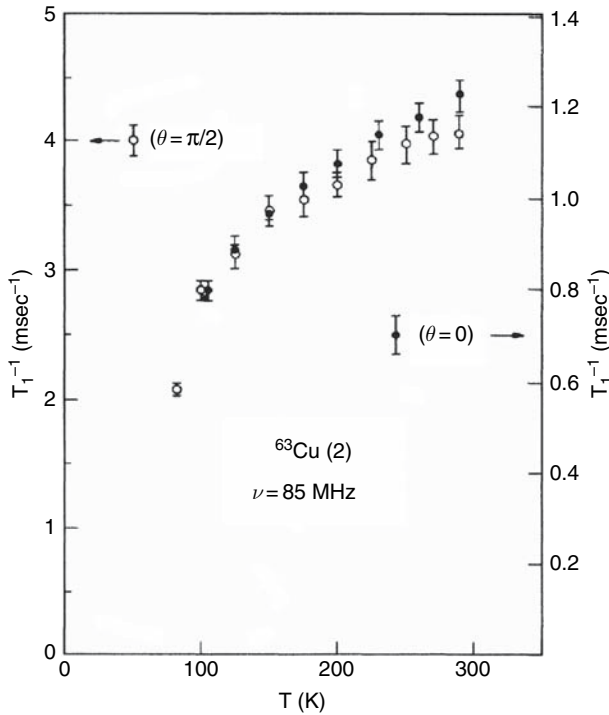


**Fig. 3.7.**  $1/T_{1ab}$  ( $\theta = \pi/2$ ) and  $1/T_{1c}$  ( $\theta = 0$ ) are plotted vs. temperature over the range  $90\text{ K} \leq T \leq 300\text{ K}$  for Cu(2) sites in an oriented powder sample of fully oxygenated YBCO7 [38]. The data are scaled so that  $T_1$  values for the two orientations coincide at  $T = 100\text{ K}$ , so as to highlight the decrease of the  $T_{1c}/T_{1ab}$  ratio over range of  $T$  measured. Reprinted figure from R.E. Walstedt, W.W. Warren, Jr., et al: Phys. Rev. B**40**, 2572 (1989). Copyright 1989 American Physical Society

Meanwhile, we also recall that the first Mila-Rice paper [2] made no attempt to apply their model to the interpretation of the peculiar temperature dependence of the  $T_1$  data. Indeed, theories addressing the behavior of  $T_1(T)$  were fairly quick to follow, but are still under discussion, as will be seen in Chap. 5.

### 3.4 Incorporating $^{17}\text{O}$ and $^{89}\text{Y}$ data into the Mila-Rice-Shastry Picture

Following the Mila-Rice (MR) paper there were many new developments, some going beyond the scope of the present chapter. There were new data on  $^{17}\text{O}$  NMR in YBCO, as well as a great deal of discussion regarding the question of a two-fluid picture of quasiparticle dynamics, i.e. whether there is evidence for a separate hole band on the oxygen sites. There were also efforts to treat

the temperature dependence of the copper  $T_1$ , along with discussion of just how the Cu(1) chain sites in YBCO differ from the Cu(2). In the midst of these many challenging questions and almost immediately following Mila and Rice, reports on the peculiar behavior of the oxygen-deficient phases made a sudden appearance. These effects, known collectively as *the pseudogap* and their interesting history in the high- $T_c$  field are the subject of Chap. 4.

We consider here the first reports on the behavior of the planar  $^{17}\text{O}$  NMR, as well as the closely related  $^{89}\text{Y}$ . Detailed theories which address the contrasting behavior of  $^{63,65}\text{Cu}$ ,  $^{17}\text{O}$ , and  $^{89}\text{Y}$  in YBCO are presented in Chap. 5. Following the discussion of the  $^{17}\text{O}$  data for YBCO7, we consider again the possible occurrence of oxygen hole bands along with the  $\text{Cu}^{2+}$ -related (Zhang-Rice) quasiparticles in the total picture of fermion dynamics.

### $^{17}\text{O}(2,3)$ NMR Data and Interpretation for YBCO7

By the middle of 1989,  $^{17}\text{O}$  NMR studies on YBCO7 had been reported by several groups [59, 60, 61, 62]. Here we shall review and discuss the results reported by Takigawa, Hammel et al. [59, 60] in some detail. A comparable set of results was reported by Horvatić et al. [61], covering a wider range of temperatures. The high temperature results for the quadrupolar and shift tensors for the O(2,3) sites from the latter study were found to agree within error bars with those from [59], and the quadrupolar data from [62] are also in accord. The HF tensor is analyzed below and compared with the MR model calculation. There is some disagreement in detail, but this, we suggest, may arise from inaccuracies in the MR quantum chemistry results.

$^{17}\text{O}$  spectra were taken on oriented powder samples of YBCO7 [59], for which  $^{17}\text{O}$ -enriched oxygen gas was used to exchange  $^{17}\text{O}$  into the sample material at a temperature of 900° C. The resulting (nearly) complete NMR spectrum for all of the oxygen sites is shown in Fig. 3.8 for the case of field oriented along the  $c$  axis. The identification of all the peaks in this spectrum is a real tour-de-force of NMR shift and quadrupole splitting analysis. Although the  $c$  axis is expected to be one of the principal axes of the EFG tensors for each oxygen site, the EFG tensors are decidedly non-axial in character. The peaks have been fitted using the  $I = \frac{5}{2}$  second-order perturbation formulas [59]

$$\left[-\frac{1}{2} \leftrightarrow \frac{1}{2}\right] : \Delta\nu = \nu_0 K_z + \frac{2}{9} (\nu_x - \nu_y)^2 / \nu_0, \quad (3.4.1a)$$

$$\left[\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}\right] : \Delta\nu = \nu_0 K_z \pm \nu_z + \frac{5}{36} (\nu_x - \nu_y)^2 / \nu_0, \quad (3.4.1b)$$

$$\left[\pm\frac{3}{2} \leftrightarrow \pm\frac{5}{2}\right] : \Delta\nu = \nu_0 K_z \pm 2\nu_z - \frac{1}{9} (\nu_x - \nu_y)^2 / \nu_0, \quad (3.4.1c)$$

where  $\nu_0 = \gamma_n H_{res}$  and  $\Delta\nu = \nu_{res} - \nu_0$ . The NMR frequency is  $\nu_{res}$ , and  $H_{res}$  is the value of the field at the peak in question. The quantities  $\nu_{x,y,z}$  are quadrupole frequency parameters defined as  $\nu_\alpha = \frac{3eQ}{20\hbar} V_{\alpha\alpha}$ . Equation (3.4.1a)

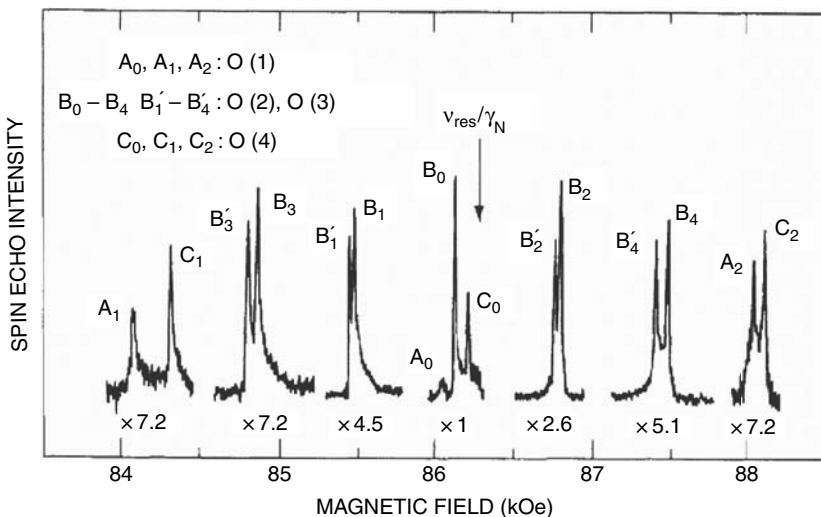


**Fig. 3.8.**  $^{17}\text{O}$  NMR spectrum taken at 49.8 MHz on an oriented powder sample of YBCO7 with enriched  $^{17}\text{O}$  content [59]. The field was oriented along the  $c$  axis. Sample temperature was 160 K. For  $^{17}\text{O}$   $\gamma_n/2\pi$  was taken to be 0.577186 kHz/Oe. The sites were identified as labelled, with the  $(B_n, B'_n)$  pairs of lines very close together for the O(2,3) sites. See text for discussion of the quadrupolar and shift tensors for the O(2,3) sites. Reprinted figure from M. Takigawa, P.C. Hammel, et al: Phys. Rev. Lett. **63**, 1865 (1989). Copyright 1989 American Physical Society

will be recognized as (2.1.3) written out with  $V_{\alpha\alpha}$  parameters. Note that no relative size or sign relationship is implied here among the  $\nu_{x,y,z}$ , except, of course, that  $\sum_{\alpha} \nu_{\alpha} = 0$ . The parameters are adjusted for each site so as to give a best fit to the spectrum shown, as well as spectra taken with  $\mathbf{H} \perp$  the  $c$  axis, an exercise of considerable complexity.

For the case of the O(2,3) sites, it was not clear from the data alone whether the principal axis of the EFG was along the  $c$  axis or along the bond axis. To decide this, trial calculations of the EFG tensor were made assuming a point-charge contribution multiplied by a Sternheimer factor  $(1 - \gamma_{\infty})$  [63], where  $\gamma_{\infty}$  was taken to be 9, plus an on-site p-electron contribution of  $(\frac{3}{20})(\frac{4}{5}e^2|Q|\langle r^{-3} \rangle)$ , where  $\langle r^{-3} \rangle$  was taken to be 3.63 a.u. [59]. On this basis, the only reasonable outcome was obtained assuming the principal axis is the bond axis, giving an estimated result (0.97, -0.42, -0.55) MHz as compared with (0.976, -0.598, -0.378) MHz shown in Table 3.5. Note that the transverse axis values are reversed between modeling and experiment, so that the fit is close, but not exact. The principal EFG values for all sites lie along the bond axes.

Our interest in the shift data shown in the table is in comparing them with the results calculated by MR, and ultimately to see whether the  $^{17}\text{O}$  data are compatible with a single-fluid description of the distribution of electronic

(i.e. hole) spin density. Shift values are given for all sites at two temperatures, 160 K and 30 K. In the latter case, we suppose that the spin susceptibility is essentially zero (see e.g. shift measurements for  $T < T_c$  in [41, 48]), so that these residual values may be regarded as orbital shifts. This surmise is verified by a detailed plot of  $K_c(T)$  vs.  $T$  by Horvatić et al., (see Fig. 4 in [61]). Subtracting the 30 K shift values from the 160 K ones, we find estimates of the spin paramagnetic shift components, listed under “ $K_s(160\text{ K})$ ”. The latter values form a tensor for each site, which has been divided into an isotropic component  $K_{iso} = (K_{\parallel} + 2K_{\perp})/3$  and an anisotropic (axial) component with  $K_{ax} = (K_{\parallel} - K_{\perp})/3$ . The latter parameters are tabulated in the final two columns. It is seen for the O(2,3) that there is a fairly large isotropic component as expected, with quite a sizeable axial shift  $K_{ax} = 0.03\%$  as well. It seems that the main hybridization is into the  $2p_{\sigma}$  orbitals as expected.

On the other hand, the MR quantum chemistry calculation predicted a rather smaller value for  $K_{ax}$  than what was found. We analyze this point by noting that the axial shift coefficient for a  $p_{\sigma}$  orbital occupied with a fraction  $f$  of the  $S = \frac{1}{2}$  moment is given by  $\alpha_{ax} = \frac{2}{5}f\langle r^{-3} \rangle/N_A$ . According to the MR quantum chemistry (Sect. 3.3),  $f = \alpha_p^2/2 = 0.058$ . Using the value  $\langle r^{-3} \rangle = 3.63\text{ a.u.}$  [59], we find  $\alpha_{\sigma} = 0.94(\text{emu}/\text{mole})^{-1}$ . With a transverse susceptibility component of  $1.01 \times 10^{-4}(\text{emu}/\text{mole Cu}(2))$  (Table 3.4), we find  $K_{ax}(\text{MR}) \simeq 0.0095\%$ . This is approximately 1/3 the experimental value in Table 3.5. So although the experimental value has a large error bar, it is certainly much larger than the MR calculated value.

Is this evidence for an oxygen hole band? We think not, but unfortunately, there is no trend with doping or even temperature dependence to check such a hypothesis. However, there is another experimental number which comes to mind here, namely the determination of the covalency of  $\text{La}_2\text{CuO}_4$  at high

**Table 3.5.** Experimental quadrupolar tensors and shift data from spectra such as Fig. 3.8 are shown at two temperatures in the left-hand columns, followed by deduced spin components, which are then broken down into isotropic and axial parts [59]. The 30 K values are taken to be of purely orbital origin. Site and orientation labels are shown at the far left. Frequencies are given in MHz and shifts in %

| Site   | Axis          | $\nu_{\alpha}$  | $K_{\alpha}(160\text{ K})$ | $K_{\alpha}(30\text{ K})$ | $K_s(160\text{ K})$ | $K_s(iso)$ | $K_s(ax)$ |
|--------|---------------|-----------------|----------------------------|---------------------------|---------------------|------------|-----------|
| O(1)   | $\perp c$     | -0.484          | 0.23                       | ...                       | ...                 | 0.10(1)    | 0.01(1)   |
|        | $\perp c$     | 1.629           | 0.22                       | 0.13(1)                   | 0.09(1)             |            |           |
|        | $\parallel c$ | -1.145          | 0.24                       | 0.13(3)                   | 0.11(3)             |            |           |
| O(2,3) | $\perp c$     | (0.986,0.966)   | 0.31                       | 0.05(1)                   | 0.26(1)             | 0.19(1)    | 0.03(1)   |
|        | $\perp c$     | -0.598          | 0.17                       | 0.01(1)                   | 0.16(1)             |            |           |
|        | $\parallel c$ | (-0.389,-0.369) | 0.18                       | 0.02(3)                   | 0.16(1)             |            |           |
| O(4)   | $\perp c$     | -0.375          | -0.02                      | -0.01(1)                  | -0.01(1)            | 0.01(1)    | 0.02(1)   |
|        | $\perp c$     | -0.721          | 0.03                       | 0.04(1)                   | -0.01(1)            |            |           |
|        | $\parallel c$ | 1.096           | 0.08                       | 0.03(1)                   | 0.05(1)             |            |           |

temperatures using  $^{17}\text{O}$  NMR shift measurements [13]. The total fraction of spin density residing on the O(2,3) with the MR result (foregoing paragraph) is  $2f = 11.6\%$ . The comparable experimental result for  $\text{La}_2\text{CuO}_4$  is 31% [13]. Scaling the foregoing estimate by the ratio of these numbers, one finds a result nearly a factor of 3 larger and in much better agreement with the O(2,3) axial shift in Table 3.5. The  $\text{La}_2\text{CuO}_4$  measurement is also in good agreement with, but actually slightly less than theoretical values given by Hüsser, et al. [14]. We suggest that the value for  $\text{La}_2\text{CuO}_4$  should not be very different from that for YBCO7. Thus, it is possible that the expected number for the  $2p_\sigma$  spin density is quite a bit larger than the MR value, and that the reported  $^{17}\text{O}(2,3)$  shift values in [59] are consistent with a one-band picture.

### *HF Tensors for $^{17}\text{O}(2,3)$ and $^{89}\text{Y}$ in YBCO7*

In Table 3.6 we collect data for the  $^{17}\text{O}(2,3)$  and  $^{89}\text{Y}$  NMR shift tensors and list the corresponding HF tensors defined in (3.3.2) and (3.3.4). For the  $^{17}\text{O}(2,3)$  case we take NMR shift data from Table 3.5. For the  $^{89}\text{Y}$  case the data are taken from Alloul et al. [64], which reports the highest numbers available for an oriented powder sample<sup>5</sup>. The HF tensors are then obtained with (3.3.4) using the spin susceptibilities in Table 3.4.

The HF constants for the various sites in and near the  $\text{CuO}_2$  in Tables 3.4 and 3.6 are expected to hold for reduced oxygen phases of YBCO7- $x$  as well. A very important test of this idea occurs in Chap. 4, where these values are compared with precisely determined relative values for the YBCO6.63 phase.

**Table 3.6.** Spin components of NMR shift are tabulated for the  $^{17}\text{O}(2,3)$  and  $^{89}\text{Y}$ ,  $^{17}K_{s\alpha}$  and  $^{89}K_{s\alpha}$ , respectively, for YBCO7 at  $T = 100\text{ K}$ . See text for the source of these data. The corresponding HF tensors obtained with (3.3.4) are also listed, along with the susceptibility tensor from Table 3.4. Note that for the  $^{89}\text{Y}$  case the denominator in (3.3.4) is “8” rather than “2”.  $C_\alpha$  and  $D_\alpha$  are given in  $kOe/\mu_B$  and  $\chi_{s\alpha}$  in  $10^{-4}(\text{emu}/\text{mole})$

| Axis     | $^{17}K_\alpha(\%)$ | $^{89}K_\alpha(ppm)$ | $C'_\alpha$ | $D'_\alpha$ | $\chi_{s\alpha}(100\text{ K})$ |
|----------|---------------------|----------------------|-------------|-------------|--------------------------------|
| <i>a</i> | 0.26(1)             | 247                  | 72(3)       | 1.71(9)     | 1.01                           |
| <i>b</i> | 0.16(1)             | 247                  | 44(2)       | 1.71(9)     | 1.01                           |
| <i>c</i> | 0.16(1)             | 315                  | 38(2)       | 1.86(9)     | 1.18                           |

<sup>5</sup> We take larger numbers for the  $^{89}\text{Y}$  NMR shift at 100 K to be a sign of full oxygenation. Moreover, the plot reported for  $^{89}K_\alpha(T)$  vs.  $T$  [64] shows a gradual increase from 300 K down to a maximum at  $T \sim 120\text{ K}$ . This is a characteristic of a fully oxygenated sample as well [47], rather than declining curves which then give smaller values of  $^{89}K_\alpha$  at  $T = 100\text{ K}$  [65].

### 3.4.1 Measurements of $T_1$ for $^{17}\text{O}$ in YBCO7

The foregoing authors also reported  $T_1$  measurements for various oxygen sites in YBCO7 [60]. As found earlier for the  $^{89}\text{Y}$  [22, 23], the  $^{17}\text{O}(2,3)$  relaxation in the normal state is very Korringa-like, with  $T_1 T \simeq 2.7 \text{ sK}$ . The authors chose to give a qualitative discussion of this result, along with their  $^{63}\text{Cu}(2)$  data, in terms of the Korringa relation (1.2.8). Following that, however, they discuss the  $T_1$  results in terms of the dynamic susceptibility  $\chi''(\mathbf{q}, \omega)$ , which became the method of choice for analyzing relaxation data. In the following sect. (3.5) we present for reference purposes a derivation of the relaxation rates for  $^{89}\text{Y}$ ,  $^{17}\text{O}(2,3)$ , and  $^{63}\text{Cu}(2)$  in YBCO in terms of  $\chi''(\mathbf{q}, \omega)$ . We shall use formulas given there for our present discussion of data from [60].

First, let us consider the simple Korringa relation (2.2.8) in relation to the current problem. One could hardly expect it to apply in any strict fashion to YBCO, owing to unknown particle dynamics,  $\mathbf{q}$ -dependent HF coupling tensors, etc. Nonetheless, it does serve a sort of qualitative purpose in comparing the behavior of different nuclear sites. The  $^{89}\text{Y}$  and  $^{17}\text{O}(2,3)$   $T_1$  processes are at least Korringa-like in their temperature dependence, though this may be somewhat illusory because of spin-spin correlation effects. Nonetheless, if you take the isotropic shift value from Table 3.5, you find for  $^{17}\text{O}(2,3)$

$$\frac{1}{K_s(iso)^2 T_1 T} \simeq 1.4 \times \left[ \frac{4\pi k_B \gamma_n^2}{\hbar \gamma_c^2} \right]. \quad (3.4.2)$$

To compare the latter result with the Cu(2) site they used  $T_{1ab}$ , because it relates to the largest on-site HF term  $A_c = -221 \text{ kOe}/\mu_B$ . Since  $A_{ab}$  is very small, however, they divided the expression (3.4.2) by two,<sup>6</sup> finding a multiplier of 11 for the Cu(2) Korringa product. So there is a very clear enhancement of the Cu(2) relaxation, with almost none for the O(2,3). If we look at the  $\mathbf{q}$ -dependent expressions for  $1/T_1$  in Sect. 3.5, the Cu(2) expression for the field  $\perp c$  axis, it is essentially independent of  $\mathbf{q}$ , whereas for both the  $^{89}\text{Y}$  and  $^{17}\text{O}(2,3)$  cases, the integrand vanishes at  $Q_{AF} = (\pi/a, \pi/a)$ . If  $\chi''(\mathbf{q}, \omega)$  has an AFM enhancement peak, the Cu(2) rate will receive full enhancement, but the  $^{89}\text{Y}$  and  $^{17}\text{O}(2,3)$  will have little or none. This is the explanation offered in [60] for the discrepancy in Korringa ratios which they find, but has been put forward by many other observers as well [66]. It was also generally thought to be related to the peculiar temperature dependence of the Cu(2) relaxation rate while the  $^{89}\text{Y}$  and  $^{17}\text{O}(2,3)$  rates were Korringa-like.

Reference [60] also presented data on relaxation rates for  $T < T_c$  for YBCO7, but discussion of those results will be combined with consideration of the Cu(2) data in Sect. 3.6.

---

<sup>6</sup> Thus, only one axis is effectively contributing to the  $T_1$  rate.

### 3.4.2 The One-Band, Two-Band Debate: $^{89}\text{Y}$ and $^{17}\text{O}(2,3)$ NMR in YBCO

The MR model theory purported to explain the  $\text{Cu}(1,2)$  NMR (in YBCO7) behavior at 100 K with a single spin fluid, where all HF couplings were assumed to originate with the  $S = 1/2$  coupled moments on the  $\text{Cu}^{2+}$  sites. At the same time or slightly later, other interpretive papers appeared as well as experimental papers with more data on the  $^{89}\text{Y}$  and  $^{17}\text{O}$  NMR shift and relaxation properties.

In this subsection we consider arguments presented on the question of one quantum fluid vs. two separate fluids needed to account for the  $T_1$  data. Monien, Pines, and Slichter [67] presented an analysis similar to MR, including the transferred HF term for the  $\text{Cu}(2)$  sites, but also considering a possible “oxygen hole band” characterized by susceptibility  $\chi_h$  as well as a  $\text{Cu}(2)$  HF coupling  $A_h$ . In similar fashion to Sect. 3.3, they concluded that the one-fluid model could not explain the data unless there were spin-spin correlations. However, they also pointed out the possibility that the  $(\chi_h, A_h)$  oxygen band, if present, could be the explanation. The question was how to decide whether the hole band was necessary.

A substantive discussion of this point was given by Mila and Rice themselves in a follow-up paper [46]. We shall briefly recap their main points here. First, they note that while one could consider the possibility of a hole band on the  $\text{O}(2,3)$  sites, the Zhang-Rice singlet picture essentially rules this out, since the singlets are magnetically inert<sup>7</sup>. Thus, one would expect that HF parameters should not depend on the doping level. In this connection they noted that in the large  $^{89}\text{Y}$  study by Alloul et al. [65], the slope of  $K$  vs.  $\chi$  plots is invariant from full doping all the way down into the insulating regime. Thus, the  $^{89}\text{Y}$  HF coupling is independent of doping, consistent with the Zhang-Rice singlet picture.

Next, they consider what one would expect if there actually were a hole band. On the basis of quantum chemistry, MR argue that such a hole band would have a much stronger HF coupling with the  $^{89}\text{Y}$  nuclei than the  $\text{Cu}^{2+}$  moments have. The reasoning is as follows. First, the  $\text{Cu}^{2+}$  are too far from the  $^{89}\text{Y}$  for direct coupling, and for the (strongly) hybridized  $2p_\sigma$  orbitals on the  $\text{O}(2,3)$ , the MR Wannier wavefunction (3.3.9) has the wrong symmetry to couple to the Y  $s$  or  $d$  orbitals. The answer, they suggest, is a possible double hybridization path through  $2p_\pi$  orbitals to the Y  $4d$ . This is, of course, very weak, and they argue that any hole band which occupies either the  $2p_\sigma$  or  $2p_\pi$  orbitals will have hybridization at least 5 times larger. Because of this, the  $^{89}\text{Y}$  HF parameter in such a case would vary sharply with hole concentration. Since it does not, they conclude that an oxygen hole band is essentially ruled out.

---

<sup>7</sup> There were, however, two-band models proposed at the time, such as that given by Emery and Reiter [68].

There was further discussion of oxygen bands in a few additional papers [48, 5], but no really cogent evidence confirming their existence. In Chap. 5 a discussion is presented of several models for calculation and interpretation of  $T_1$  data for various nuclear species in the YBCO family of compounds. With the development of various theoretical models and schemes for interpretation of relaxation effects, there seemed less and less motivation to include oxygen hole bands. There was no evidence to support their suggested existence once it was realized that  $q$ -dependence susceptibilities and HF couplings could account for the observed behavior. There, however, we shall also reconsider the possibility of an orbital relaxation term (see Sect. 5.6).

### 3.5 Formulation of $T_1$ in Terms of $\chi''(q, \omega)$ and $q$ -Dependent HF Couplings

Even though transferred HF couplings quite obviously underlie the shift and relaxation effects of the  $^{89}\text{Y}$  nuclei in YBCO [22, 23, 35, 36], their presence – and the concomitant effects of antiferromagnetic (AFM) spin-spin correlations – were brought to our attention by the MR [2] analysis. However, the spin-spin correlation picture was not destined to become the language of choice for this problem, but rather that of the well-known dynamical susceptibility  $\chi(\mathbf{q}, \omega)$  [69, 70]. While these pictures are, as will be seen below, completely equivalent, the  $q$ -space methodology is perhaps a bit more convenient, as well as tying in directly with INS measurements. While the potential of this approach to distinguish the behavior of  $^{63,65}\text{Cu}$ ,  $^{17}\text{O}$ , and  $^{89}\text{Y}$  in YBCO was noted early on [34], its dramatic consequence of cancelling AFM fluctuations at the planar oxygen was first articulated by the analysis of Shastry [3]. Subsequently, it has been widely invoked for discussion of  $T_1$  effects [6, 7, 46, 60, 66, 71].

#### 3.5.1 Derivation of Dynamical Susceptibility $T_1$ Equation

The formula for  $T_1$  in terms of  $\chi''(\mathbf{q}, \omega)$  and  $q$ -dependent HF couplings is widely quoted. For reference, we give here a simple derivation of this result, starting from the master equation for the interaction representation density matrix for nuclear spins  $\rho^*(t)$  [72],

$$\frac{d\rho^*}{dt} = - \int_0^\infty d\tau \overline{[\mathcal{H}_1^*(t), [\mathcal{H}_1^*(t-\tau), \rho^*(t)]]}, \quad (3.5.1)$$

where  $\mathcal{H}_1$  is the spin-lattice interaction being treated here as a perturbation, and the overline represents an average over  $t$  which is long compared with the correlation time scale of  $\tau$ , but short compared with the time for the nuclear spin polarization to change. The star indicates operators which have been transformed into the interaction representation as in  $\mathcal{O}^*(t) = \exp(i(\mathcal{F} + \mathcal{H}_0)t)\mathcal{O}\exp(-i(\mathcal{F} + \mathcal{H}_0)t)$ , where  $\mathcal{H}_0$  is the unperturbed nuclear

spin Hamiltonian, and  $\mathcal{F}$  is the Hamiltonian for the rest of the dynamical variables in the system. Here, for simplicity we take  $\mathcal{H}_0$  to be a Zeeman term with a field  $H$  applied along the cartesian axis labelled  $\alpha$ ,

$$\mathcal{H}_0 = -\omega_0 \sum_i I_{\alpha i}, \quad (3.5.2)$$

where  $\omega_0 = \gamma_n H$ . The density matrix for spin-lattice relaxation in such a case is simply  $\rho^*(t) = \rho(t) = a(t) \sum_i I_{\alpha i}$ , where  $a(t)$  is a variable which represents the changing nuclear magnetization during a  $T_1$  experiment.

We illustrate the  $\mathbf{q}$ -dependent HF coupling effects with  $\mathcal{H}_1$  for the Cu(2) sites,

$$\mathcal{H}_1 = \sum_{j,\beta} I_{j\beta} \left[ A_\alpha S_{j\beta} + B \sum_{k=nn} S_{k\beta} \right], \quad (3.5.3)$$

where the  $B$  term is an isotropic coupling between  $\mathbf{I}_j$  and the four  $nn$  spins  $\mathbf{S}_k$  to the  $j$  site. It will simplify the procedure if we neglect the imaginary part of the time factors  $\exp(\pm i\omega_0 t)$  which occur for each of the operators  $I_{j\beta}$  in the interaction representation, and simply represent them as a factor  $\cos\omega_0\tau$  times the correlation functions. The correlation functions are assumed to be even in the variable  $\tau$ , and the  $\sin\omega_0\tau$  terms will always vanish in the applications considered here.

A second simplification occurs if we operate on both sides of (3.5.1) with  $\text{Tr}(I_{i\alpha} \dots)$ . Since the spin correlation functions are even functions of  $\tau$  so that  $S_{j\beta}(t)S_{k\beta}(t+\tau) = S_{j\beta}(t+\tau)S_{k\beta}(t)$ , we may write (3.5.1), in part, as

$$a^{-1} \frac{da}{dt} = - \sum_i^{(N)} \int_0^\infty d\tau \cos\omega_0\tau \overline{[A_x S_{ix}(t) + B \sum_{k=nn} S_{kx}(t)] [A_x S_{ix}(t+\tau) + B \sum_{k=nn} S_{kx}(t+\tau)]}, \quad (3.5.4)$$

where we are displaying only the  $x$  axis fluctuation term as an example.

The next step is to Fourier transform the spin operators with

$$S_{i\beta}(t) = \sum_{\mathbf{q}}^{(N)} e^{i\mathbf{q} \cdot \mathbf{r}_i} S_{\mathbf{q}}(t), \quad \beta = x, y, z, \quad (3.5.5)$$

where the summations are normalized so that  $\sum_{\mathbf{q}}^{(N)} \exp[i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}_i)] = \delta_{\mathbf{r}, \mathbf{r}_i}$ , etc. In (3.5.5)  $S_{\mathbf{q}}(t)$  is defined to be an isotropic,  $\mathbf{q}$ -dependent spin fluctuation operator. Using (3.5.5) in both factors in (3.5.4) and noting that  $\sum_i^{(N)} \exp[i(\mathbf{q} + \mathbf{q}') \cdot \mathbf{r}_i] = \delta_{\mathbf{q}, -\mathbf{q}'}$ , (3.5.4) becomes

$$a^{-1} \frac{da}{dt} = - \sum_{\mathbf{q}}^{(N)} A_x(\mathbf{q})^2 \int_0^\infty d\tau \overline{S_{\mathbf{q}}(t) S_{-\mathbf{q}}(t+\tau)} \cos\omega_0\tau, \quad (3.5.6)$$

where  $A_x(\mathbf{q}) = [A_x + 2B(\cos(q_x a) + \cos(q_y a))]$ . In (3.5.6) the  $A_x(\mathbf{q})$  are in circular frequency units per unit of spin. We now proceed to replace the time average with an ensemble average

$$\int_0^\infty d\tau \overline{S_{\mathbf{q}}(t)S_{-\mathbf{q}}(t+\tau)} \cos \omega_0 \tau = \int_0^\infty d\tau \langle S_{\mathbf{q}}(0)S_{\mathbf{q}}(\tau) \rangle_{Ens} \cos \omega_0 \tau = S(\mathbf{q}, \omega_0), \quad (3.5.7)$$

where we have also assumed that  $S_{\mathbf{q}}(t)$  has inversion symmetry. The quantity on the far right of (3.5.7) is known as the *dynamical structure factor*.

### 3.5.2 The Fluctuation-Dissipation Theorem

The dynamical structure factor may be related to  $\chi(\mathbf{q}, \omega_0)$  using the *fluctuation-dissipation theorem* [4], which says

$$Im[\chi_s(\mathbf{q}, \omega_0)] = \chi_s''(\mathbf{q}, \omega_0) = \frac{(e^{\hbar\omega_0\beta} - 1)}{\hbar e^{\hbar\omega_0\beta}} S(\mathbf{q}, \omega_0), \quad (3.5.8)$$

where  $\beta = 1/k_B T$  and we note that  $\hbar\omega_0\beta \ll 1$ . The subscript “s” is a reminder that the spin-only susceptibility defined by (3.5.8) has a dimension of inverse energy. Inserting this into (3.5.6) and combining terms for  $x$  and  $y$ -axis fluctuations yields for  $-a^{-1}da/dt$ ,

$$\frac{1}{T_{1\alpha}} = \frac{\gamma^2 k_B T}{\mu_B^2} \sum_{\mathbf{q}} \sum_{\xi}^{(N)} A_{\xi}(\mathbf{q})^2 \chi_{\xi}''(\mathbf{q}, \omega_0) / (g_{\xi}^2 \omega_0). \quad (3.5.9)$$

The latter expression for  $1/T_{1\alpha}$  uses  $A_{\xi}(\mathbf{q})$  in Gauss per unit of spin (see Sect. 2.3.1) and a conventional susceptibility per formula unit of  $\text{CuO}_2$ . The sum on  $\xi$  is over the two directions normal to  $\alpha$ .

Next, we introduce a convenient simplification. One could use (3.5.9) by absorbing the  $g$ -factor denominator into the HF coefficients and work with the primed coefficients via (3.3.4). Following Auler et al., [73], we find it more convenient to define an *isotropic susceptibility* via  $\chi_{iso}''(\mathbf{q}, \omega) = 4\chi_{\xi}''(\mathbf{q}, \omega)/g_{\xi}^2$ , whereupon (3.5.9) becomes

$$\frac{1}{T_{1\alpha}} = \frac{\gamma^2 k_B T}{4\mu_B^2} \sum_{\mathbf{q}} \sum_{\xi}^{(N)} A_{\xi}(\mathbf{q})^2 \chi_{iso}''(\mathbf{q}, \omega_0) / \omega_0. \quad (3.5.10)$$

In this way only the natural anisotropy of the HF couplings from (3.3.2) comes into the  $T_1$  formula.

We now present expressions for  $1/T_1$  for the various nuclear species in YBCO, using the HF tensors developed in the text. For the  $c$  axis relaxation of  $\text{Cu}(2)$ ,  $A_{\xi} = A_{ab}$ , for both terms, so (3.5.9) becomes

$$\left. \frac{1}{T_{1c}} \right|_{\text{Cu}(2)} = \frac{\gamma^2 k_B T}{2\mu_B^2} \sum_{\mathbf{q}}^{(N)} [A_{ab} + 2B(\cos q_x a + \cos q_y a)]^2 \chi_{iso}''(\mathbf{q}, \omega_0) / \omega_0, \quad (3.5.11)$$

where the susceptibility is per  $\text{CuO}_2$ . For the field in the  $ab$  plane, we have

$$\left. \frac{1}{T_{1ab}} \right|_{\text{Cu}(2)} = \left. \frac{1}{2T_{1c}} \right|_{\text{Cu}(2)} + \frac{\gamma^2 k_B T}{4 \mu_B^2} \sum_{\mathbf{q}}^{(N)} [A_c + 2B (\cos q_x a + \cos q_y a)]^2 \chi''_{iso}(\mathbf{q}, \omega_0) / \omega_0. \quad (3.5.12)$$

However, for the  $\text{Cu}(2)$  HF couplings given in Table 3.4,  $A_c$  is the dominant term, so that for  $1/T_{1ab}$  the contribution of  $1/2T_{1c}$  is essentially negligible. Unless the correlations are known to be large, a good estimate can be obtained by dropping the “B” term as well, so that the HF coupling becomes essentially independent of  $\mathbf{q}$ .

For the planar oxygen sites and the yttrium sites in YBCO the HF couplings are dominated by hybridization effects with the  $2s$  [3] and  $4d$  [35] holes, giving HF coupling terms

$$A_{O,\xi}(\mathbf{q}) = 2C_\xi \cos q_x a / 2 \quad \text{and} \quad A_{Y,\xi}(\mathbf{q}) = 8D_\xi \cos q_x a / 2 \cos q_y a / 2, \quad (3.5.13)$$

respectively, where it is noted that the HF coupling for the  $\text{Y}^{3+}$  is thought to be dominated by the  $4d$  core-polarization HF field [35].

The corresponding expression for the  $^{17}\text{O}$  relaxation rate is, e.g.,

$$\left. \frac{1}{T_{1c}} \right|_O = \frac{\gamma^2 k_B T}{2 \mu_B^2} \sum_{\mathbf{q}}^{(N)} [C_x^2 (1 + \cos q_y a) + C_y^2 (1 + \cos q_x a)] \chi''_{iso}(\mathbf{q}, \omega_0) / \omega_0, \quad (3.5.14)$$

where  $T_1$  along other axes is analogous to the case for  $\text{Cu}(2)$ .

For the case of  $^{89}\text{Y}$ , we give here an expression in which interplanar correlations are neglected. Thus,

$$\left. \frac{1}{T_{1c}} \right|_Y = \frac{4\gamma^2 k_B T}{\hbar \mu_B^2} \sum_{\mathbf{q}}^{(N)} [D_x^2 + D_y^2] (1 + \cos q_x a) (1 + \cos q_y a) \chi''_{iso}(\mathbf{q}, \omega_0) / \omega_0. \quad (3.5.15)$$

### $\mathcal{K}_{ij}$ and $\mathcal{X}_{at}$ Expressed in Terms of $\chi''(\mathbf{q}, \omega)$

Dynamical AFM spin-spin correlation effects in these relaxation processes are embodied in the factors such as  $(1 + \cos q_{x,y} a)$ , the mean value of which will approach zero in the event of strong correlations. Such correlation factors were introduced by Mila and Rice [2], where in Sect. 3.3 they took the form  $\mathcal{K}_{ij} = 4\langle S_{i\alpha} S_{j\alpha} \rangle$ . It is useful to introduce an equivalent definition of the  $\mathcal{K}_{ij}$  in terms of  $\chi''(\mathbf{q}, \omega)$ . For example, the sum on  $\mathbf{q}$  in (3.5.14) can be put into the form

$$\sum_{\mathbf{q}}^{(N)} [\ ] = [C_x^2 + C_y^2] [1 + \mathcal{K}_{01}] \mathcal{X}_{at}, \quad (3.5.16)$$

where

$$\mathcal{X}_{at} = \sum_{\mathbf{q}}^{(N)} \frac{\chi''_{is}(\mathbf{q}, \omega_0)}{\omega_0} \text{ and } \mathcal{K}_{01} = \frac{1}{\mathcal{X}_{at}} \sum_{\mathbf{q}}^{(N)} \cos k_{x,y} a \frac{\chi''_{is}(\mathbf{q}, \omega_0)}{\omega_0}. \quad (3.5.17)$$

The quantity  $\mathcal{X}_{at}(T)$  is a fundamental dynamical index for  $\chi''_{is}(\mathbf{q}, \omega)$  at low frequencies. It contains the basic correlation time for the spin fluctuations. Furthermore, the quantity  $(k_B T)/\mu_B^2 \mathcal{X}_{at} \sim \hbar k_B T N(0)^2$  gives the correlation time along with the statistical weight of the  $T_1$  process, where  $N(0)$  is the density of states/atom at the Fermi surface for one direction of spin in an energy band environment. The other factor  $(1 + \mathcal{K}_{01}(T))$  gives the temperature variation of  $T_1$  arising from dynamical correlations for the case of transferred HF interactions. Equation (3.5.16) therefore effects a separation of these two fundamental – and physically very different – factors in the temperature dependence of  $T_1$ .

To complete the picture of spin–spin correlations used for the YBCO family of compounds, we have, in analogy with (3.5.17),

$$\begin{aligned} \mathcal{K}_{12} &= \frac{1}{\mathcal{X}_{at}} \sum_{\mathbf{q}}^{(N)} \cos k_x a \cos k_y a \frac{\chi''_{iso}(\mathbf{q}, \omega_0)}{\omega_0} \text{ and} \\ \mathcal{K}_{13} &= \frac{1}{\mathcal{X}_{at}} \sum_{\mathbf{q}}^{(N)} \cos 2k_{x,y} a \frac{\chi''_{iso}(\mathbf{q}, \omega_0)}{\omega_0}. \end{aligned} \quad (3.5.18)$$

We may now introduce these forms into the  $T_1$  expressions (3.5.11)–(3.5.15). As an example we consider the expression (3.5.11), where the HF coefficient factor  $[\ ]^2$  may be expanded as

$$\begin{aligned} A_\alpha^2 + 4B^2 + 2B^2 (\cos 2q_x a + \cos 2q_y a) + 8B^2 \cos q_x a \cos q_y a \\ + 4A_\alpha B (\cos q_x a + \cos q_y a). \end{aligned} \quad (3.5.19)$$

Using the definitions (3.5.17) and (3.5.18), the expression for  $1/T_1$  becomes

$$\left. \frac{1}{T_{1c}} \right|_{Cu(2)} = \frac{\gamma_{63}^2 k_B T}{2 \mu_B^2} \mathcal{X}_{at} \{ A_{ab}^2 + 4B^2 [1 + 2 \mathcal{K}_{12} + \mathcal{K}_{13}] + 8A_{ab} B \mathcal{K}_{01} \}, \quad (3.5.20)$$

where we recognize the same expression for the HF constants and correlation functions as in (3.3.14) and (3.3.15). Expressions such as (3.5.20) give a more direct idea of the dependence of  $T_1$  on the spin-spin correlations than expressions given earlier in terms of  $\chi''(\mathbf{q}, \omega)$ .

The corresponding equations for  $^{17}\text{O}(2,3)$  and  $^{89}\text{Y}$  are

$$\left. \frac{1}{T_{1z}} \right|_{\text{O}} = \frac{\gamma_{17}^2 k_B T}{2 \mu_B^2} \mathcal{X}_{at} [C_x^2 + C_y^2] [1 + \mathcal{K}_{01}], \quad (3.5.21)$$

and

$$\left. \frac{1}{T_{1z}} \right|_Y = \frac{4\gamma_{89}^2 k_B T}{\mu_B^2} \mathcal{X}_{at} [D_x^2 + D_y^2] [1 + 2\mathcal{K}_{01} + \mathcal{K}_{12}], \quad (3.5.22)$$

for any permutation of axes (x,y,z). Equations (3.5.20), (3.5.21), and (3.5.22) are quite general and are useful for discussing cases where  $\mathcal{X}_{at}(T)$  and the  $\mathcal{K}_{ij}(T)$ 's are both changing substantially with temperature.

The formulation of  $T_1$  in terms of  $\mathcal{X}_{at}$  and the  $\mathcal{K}_{ij}$ 's described here is the theoretical basis for the comprehensive  $T_1$  data interpretation scheme pioneered by Uldry and Meier [58], which is discussed in Chap. 5.

### 3.6 A d-Wave Model for the NMR Shift and $T_1$ at $T < T_c$

Following Mila and Rice, a number of relaxation model calculations were developed which made use of the random phase approximation (RPA) to include the effects of electron-electron interactions. Several of these model calculations are reviewed in Chap. 5, as well as a proposed orbital relaxation term for the  $^{63}\text{Cu}(2)$  based on the marginal Fermi liquid hypothesis [74].

Among the RPA schemes which appeared early on was an interacting Fermi liquid theory with strong AFM exchange couplings put forward by Monien and Pines (MP) [5], where they used the RPA to construct a model for  $\chi''(\mathbf{q}, \omega)$  with an adjustable enhancement level in the vicinity of  $Q_{AF}$ . An important innovation in this work was the introduction of an energy gap with d-wave symmetry for  $T_1$  and NMR shift calculations for  $T < T_c$ . Even though there were theoretical developments from very early on suggesting the suitability of d-wave superconductivity for the cuprates [75, 76, 77], up to this point no one had tried to interpret NMR data with the d-wave picture. In spite of the apparent success of this interpretation as seen in [5], widespread acceptance of d-wave symmetry did not occur until the dramatic confirmation of d-wave superconductivity in the cuprates by means of phase jumps at Josephson junction boundaries, which was still several years away [78, 79]. The NMR modeling described here followed closely upon a successful application of d-wave theory to Raman scattering experiments [80].

The RPA theory of [5] was applied to giving a realistic account of the shift and of  $T_1$  vs.  $T$  at the Cu sites in YBCO7 for  $T < T_c$ . This first NMR test of d-wave calculations was an important step along the path of eventual adoption of the singlet d-wave interpretation of cuprate superconductivity. By this point in time, there was ample  $T_1$  data below  $T_c$  on which to apply calculations such as this. As we shall see, however, *both the theoretical details and some of the data* were destined to undergo revision in later years. Nonetheless, these preliminary exercises in understanding the cuprate NMR data were both very encouraging and highly suggestive.

### 3.6.1 The NMR Shift Behavior for $T < T_c$

To discuss the Cu(1,2) NMR shift below  $T_c$ , we must first address the experimental situation. We therefore digress briefly here to discuss the NMR shift measurements conducted by Takigawa et al., [81] and by Barrett et al., [48]. Both papers appear to be very careful pieces of work. The biggest problem involved in such measurements is accounting for the diamagnetic shift of the internal field in the superconducting vortex state. This was dealt with in sharply contrasting ways in the two papers cited, leading, unfortunately, to slightly different results. Here we suggest a compromise interpretation.

#### *Correcting for Diamagnetism via Magnetization*

In [81] the internal field was corrected for using an effective demagnetizing factor, which is applied to the measured magnetization of the oriented powder sample. The demagnetizing factor was determined with a careful calibration procedure, which is too lengthy to discuss here. However, the risk with such a procedure lies perhaps not in the demagnetizing factors, but in using magnetization measurements on a powder sample set in epoxy. There is a risk of non-intrinsic Curie-Weiss-like anomalies affecting such a procedure. Indeed, the  $c$ -axis shift for Cu(2) has an upturn below  $\sim 50K$  which we suggest may be spurious. This is shown in Fig. 3.9(a) where the Cu(2)-site shift results are plotted with corrections. Interestingly, no such feature is found for the  $ab$ -plane result. This same kind of anisotropic Curie-Weiss background effect was also reported later in an attempt to determine the intrinsic normal-state susceptibility of YBCO [50]. In the present case we note that the shift corrections become nearly 0.25% as  $T \rightarrow 0$ . The size and temperature dependence of this effect does not seem compatible with superconducting diamagnetism.

#### *Calibration of Internal Field with the $^{89}\text{Y}$ Shift*

On the other hand, in [48] the  $^{89}\text{Y}$  NMR line was used as a reference for the internal field at low temperatures, which is a very sound method in principle, as long as the  $^{89}\text{Y}$  NMR shift is reliably known. If, for example, the resonance frequencies  $\nu_{63}$  and  $\nu_{89}$  were measured in the same field, then we have

$$K_{Cu} = \left( \frac{\nu_{63}\gamma_{89}}{\nu_{89}\gamma_{63}} \right) + K_Y - 1. \quad (3.6.1)$$

In practice,  $K_Y \simeq -0.03\%$  at  $T = 100\text{ K}$ , and it was assumed [48] that  $K_Y \propto Y_s(T)$ ,  $Y_s(T)$  being the Yosida function [82] for  $s$ -wave gap symmetry. Since one may be looking here for a  $d$ -wave Yosida function effect, the foregoing assumption may cause a problem, but in fact the difference is small enough to be within the error bars. The Cu(2) shift results are shown in Fig. 3.9(b) and (c). It is noteworthy that the maximum  $c$ -axis internal field correction (for  $K_s(c)$ ) is  $\sim 0.05\%$  or only  $\sim 20\%$  of that found at low  $T$  in Fig. 3.9(a).

Although the latter correction cannot be arbitrarily curtailed, it seems likely that it is primarily responsible for the discrepancy between the  $c$ -axis results. The  $ab$ -plane results are also slightly outside error bars [0.37(2)% for [81] and 0.30(2)% for [48]]. However, this difference is as much a result of disparate normal-state shifts as it is of low- $T$  corrections, which are similar.

We suggest the following composite picture based on the combined results of [81] and [48]. The  $c$ -axis result of [48] is to be accepted as is, which says that  $K_s(c)$  is negligibly small on the scale of  $K_s(ab)$ . The axial and isotropic shifts thus behave in a very similar fashion, since they both reflect the behavior of  $K_s(ab)$ . Thus, we suggest that the contrasting behaviors of  $K_{ax}(T)$  and  $K_{iso}(T)$  highlighted in [81] may have been generated, in part, by subtracting and adding the strongly corrected  $c$ -axis shift, respectively. It is suggested that the sharp contrast which results is unreliable. On the other hand, the corrected  $K_{ab}(T)$  curve in Fig. 3.9(a) shows a very interesting linear- $T$  behavior below 50 K which is clearly not a result of the correction process. This may therefore be a sign of  $d$ -wave symmetry behavior, as reflected in the MP interpretation below. The behavior of  $K_{ax}(T)$  in Fig. 3.9(b) and (c) is also compatible with  $d$ -wave, as we shall see below. Both of these papers considered the isotropic

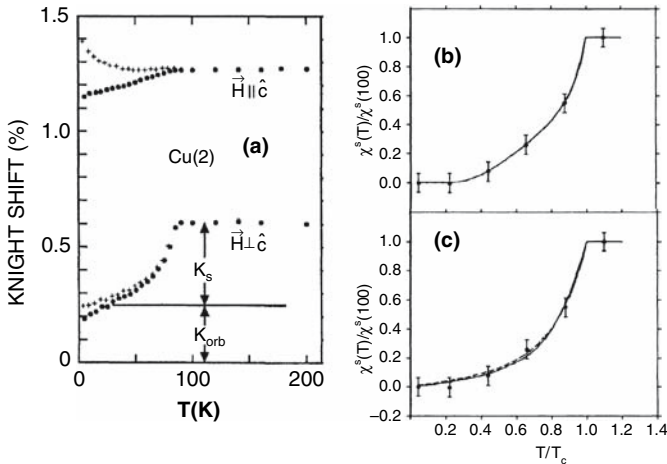


**Fig. 3.9.** (a) Corrected and uncorrected NMR shift data for Cu(2) in YBCO7 from [81] are shown plotted as a function of temperature for field parallel (top) and perpendicular (bottom) to the  $c$  axis. The correction scheme is described in the text. Figure reprinted from M. Takigawa, P.C. Hammel, R.H. Heffner, Z. Fisk, Phys. Rev. B **39**, 7371 (1989). Copyright 1989 American Physical Society. In (b) and (c), Cu(2) NMR shift data for YBCO7, i.e.  $K_s(c) - K_s(ab)$  normalized to 1 at 100 K, are plotted vs.  $T/T_c$  [48]. Yosida function fits to the data are shown using  $s$ -wave symmetry (b) and  $d$ -wave ( $d'$ -wave) symmetries (c) from Fig. 3.10(a) as a solid (dashed) line. Fit parameters are shown in Table 3.7 and discussed in the text. Figure reprinted from S.E. Barrett, D.J. Durand, et al., Phys. Rev. B **41**, 6283 (1990). copyright 1990 American Physical Society

component of shift as heavily contaminated with “oxygen hole band” effects. Following MR and MR2 [2, 46], we maintain their occurrence to be unlikely.

### 3.6.2 The Monien-Pines Calculations of NMR Shifts below $T_c$

MP began by applying different pairing symmetries to the interpretation of NMR shift variation below  $T_c$ . For comparison purposes they applied the pairing symmetries shown in Fig. 3.10(a). The pure s-wave and d-wave are flat and  $\propto \cos \phi$ , respectively, where  $\phi$  is the azimuthal angle for the cylindrical 2D Fermi surface for the  $\text{CuO}_2$  planes. They argue in detail that triplet pairing states are inappropriate for this case [5]. Then, still concerned about the possibility of an oxygen hole band, following [81] they consider only the axial component of the shift, which they suggest would reflect only the spin paramagnetism of the  $\text{Cu}(2)^{2+}$  sites <sup>8</sup> The data which were fitted are shown in Fig. 3.10(b) [81] and in Fig. 3.9(b) and (c).

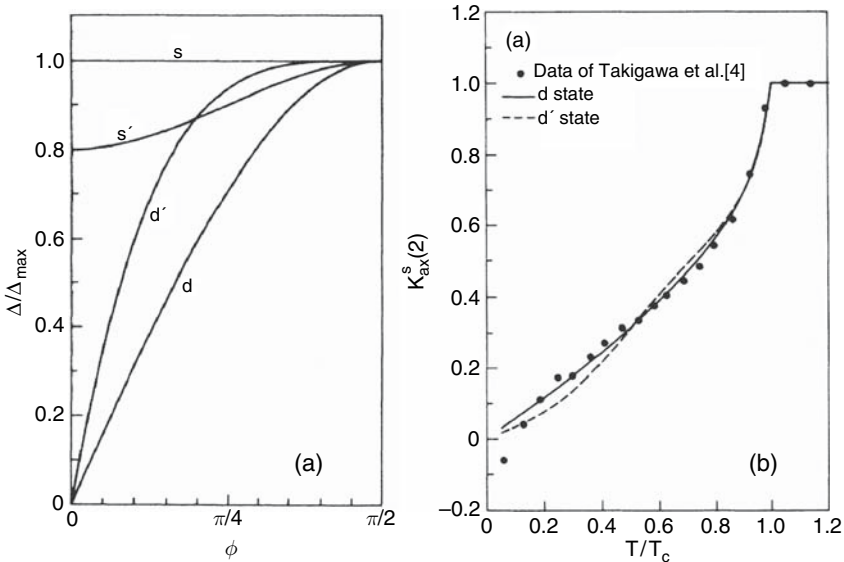


**Fig. 3.10.** (a) Gap energy variation for several choices of gap symmetry from [5] shown as a function of azimuthal angle  $\phi$  over one quadrant. (b) Plot of  $K_s^s(ax)$  from [81] as a function of  $T/T_c$  (dots) for temperatures in the superconducting state. The solid and dashed lines are calculated fits for gap functions labelled “d” and “d’” in the (a) portion [5], as described in the text. Noteworthy is the d-wave-like linear T behavior at the lowest temperatures. Figure reprinted from H. Monien, D. Pines, Phys. Rev. B **41**, 6297 (1990). Copyright 1990 American Physical Society

<sup>8</sup> The essential assumption here is that any oxygen hole-band NMR shift would be isotropic.

### Calculating the Yosida Function

To compare with NMR shift data, the Yosida function  $Y(T)$  is calculated using the weak-coupling BCS formula for an anisotropic, singlet superconductor,

$$Y(T) = \int_{-\infty}^{\infty} dE \left( -\frac{\partial f}{\partial E} \right) N(E), \quad (3.6.2)$$

where  $N(E)$  is the density of states, and  $f$  is the Fermi distribution function. The behavior of  $Y(T)$  for an s-state gap is  $Y_s(T) \propto \exp(-\Delta_{min}/k_B T)$  for  $T \ll T_c$ ,  $\Delta_{min}$  being the minimum gap energy as  $T \rightarrow 0$ . In contrast, for the case of a d-state gap  $N(E) \propto E$  for  $E \ll \Delta(0)$ , leading to a linear variation of  $Y_d(T)$  with  $T$  for  $T \ll T_c$ . MP used the maximum gap value  $\Delta(0)/k_B T_c$  and the specific heat jump at  $T_c$

$$\Delta C/C \propto \left( \frac{\partial \Delta^2}{\partial T} \right)_{T_c} \quad (3.6.3)$$

as parameters for calculating  $Y_d(T)$ , which is plotted in Fig. 3.10(b). The d-wave result is seen to be in good agreement with the Cu(2)-site  $K_{ax}$  data from [81]. Values of the parameters for the cases of (i) weak-coupling BCS theory and (ii), (3.6.2) fitted to the NMR shift data in Fig. 3.10(b) and in Fig. 3.9(b) and (c), are given in Table 3.7. Strong coupling effects are seen to be appreciable, but also, the d-wave calculation is quite successful in reproducing the linear temperature behavior of the shift data.

### 3.6.3 Calculating the Relaxation Decay Curve

By fitting the relaxation, the viability of using d-wave gap symmetry to interpret NMR data was tested BCS theory of  $T_1$  for the d-wave case. We begin

**Table 3.7.** Table of fitting parameters  $\Delta_0/k_B T_c$  and  $\Delta C/C$  from [5] for the NMR shift data in Fig. 3.10(b) [81] (top part) and for the data in Fig. 3.9(b) and (c) (bottom). The values of these parameters for weak-coupling BCS theory are shown on the left-hand side for comparison. The pairing states shown in Fig. 3.10(a) were used for these calculations

| Data Plot       | Pairing State | Weak Coupling $\Delta_0/k_B T_c$ | Weak Coupling $\Delta C/C$ | Optimal Fit $\Delta_0/k_B T_c$ | Optimal Fit $\Delta C/C$ |
|-----------------|---------------|----------------------------------|----------------------------|--------------------------------|--------------------------|
| Fig. 3.10(b) d  |               | 2.13                             | 0.95                       | 2.44                           | 1.97                     |
| Fig. 3.10(b) d' |               | 1.93                             | 1.17                       | 1.74                           | 2.36                     |
| Fig. 3.9(b) s   |               | 1.76                             | 1.43                       | 1.90                           | 2.77                     |
| Fig. 3.9(b) s'  |               | 2.10                             | 1.27                       | 2.16                           | 2.49                     |
| Fig. 3.9(c) d   |               | 2.13                             | 0.95                       | 14.7                           | 1.76                     |
| Fig. 3.9(c) d'  |               | 1.93                             | 1.17                       | 3.13                           | 2.14                     |

with a brief synopsis of the calculation of  $T_1$  [5]. In the presence of an AFM interaction  $J_{eff}(\mathbf{q}, T)$  the RPA expression for the dynamic susceptibility becomes

$$\chi(\mathbf{q}, \omega, T) = \frac{\chi_0(\mathbf{q}, \omega)}{1 - N(0)J_{eff}(\mathbf{q}, T)\chi_0(\mathbf{q}, \omega)}, \quad (3.6.4)$$

where  $\chi_0(\mathbf{q}, \omega)$  is the "bare spin-spin correlation function" [5]. For a  $T_1$  calculation such as (3.5.9) from the previous subsection, one only needs the imaginary or dissipative part  $\chi''(\mathbf{q}, \omega)$ . Monien and Pines make the following approximations to treat  $T_1$  behavior below  $T_c$ . Assuming AFM enhancement effects are large (such as for Cu(2) in YBCO), the enhancement denominator in (3.6.4) is first replaced by its average, temperature-dependent value at  $Q_{AF}$ , so that (3.6.4) becomes

$$\frac{1}{T_1} = \frac{1}{(T_1)_{free}} \frac{1}{[1 - \lambda(T)]^2}, \quad (3.6.5)$$

where

$$\lambda(T) = \langle N(0)J_{eff}(\mathbf{Q}_{AF}, T)\chi'_0(\mathbf{Q}_{AF}, T) \rangle. \quad (3.6.6)$$

It was then further assumed that the real part of the dynamic susceptibility at  $Q_{AF}$ ,  $\chi'_0(\mathbf{Q}_{AF}, T)$ , scales with temperature like the noninteracting uniform susceptibility  $\chi'_0(\mathbf{q} = 0, T)$ .  $T_1$  (3.6.5) can then be expressed in terms of the Yosida function (see Sect. 1.2.2)

$$Y(T) = \chi'_0(\mathbf{q} = 0, T)/\chi'_0(\mathbf{q} = 0, T_c) \quad (3.6.7)$$

as

$$\frac{1}{T_1} = \frac{1}{(T_1)_{BCS}} \frac{1}{[1 - \lambda(T_c)Y(T)]^2}, \quad (3.6.8)$$

where  $1/(T_1)_{BCS}$  may be calculated for any pairing symmetry desired in the absence of quasiparticle interactions. In this simple approximation the falloff of  $1/T_1$  below  $T_c$  will be enhanced by the decline of the enhancement factor, which in turn falls off according to how the Yosida function diminishes below  $T_c$ .

For other than s-wave gap symmetries, we may write the BCS relaxation expression (cf. Sect. 1.2.2)

$$\frac{1}{(T_1 T)_{BCS}} \propto \int_{-\infty}^{\infty} dE \left( -\frac{\partial f}{\partial E} \right) [N^2(E) + M^2(E)], \quad (3.6.9)$$

where  $N(E)$  and  $M(E)$ , which account for the BCS coherence factor, are defined by [83]

$$N(E) = \left\langle \text{Re} \left[ \frac{E}{(E^2 - \Delta_k^2)^{1/2}} \right] \right\rangle_{FS} \quad \text{and} \quad M(E) = \left\langle \text{Re} \left[ \frac{\Delta_k}{(E^2 - \Delta_k^2)^{1/2}} \right] \right\rangle_{FS}. \quad (3.6.10)$$

The latter definitions allow for the possibility of a complex gap function. Combining (3.6.8) with (3.6.10) yields an expression for the relaxation rate which will decline below  $T_c$ , both because of the growth of the superconducting energy gap and because of the decline of the enhancement factor owing to the decrease in  $Y(T)$ . Because of the d-wave gap function described above, the linear-E density of states will lead to asymptotic  $1/T_1 \propto T^3$  behavior for  $T \ll T_c$ .

### *Application of MP $T_1$ Calculations to Cu(2) Data for YBCO7*

MP illustrated the above formalism by using it to fit the NQR  $T_1$  data on  $^{63}\text{Cu}(2)$  in YBCO7 by Imai et al., [84]. The fitting function is shown as a solid line in Fig. 3.11(a), and is seen to give an excellent representation of the data over two full orders of magnitude of the decline of  $1/T_1$  below  $T_c$ . We make a number of remarks regarding this  $T_1$  fit. First, for the d-wave gap function (see Fig. 3.10(a)), there is no vestige of the coherence peak, unlike what is found for the s-wave cases [5]. Moreover, the very steep decline found just below  $T_c$  can be achieved in two different ways. This is illustrated by the fit parameters shown in Table 3.8. The actual curve plotted in Fig. 3.11 does not allow the enhancement factor to change below  $T_c$ , for reasons to be discussed presently. As a consequence, a very large gap parameter of  $5.12k_B T_c$  is needed to cause the steep fall-off near  $T_c$ . However, MP have calculated another fit curve for the data shown, corresponding to the second row of parameters in the table, which is almost indistinguishable from the first ([5], Fig. 3(d)). In the latter case the enhancement parameter  $\lambda \simeq 0.5$  (see ([5])) contributes to the decline of  $1/T_1$ , but the gap parameter  $\Delta_0/k_B T_c = 2.44$  is only half as great as for the calculation shown. This may be a more physically reasonable scenario. The corresponding (second row) parameters from Table 3.8 is in fact the same set used to fit the shift data in Fig. 3.9(c).

Referring to Fig. 3.11(b), the solid dots plot the same data as in the (a) panel. There we compare the decline of  $1/T_1$  with a line of slope  $\propto T^3$  in the middle region and a linear  $T$  curve at the lowest temperatures. The  $\propto T^3$  behavior is expected at low  $T$  as mentioned earlier, because of the

**Table 3.8.** Table of fitting parameters for the  $T_1$  data of Fig. 3.11(a) using a d-wave gap function [5]. The top line shows parameter values for a fit assuming a constant enhancement below  $T_c$ . In this case the effective value of  $\lambda$  is zero. The second line shows an essentially equivalent fit in which  $\lambda$  is allowed to decay below  $T_c$  according to the d-wave Yosida function. The remaining parameters are those used to fit the NMR shift data, as shown in Fig. 3.9(c)

| Weak Coupling      | Weak Coupling | Optimal Fit        | Optimal Fit  |                |
|--------------------|---------------|--------------------|--------------|----------------|
| $\Delta_0/k_B T_c$ | $\Delta C/C$  | $\Delta_0/k_B T_c$ | $\Delta C/C$ | $\lambda(T_c)$ |
| 2.13               | 0.95          | 5.12               | 1.89         | 0.0            |
| 2.13               | 0.95          | 2.44               | 1.97         | 0.5            |

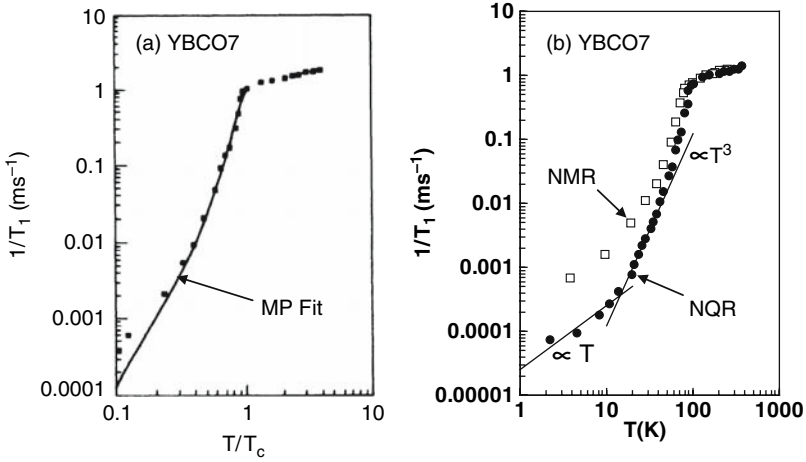


**Fig. 3.11.** (a) NQR  $T_1$  data for Cu(2) in YBCO [84] is plotted vs.  $T/T_c$  for temperatures above and below  $T_c$ . The MP theoretical fit described in the text is shown as a solid line. Figure reprinted from H. Monien, D. Pines, Phys. Rev. B **41**, 6297 (1990). copyright 1990 American Physical Society (b) The same data as in part (a) are plotted as dots on a scale of absolute temperature. Also plotted for comparison are a set of NMR data (open squares) for the same nominal compound taken in a field of  $7.4 T$  [60]. For the NQR data the regions of data which vary as  $T^3$  and as  $T$  are indicated with straight lines (see text for discussion). Figure reprinted from P.C. Hammel, M. Takigawa et al., Phys. Rev. Lett. **63**, 1992 (1989). Copyright 1989 American Physical Society

linear-E character of  $N(E)$  which results from the d-wave gap having a line of nodes. Further, the suggested crossover to linear  $T$  behavior often results from disorder in the sample causing quasiparticle states to occur in the gap region. The progression of  $T^3 \rightarrow T$  behavior has been found to occur below  $T_c$  in many non-cuprate unconventional superconductors. A few cases we could mention are  $^{115}\text{In}$  in  $\text{CeIrIn}_5$  [85],  $^{69}\text{Ga}$  in  $\text{PuCoGa}_5$  [86],  $^{69}\text{Ga}$  in  $\text{PuRhGa}_5$  [87], and  $^{23}\text{Na}$  in  $\text{Na}_{0.35}\text{CoO}_2 \cdot y\text{H}_2\text{O}$  [88].

### ***Does AFM Enhancement Decay Below $T_c$ ?***

Next, we discuss the difference between the NMR and NQR data shown in Fig. 3.11(b). Along with the NMR data shown, Hammel et al., also reported a  $T_1$  curve for the (planar) O(2,3) sites over the same temperature range. Their NMR data for the Cu(2) and the O(2,3) created something of a sensation when the variation below  $T_c$  turned out to be precisely the same for these two nuclei over two decades. In terms of the MP theory outlined above the implication is that even though the Cu(2) undergoes substantial enhancement in the normal state, *any such enhancement becomes temperature independent below  $T_c$* . This was taken to be a constraint on the theory, and is the reason

why MP calculated the solid curve fit in Fig. 3.11(a) without allowing the enhancement to vary with temperature.

However, the contrast between the NQR and NMR measurements suggests very strongly that there is an additional  $T_1$  mechanism operating in a high magnetic field. Detailed studies which came later showed this to be the case, namely relaxation to the normal cores in the vortex state just as occurred in  $V_3Si$  (see Fig. 2.13). For that reason, the Cu(2) and O(2,3) relaxation curves in [60] are not really intrinsic superconducting behavior. Later studies, as we shall see in Chap. 5, show that the AFM enhancement in the SC state really does decay away to zero at low temperatures. Therefore, for the data of Fig. 3.11(a), the fit calculated including enhancement decay is probably the more realistic one.

In sum, we find that the d-wave description of the YBCO7 NMR effects for  $T < T_c$  according to the MP model theory was successful in an essentially quantitative way. Fitted parameter values suggest that strong-coupling effects are quite important. It remained to be seen whether this kind of RPA model for the dynamic susceptibility could be applied to interpret the disparate temperature dependences which occur in the normal state. This is the theme of a series of theory papers which came soon after MP and which are expounded in some detail in Chap. 5. We shall see that the latter papers uphold the continued success of the single quantum fluid picture of these systems which was initiated by the calculations of Mila and Rice. Meanwhile, the pseudo-gap effect for low-doping materials came to light, and as we shall see in the next chapter, this effect became a major sub-theme of cuprate physics.

## References

1. R.M. Hazen, in *Physical Properties of High Temperature Superconductors*, Vol. II, ed. by D.M. Ginsburg (World Scientific, Singapore, 1990), p. 121-67
2. F. Mila, T.M. Rice, *Physica C* **157**, 561 (1989) 67, 73, 81, 84, 85, 86, 87, 90, 92, 99, 102, 107
3. B.S. Shastry, *Phys. Rev. Lett.* **63**, 1288 (1989) 67, 73, 81, 82, 99, 102
4. T. Moriya, *J. Phys. Soc. Japan* **18**, 516 (1963) 68, 101
5. H. Monien, D. Pines, *Phys. Rev. B* **41**, 6297 (1990) 68, 99, 104, 107, 108, 109, 110
6. A.J. Millis, H. Monien, D. Pines, *Phys. Rev. B* **42**, 167 (1990) 68, 99
7. A.J. Millis, H. Monien, *Phys. Rev. B* **45**, 3059 (1992) 68, 99
8. J.G. Bednorz, K.A. Mueller, *Z. Phys.* **B64**, 189 (1986) 68
9. R.J. Cava, R.B. Van Dover, B. Batlogg, E.A. Rietman, *Phys. Rev. Lett.* **58**, 408 (1987) 68
10. M.K. Wu, J.R. Ashburn, et al., *Phys. Rev. Lett.* **58**, 908 (1987) 68
11. J.D. Jorgensen et al., *Phys. Rev. Lett.* **58**, 1024 (1987) 68, 69
12. J.D. Jorgensen et al., *Phys. Rev. B* **36**, 5731 (1987) 69, 70
13. R.E. Walstedt, S.-W. Cheong, *Phys. Rev. B* **64**, 014404 (2001) 69, 86, 89, 96
14. P. Hüsler, H.U. Suter, E.P. Stoll, P.F. Meier, *Phys. Rev. B* **61**, 1567 (2000) 69, 86, 89, 96
15. N.F. Mott, *Proc. Phys. Soc. London Sect. A* **62**, 416 (1949) 69
16. F.C. Zhang and T.M. Rice, *Phys. Rev. B* **37**, 3759 (1988) 70, 71, 82
17. V. Barzykin, D. Pines, *Phys. Rev. B* **52**, 13585 (1995) 70

18. C.M. Varma, Phys. Rev. Lett. **77**, 3431 (1996) 70
19. P.W. Anderson, Science **235**, 1196 (1987) 71, 78
20. P.W. Anderson, in *Frontiers and Borderlines in Many-Particle Physics*, ed. by R.A. Broglia, J.R. Schrieffer, International School of Physics "Enrico Fermi," Course CIV (North-Holland, Amsterdam, 1988) 71, 78
21. S. Trugman, Phys. Rev. **B37**, 1597 (1988); B.J. Shraiman, E.D. Siggia, Phys. Rev. Lett. **60**, 740 (1988); S. Sachdev, Phys. Rev. **B39**, 12232 (1989); C.K. Lane, P.A. Lee, N. Read, Phys. Rev. **B39**, 6880, (1989) 71
22. J.T. Markert, T.W. Noh, S.E. Russek, R.M. Cotts, Sol. St. Comm. **63**, 847 (1987) 73, 74, 97, 99
23. D. Brinkmann, L. Pauli, J. Roos, H. Zimmermann, Phys. Lett. A **124**, 112 (1987) 73, 74, 75, 97, 99
24. W.W. Warren, Jr., R.E. Walstedt, et al., Phys. Rev. Lett. **59**, 1860 (1987) 73, 74, 75, 76
25. H. Lütgemeier, M.W. Pieper, Sol. St. Comm. **64**, 267 (1987) 73, 76
26. I. Furo, A. Jánossy, L. Mihály et al., Phys. Rev. **B36**, 5690 (1987) 73, 76
27. C.H. Pennington, D.J. Durand et al., Phys. Rev. **B37**, 7944 (1988) 74, 76
28. T. Shimizu, H. Yasuoka, T. Imai et al., J. Phys. Soc. Japan **57**, 2494 (1988) 74, 76, 80
29. C.H. Pennington, D.J. Durand, C.P. Slichter, Phys. Rev. **B39**, 274 (1989) 74, 79, 80, 81, 84
30. F. Adrian, Phys. Rev. **B38**, 2426 (1988) 74
31. C.H. Pennington, D.J. Durand, C.P. Slichter et al., Phys. Rev. **B39**, 2902 (1989) 74
32. R.E. Walstedt, W.W. Warren, Jr., et al., Phys. Rev. **B36**, 5727 (1987) 75, 76, 80
33. M. Takigawa, P.C. Hammel, R.H. Heffner, Z. Fisk, Phys. Rev. **B38**, 2832 (1988) 76, 79, 81, 84, 85
34. R.E. Walstedt, W.W. Warren, Jr., et al., Phys. Rev. **B38**, 9299 (1988) 76, 85, 99
35. H. Alloul, P. Mendels, et al., Phys. Rev. Lett. **61**, 746 (1988) 76, 82, 99, 102
36. G. Balakrishnan, R. Dupree et al., J. Phys. C: Solid State Phys. **21** L847 (1988) 77, 99
37. R.E. Walstedt, W.W. Warren, Jr., R. Tycko et al., Phys. Rev. **B38**, 9303 (1988) 79, 81, 91
38. R.E. Walstedt, W.W. Warren, Jr., et al., Phys. Rev. **B40**, 2572 (1989) 79, 80, 81, 91, 92
39. Y. Yafet, V. Jaccarino, Phys. Rev. **133**, A1630 (1964) 79
40. B. Bleaney, K.D. Bowers, M.H.L. Pryce, Proc. R. Soc. London **A228**, 166 (1955) 79
41. M. Takigawa, P.C. Hammel et al., Phys. Rev. **B39**, 300 (1989) 79, 81, 84, 85, 95
42. A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, (Clarendon Press, Oxford, 1970), p. 455 80, 83, 86, 89
43. P.W. Anderson, Phys. Ref. Lett. **3**, 325 (1959) 80
44. D.E. Farrell et al., Phys. Rev. **B36**, 4025 (1987) 80
45. R.E. Watson, A.J. Freeman, *Hyperfine Interactions*, ed A.J. Freeman, R.B. Frankel (Academic Press, New York, 1967), p. 53 81
46. F. Mila and T.M. Rice, Phys. Rev. **B40**, 11382 (1989) 81, 82, 98, 99, 107
47. R.E. Walstedt et al., Phys. Rev. **B45**, 8074 (1992) 83, 96
48. S.E. Barrett, D.J. Durand, et al., Phys. Rev. **B41**, 6283 (1990) 84, 85, 95, 99, 105, 106
49. W.C. Lee, D.C. Johnston, Phys. Rev. **B41**, 1904 (1990) 85, 87
50. R.E. Walstedt, W.W. Warren, Jr., et al., Phys. Rev. **B41**, 9574 (1990) 85, 105
51. A.K. McMahan, R.M. Martin, and S. Satpathy, Phys. Rev. **B38**, 6650 (1988) 86
52. J. Owen, J.H.M. Thornley, Rep. Prog. Phys. **29**, 675 (1966) 86

53. D.L. Randles, Proc. Roy. Soc. London, Ser. A**331**, 85 (1972) 86
54. F. Mila, Phys. Rev. B**38**, 11358 (1988) 87
55. T. Moriya, J. Phys. Soc. Japan **19**, 681 (1964) 88
56. V. Heine, Phys. Rev. **107**, 1002 (1957) 89
57. J.A. Martindale, S.E. Barrett et al., Phys. Rev. Lett. **68**, 702 (1992) 91
58. A. Uldry and P.F. Meier, Phys. Rev. B**72**, 094508 (2005) 91, 104
59. M. Takigawa, P.C. Hammel, et al., Phys. Rev. Lett. **63**, 1865 (1989) 93, 94, 95, 96
60. P.C. Hammel, M. Takigawa et al., Phys. Rev. Lett. **63**, 1992 (1989) 93, 97, 99, 111, 112
61. M. Horvatić, Y. Berthier, et al., Physica C**159**, 689 (1989) 93, 95
62. C. Coretsopoulos et al., Phys. Rev. B**39**, 781 (1989) 93
63. R. Sternheimer, Phys. Rev. **84**, 244 (1951); **86**, 316 (1952); **95**, 736 (1954) 94
64. H. Alloul, A. Mahajan, H. Casalta, O. Klein, Phys. Rev. Lett. **70**, 1171 (1993) 96
65. H. Alloul, T. Ohno, P. Mendels, Phys. Rev. Lett. **63**, 1700 (1989) 96, 98
66. N. Bulut, D.W. Hone et al., Phys. Rev. B**41**, 1797 (1990); Phys. Rev. Lett. **64**, 2723 (1990) 97, 99
67. H. Monien, D. Pines, C.P. Slichter, Phys. Rev. B**41**, 11120 (1990) 98
68. V.J. Emery, G. Reiter, Phys. Rev. B**38**, 4547 (1988) 98
69. T. Moriya, J. Phys. Soc. Japan **18**, 516 (1963) 99
70. V. Jaccarino, in *Physics of Solids*, International School of Physics "Enrico Fermi", Course XVIII (Academic, New York, 1967) 99
71. H. Monien, D. Pines, Phys. Rev. B**41**, 6297 (1990); N. Bulut, D. Scalapino, Phys. Rev. B**45**, 2371 (1992) 99
72. A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1983) 99
73. T. Auler, M. Horvatic et al., Physica C**313**, 255 (1999) 101
74. C.M. Varma, P. Littlewood et al., Phys. Rev. Lett. **63**, 1996 (1989) 104
75. C. Gros, R. Joynt, T.M. Rice, Z. Phys. B**68**, 425 (1987) 104
76. F.C. Zhang, C. Gros, T.M. Rice, H. Shiba, Supercond. Sci. Technol. **1**, 36 (1988) 104
77. G. Kotliar, J. Liu, Phys. Rev. B**38**, 5142 (1988) 104
78. J. Kirtley, C.C. Tsuei, et al., Nature (London) **373**, 225 (1995) 104
79. D.H. Wollman, D.J. van Harlingen, et al., Phys. Rev. Lett. **74**, 797 (1995) 104
80. H. Monien, A. Zawadowski, Phys. Rev. Lett. **63**, 911 (1989) 104
81. M. Takigawa, P.C. Hammel, R.H. Heffner, Z. Fisk, Phys. Rev. B**39**, 7371 (1989) 105, 106, 107, 108
82. K. Yosida, Phys. Rev. **110**, 769 (1958) 105
83. D.E. MacLaughlin, "Magnetic Resonance in the Superconducting State", in *Solid State Physics*, Vol. 31, ed. by H. Ehrenreich, F. Seitz, D. Turnbull (Academic Press, New York, 1976), p. 1 109
84. T. Imai, T. Shimizu, H. Yasuoka, J. Phys. Soc. Jpn. **57**, 2280 (1988) 110, 111
85. G.-q. Zheng, et al., Phys. Rev. Lett. **86**, 4664 (2001) 111
86. N.J. Curro, et al., Nature **434**, 622 (2005) 111
87. H. Sakai, Y. Tokunaga, et al., J. Phys. Soc. Japan **74**, 1710 (2005) 111
88. T. Fujimoto, G.-q. Zheng, et al., Phys. Ref. Lett. **92**, 047004 (2004) 111

## Pseudogap Effects in Cuprate NMR Studies

Up to this point the discussion has focused on fully oxygenated YBCO7 and nearby compositions, for which  $T_c$  is very near its peak value  $\simeq 92\text{ K}$  for this compound. In 1989, detailed studies began to appear for *underdoped* YBCO7- $x$ ,  $x \sim 0.4$ , as well as for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  over its entire range of superconducting behavior  $0.05 \leq x \leq 0.35$ . These phases brought new and surprising effects to light, detailed theories for which are only recently beginning to appear. The principal new effect was a gapped appearance to the NMR shifts, susceptibility, and low-energy excitations via  $1/T_1T$ . These effects were at first attributed to pairing correlations forming at temperatures well above  $T_c$ , since there appeared to be no clear distinction between the pseudogaps and superconducting gaps. In the prevailing notion of “spin-charge separation” these effects were initially called “spin gaps” in the mistaken belief that they only affected spin-magnetic properties. Eventually, energy gaps were observed with a wide variety of probes (e.g. ARPES), uncovering a major element in the phenomenology of cuprate superconductivity. In this chapter we recount the beginnings as well as the current status of the pseudogap effect.

In the pre-pseudogap days, the behavior of YBCO7 did not appear to be affected by pseudogap effects. With its relatively flat susceptibility and Korringa-like relaxation for the  $^{89}\text{Y}$  and  $^{17}\text{O}$ , the NMR properties seemed to resemble a normal Fermi liquid. However, in retrospect, such a simple picture was illusory. A cuprate with no trace of a pseudogap is clearly a very *special case*, and the vast majority of other phases which came to light were dominated by pseudogap behavior. Typically, as the doping level decreases from the optimum  $T_c$  value, (i) the susceptibility develops a *gapped appearance*, beginning at progressively higher temperatures, (ii) the temperature variation of  $1/T_1T$  for  $^{89}\text{Y}$  and  $^{17}\text{O}$  develops a similar shape, while that for  $^{63,65}\text{Cu}(2)$  remains *non-monotonic* with a peak at a lower temperature, and (iii) instead of a sharp break downward in the NMR shift and  $1/T_1T$  below  $T_c$ , *these quantities execute smooth, declining curves through  $T_c$  without any noticeable discontinuity in slope*. Among conventional superconductors, behavior such as this is unknown.

We illustrate these effects with data from two early NMR papers on the pseudogap [1, 2]. Similar results for the Cu(2) were given by Horvatić et al. [3] and Yasuoka et al. [4]. Warren et al. presented NQR curves for  $1/T_1T$  vs.  $T$  for  $^{63}\text{Cu}(2)$  and similar NMR measurements for  $^{89}\text{Y}$  in the  $T_c \simeq 64\text{K}$  phase of YBCO7- $x$ ,  $0.3 \leq x \leq 0.5$ <sup>1</sup>. These are shown in Fig. 4.1

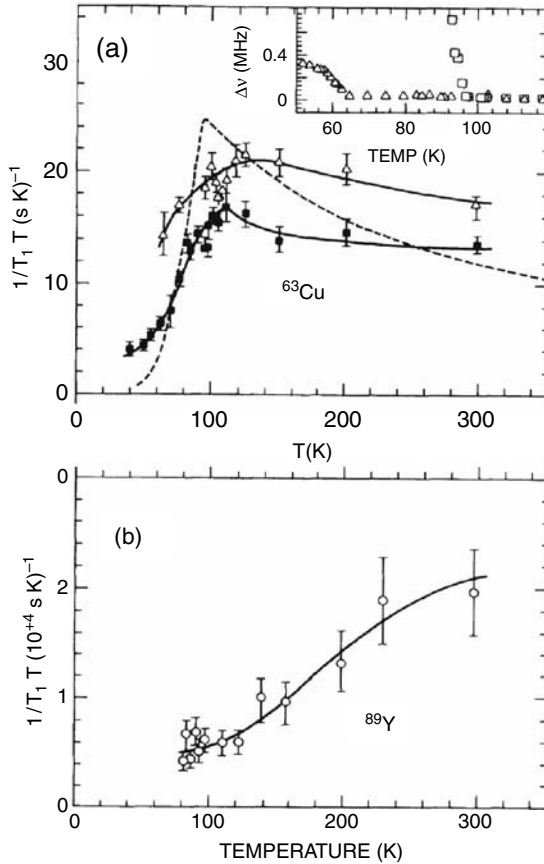


**Fig. 4.1.** (a)  $1/T_1T$  is plotted vs.  $T$  over the interval  $40\text{K} \leq T \leq 300\text{K}$  for two NQR peaks associated with  $^{63}\text{Cu}(2)$  sites in YBCO6.64 ( $T_c \simeq 64\text{K}$ ) [1]. For comparison, the dashed line shows the behavior recorded earlier for the YBCO7 phase ( $T_c \simeq 90\text{K}$ ). The inset shows the shift in the resonance frequency of the NQR coil which occurs as the sample goes superconducting at  $T \simeq 64\text{K}$ . (b)  $1/T_1T$  is plotted vs.  $T$  for  $^{89}\text{Y}$  NMR in the same sample used as in (a). These data show a sharp deviation from YBCO7-phase Korringa behavior, which is characteristic of the pseudogap. Figure reprinted from W.W. Warren, Jr., R.E. Walstedt, et al., Phys. Rev. Lett. **62**, 1193 (1989). Copyright 1989 American Physical Society

<sup>1</sup> Although a continuum of  $T_c$  values has been reported for YBCO7- $x$ , the  $60\text{K}$  phase is the most homogeneous underdoped phase, since  $dT_c/dx$  is quite small in that region.

where the low-frequency excitation spectrum ( $\sum_q A_q^2 \chi''(q, \omega)/\omega$ ) is seen to decline at low temperatures as though an energy gap had set in below  $T \sim 300\text{ K}$ . At  $T_c \simeq 64\text{ K}$  there is no break or other feature in the  $\text{Cu}(2)$   $T_1$  data (Fig. 4.1(a)), in complete contrast with the sharp drop which takes place for the YBCO7 phase (see Fig. 3.11). Nonetheless, monitoring the rf coil susceptibility (Fig. 4.1(a), inset) gives good evidence that the sample material undergoes a transition to bulk superconductivity at that temperature. This behavior will be confirmed below for this as well as other cuprates.

A second body of both NMR shift and relaxation data for  $^{89}\text{Y}$  in  $\text{YBCO6}+x$  is shown in Fig. 4.2, where curves with very similar shapes for both parameters are presented [2]. There, a progressive gapping effect is seen to advance steadily from  $x \sim 1.0$  to the non-superconducting phase at  $x \sim 0.4$ . Although these results were first interpreted on a Fermi-liquid model, that interpretation was later revised [5]. In retrospect, the results concerned appear to establish another important pseudogap result contrary to the usual Korringa behavior. The relaxation rate product  $1/T_1 T$  is very nearly proportional to  $K_s(T)$  and therefore to the spin susceptibility  $\chi_s(T)$ . In Sect. 4.1 we will discuss the physical meaning of this along with a theoretical model which yields this result.

Reference was made [2] to the theoretical prediction by Friedel [6] that precursive pairing effects in 2D superconductors might give rise to a “pseudogap” well above  $T_c$  in the excitation spectrum. As we shall see in Sect. 4.2, the pseudogap also turned up fairly quickly in charge-related effects such as specific heat and ARPES data.

We mention one final result which appeared around the same time as the foregoing effects were reported, namely the susceptibility scaling effect for underdoped LSCO which was reported by D.C. Johnston [7]. It was found that  $\chi_s(T)$  for a series of underdoped samples of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  not only exhibited a gap-like feature, but were found to scale rather precisely with a reduced temperature variable  $T/T^*$ . Although this effect was interpreted at the time in terms of a theoretical model for insulating antiferromagnets and was not linked for some time with the pseudogap effect, it seems clear in retrospect that it was, in fact, closely related to the effects presented above for YBCO7- $x$ . Later in this chapter we shall also discuss pseudogap effects in the high- $T_c$  systems LSCO and Y248.

## 4.1 The Pseudogap in Oxygen-Deficient YBCO7-x

Since spin pseudogap effects in the NMR data first came to light in studies of YBCO7- $x$  with some depletion of the oxygen content (and thus of hole doping), it was for this system that the most precise and comprehensive bodies of data were first developed. In this section we present and discuss a set of results on both the NMR shifts and relaxation rates for  $^{89}\text{Y}$ ,  $^{17}\text{O}(2,3)$ , and

$^{63}\text{Cu}(2)$  for a representative composition YBCO6.63 [8, 9, 10]. This compound is a well-characterized example of a high- $T_c$  pseudogap system.

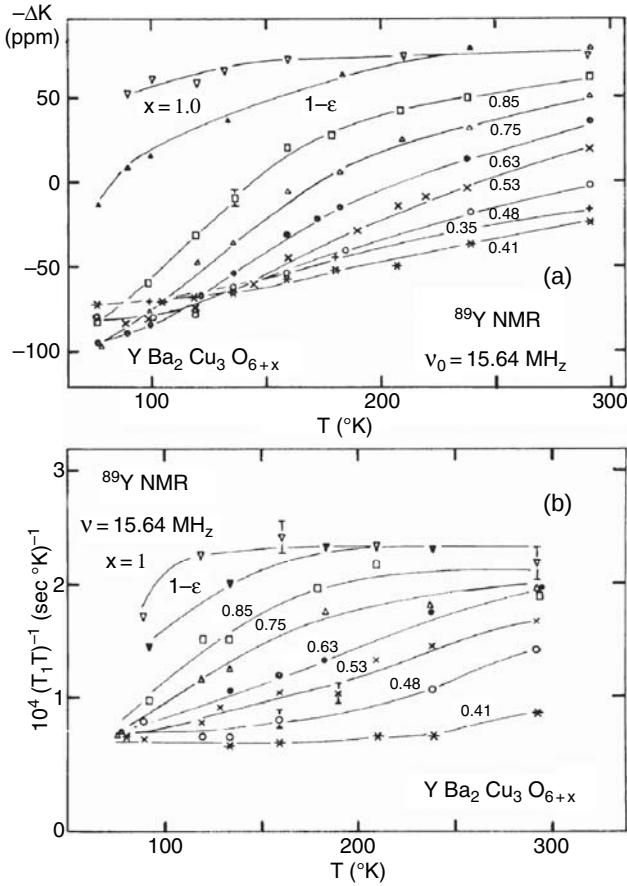


**Fig. 4.2.** (a) The negative of the  $^{89}\text{Y}$  NMR shift  $\Delta K$  is plotted as a function of temperature for a series of compositions YBCO6+ $x$ , for  $0.4 \leq x \leq 1.0$  [2].  $\Delta K$  is measured relative to the  $^{89}\text{Y}$  gyromagnetic ratio found with a solution of  $\text{YCl}_3$ . In Sect. 4.1 the chemical shift is determined to be  $^{89}K_{orb,\alpha} \simeq 160 \text{ ppm}$ , where  $\alpha = ab, c$ . (b) Plots of  $1/T_1 T$  vs.  $T$  for the same series of compositions used in (a) [2]. In both cases the data show the progressive development of a pseudogap effect in which they exhibit a maximum at progressively higher  $T$  for increasing dilution of hole carriers. These data can also be plotted to show the relation  $1/T_1 T \propto (^{89}K_{orb,\alpha} - \Delta K_\alpha(T))$  characteristic of the pseudogap region. Figure reprinted from H. Alloul, T. Ohno, P. Mendels, Phys. Rev. Lett. **63**, 1700 (1989). Copyright 1989 American Physical Society

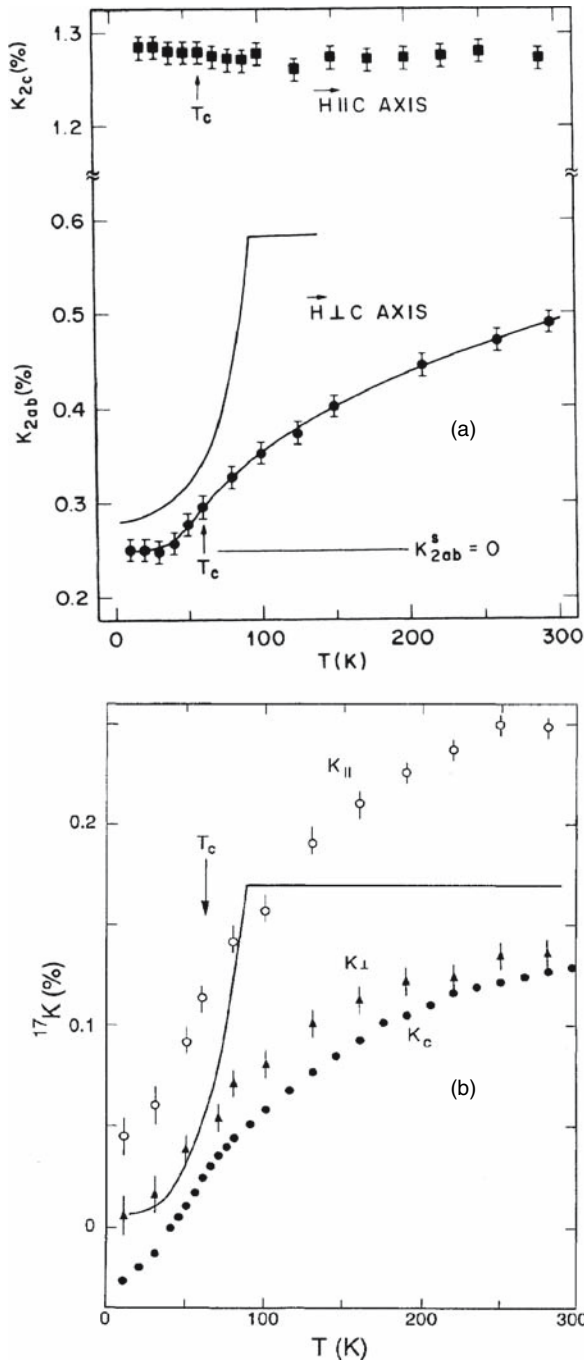


Fig. 4.3. Continued

### 4.1.1 HF Parameters for YBCO6.63 from Scaling of Shift Data

We first discuss NMR shift and susceptibility data for YBCO6.63. In Fig. 4.3(a) NMR shift data for  $^{63}\text{Cu}(2)$  in an oriented powder specimen are plotted for field orientation both parallel to and perpendicular to the  $c$  axis [1]. The  $c$  axis data show only a slight increase below  $T_c$ , so that  $^{63}K_{orb,c} = 1.28(1)\%$  and  $^{63}K_{s,c} = -0.01(1)\%$  (near 300K). This result for  $^{63}K_{orb,c}$  is indistinguishable from that for YBCO7.0 [11]. The zero-temperature intercept for  $^{63}K_{ab}(T)$  is  $^{63}K_{orb,ab} = 0.25(2)\%$ , which is also unchanged from YBCO7 [11]. The downward-curving spin paramagnetism is the essence of spin pseudogap behavior.

In Fig. 4.3(b) are plotted  $^{17}\text{O}$  NMR shift values ( $^{17}K_{\parallel}$ ,  $^{17}K_{\perp}$ ,  $^{17}K_c$ ) as functions of temperature for the three principal axes of the O(2,3) sites [9]. The quadrupole tensor has also been evaluated and is virtually indistinguishable from what was determined for YBCO7 (see Fig. 3.8 and discussion). The shift  $^{17}K_{\parallel}(T)$  corresponding to the Cu(2)-Cu(2) bond axis is seen to be more than half again as large as the transverse components. The latter ( $^{17}K_{\perp}(T)$  and  $^{17}K_c(T)$ ) have slightly different chemical (i.e. orbital) shifts, but their temperature variation is essentially indistinguishable. The  $^{17}\text{O}(2,3)$  shift can therefore be characterized by axial and isotropic components defined by  $^{17}K_{ax} = (^{17}K_{\parallel} - ^{17}K_{\perp})/3$  and  $^{17}K_{iso} = (^{17}K_{\parallel} + ^{17}K_{\perp} + ^{17}K_c)/3$ . As with YBCO7 (Sect. 3.4) there is a dominant isotropic HF effect from 3d-2s hybridization [12] and a lesser axial shift term corresponding to dipolar coupling from the 3d-2p $_{\sigma}$  hybridization, although the latter admixture is much greater than the former.

The  $^{17}\text{O}$  NMR shifts for  $^{17}K_{\parallel}$  and  $^{17}K_{\perp}$ , plus that for  $^{63}\text{Cu}(2)$  [9] have been scaled to coincide with  $^{17}K_c(T)$ , the most accurate data set, between  $T_c$  and 300K, and are plotted with separate vertical axes in Fig. 4.4. All shifts are seen to follow a common temperature variation very closely, i.e. that of the spin susceptibility. From the scaling fits the following relations are obtained:



**Fig. 4.3.** (a) The NMR shift for  $^{63}\text{Cu}(2)$  in an oriented-powder sample of YBCO6.64 [8] is plotted vs. temperature for field orientation parallel and perpendicular to the  $c$  axis. The upper solid line is a representation of data for YBCO7, while the lower one is a guide to the eye. As with YBCO7 it is assumed that the orbital shifts are independent of temperature and that the spin susceptibility goes to zero at  $T \ll T_c$ . The breakdown of both shifts into spin and orbital components is given in the text. Figure reprinted from R.E. Walstedt, W.W. Warren, Jr., et al., Phys. Rev. B**41**, 9574 (1990). copyright 1990 American Physical Society (b) Data for the  $^{17}\text{O}(2,3)$  NMR shift is plotted as a function of temperature up to 300K for an oriented powder sample with field oriented along three mutually perpendicular axes, where the axis for  $^{17}K_{\parallel}$  is the Cu(2)-Cu(2) bond axis [9]. The solid line is the variation of  $^{17}K_c(T)$  for YBCO7 [11]. Analysis of these results is given in the text. Figure reprinted from M. Takigawa, A.P. Reyes, P.C. Hammel, Phys. Rev. B**43**, 247 (1991). copyright 1991 American Physical Society

$$^{17}K_{ax}(T) = 0.1886 \times ^{17}K_c(T) + 0.0151\%, \quad (4.1.1a)$$

$$^{17}K_{iso}(T) = 1.057 \times ^{17}K_c(T) + 0.039\%, \quad (4.1.1b)$$

$$^{63}K_{ab}(T) = 1.522 \times ^{17}K_c(T) + 0.32\%. \quad (4.1.1c)$$

This result gives additional strong evidence for a one-component quasiparticle state, since multiple bands would have to have susceptibilities with precisely matching spin-gapped temperature variation to produce this result. Such an effect seems quite implausible.

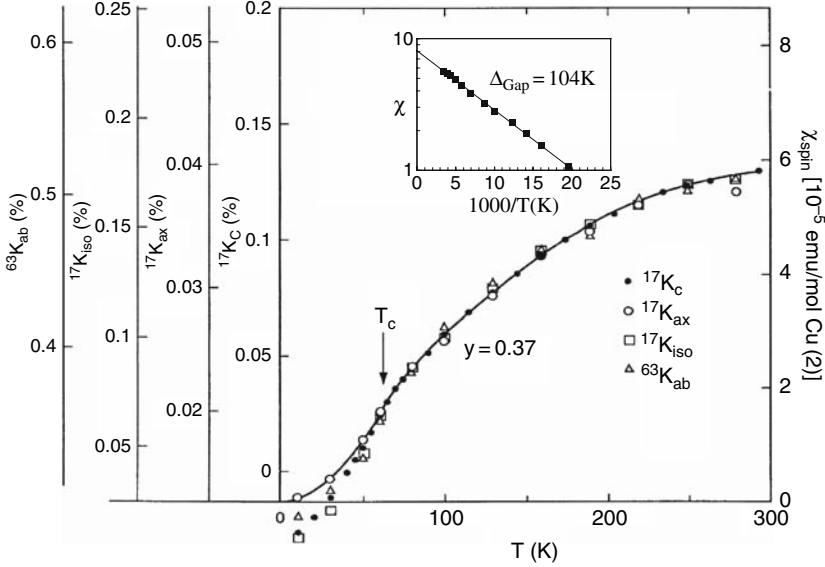


**Fig. 4.4.** (a) Data for  $^{63}K_{ab}(T)$  for the Cu(2) sites [9] (similar to Fig. 4.3(a)) as well as for  $^{17}K_{\parallel}(T)$  and  $^{17}K_{\perp}(T)$  have been scaled to  $^{17}K_c(T)$  and are plotted with the latter data as a function of temperature. The  $T \rightarrow 0$  (orbital shift) limits of these shifts plots have been determined as discussed in the text, leading to an estimate for the zero of the spin components of the shifts and of the spin susceptibility. Scales for the various shift components are shown on the left. The scale for  $\chi_s(T)$  has been estimated from the knowledge of HF constants (see text) and is shown on the right side of the plot. The solid line represents the estimate of  $\chi_s(T)$  so determined. The inset shows an Arrhenius plot of  $\ln(\chi_s(T))$  vs.  $1000/T(K)$ . The linear behavior suggests an energy-gap nature for  $\chi_s(T)$ , where  $\Delta_{Gap} \simeq 104K$ . Figure reprinted from M. Takigawa, A.P. Reyes, P.C. Hammel, Phys. Rev. B **43**, 247 (1991). copyright 1991 American Physical Society

The scaled curves in Fig. 4.4 come apart a bit below  $T_c$ , an effect which is attributed to varying levels of diamagnetic shielding for the different cases. However, because  $^{17}K_{\parallel}$  and  $^{17}K_{\perp}$  are both measured with field  $\perp c$  axis, there is no diamagnetic correction to  $^{17}K_{ax}$ . Directly from extrapolating the

curves in Fig. 4.3(b) to  $T = 0$ , then, one finds  $^{17}K_{ax}(0) = 0.013(2)\%$ . One can then use the (4.1.1) to obtain the other orbital (i.e. zero temperature) shift values. One finds  $^{17}K_c(0) = -0.014(7)\%$ ,  $^{17}K_{iso}(0) = 0.024(11)\%$ , and  $^{63}K_{ab}(0) = 0.30(2)\%$ . These values are virtually unchanged from  $^{17}\text{O}$  orbital shifts determined earlier for YBCO7 (See Table 3.2).

Using the relation  $\chi_s(T) = ^{63}K_{ab}(T)/f_{Cu}(A_{ab} + 4B)$ , where  $A_{ab} + 4B \simeq 198 \text{ kOe}/\mu_B$  [13], and the estimate  $f_{Cu} \simeq 0.7$  for the fraction of  $\chi_s$  which resides on the Cu(2) site, the scale shown for  $\chi_{spin}(T)$  in Fig. 4.4 has been determined. The parameters derived from a Mila-Rice fit to the data in Sect. 3.2 (see Table 3.4) would give a slightly larger value for  $(A_{ab} + 4B)$ . Other fits to the shift and relaxation data in Chap. 5 will also give slightly different values for the scale of  $\chi_s(T)$ . We only note that this scaling factor is not critical at this point. It will be discussed further in Chap. 5.

Regardless of the scale of  $\chi_s(T)$ , we may examine the question of its gapped nature by plotting the data of Fig. 4.4 in an Arrhenius plot, i.e. as  $\chi_s(T) = \chi_0 \exp(-\Delta_{Gap}/T)$ . Such a plot is shown in the inset to Fig. 4.4,<sup>2</sup> where it is found to yield a very accurate representation of the data, with  $\Delta_{Gap} \simeq 104\text{K}$ . Such a result was implied by the fitting procedure of Uldry and Meier [14], to be discussed in Chap. 5. To our knowledge, this representation has not been predicted by any model calculation up to now and has not been emphasized in the literature. This result will be compared with INS data on a similar sample below.

The  $^{89}\text{Y}$  NMR shift and relaxation data which came two years later [10] completed the NMR data picture for YBCO6.63. The corresponding shift data for both YBCO6.63 and YBCO7 cases were plotted vs.  $T$  as in Fig. 4.5(a), where the “6.63” data are seen to exhibit a very similar temperature dependence as the scale plot Fig. 4.4. This idea is tested in Fig. 4.5(b) where the latter data for both field orientations are plotted vs.  $^{17}K_c(T)$  data from Fig. 4.3. The resulting curves are straight lines within narrow error limits, and the extrapolation to  $^{17}K_c(0) = -0.014(7)\%$  then gives the chemical shifts  $^{89}K_{orb,c} = 160(15)$  and  $^{89}K_{orb,ab} = 152(10)$  ppm. Thus, the  $^{89}\text{Y}$  shift data also follow the curve in Fig. 4.4 to high precision.

### *Scaling of HF Coefficients to Match YBCO7.*

We therefore have a complete characterization of NMR shifts for all significant sites and field orientations in YBCO6.63 in terms of a single universal curve [9]. The resulting shift values at  $T = 300\text{K}$  are listed in Table 4.1 (“300K Values”). Also listed there is the estimated Cu(2) susceptibility tensor at 300K from [9]. We suggest, however, that the latter values are very approximate and that better values for both the susceptibility tensor and the HF coefficients can be assigned by scaling the HF tensor components so that they match the

---

<sup>2</sup> Please note that this inset was not part of the original figure in [9], but was added later.

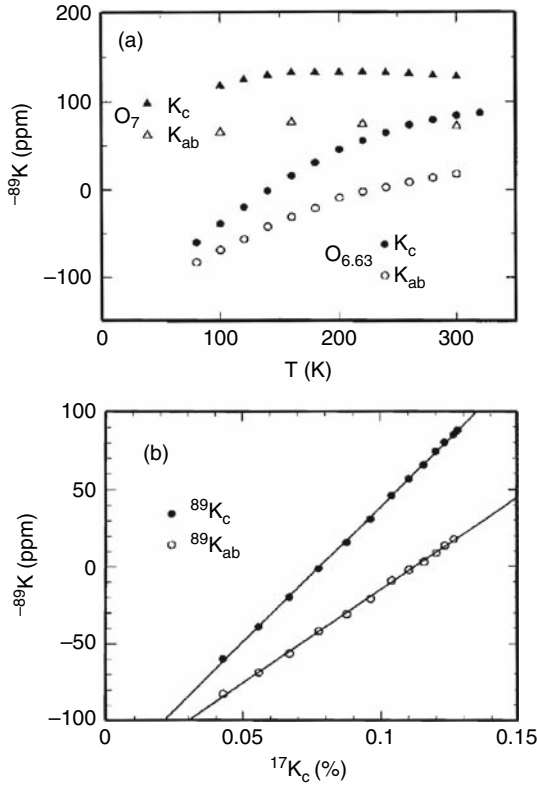


**Fig. 4.5.** (a) The negative of the  $^{89}\text{Y}$  NMR shift in YBCO6.63 is plotted as a function of temperature for applied field both parallel and perpendicular to the  $c$  axis of an oriented powder sample [10], which is actually the same sample used in the foregoing Cu(2) and O(2,3) NMR studies [9]. For comparison, previous data on YBCO7 [10] are also shown. (b) The YBCO6.63 shift data from part (a) are plotted vs. the oxygen shift data  $^{17}\text{K}_c(T)$  from [9]. Extrapolation of these curves to  $^{17}\text{K}_c(0)$  yields the chemical shift values for  $^{89}\text{Y}$  given in the text. These linear fits also demonstrate that all NMR shifts in YBCO6.63 follow the same temperature dependence, namely that of  $\chi_s(T)$ . Figure reprinted from M. Takigawa, W.L. Hufts, J.L. Smith, Phys. Rev. Lett. **71**, 2650 (1993). Copyright 1993 American Physical Society

YBCO7 values from Tables 3.4 and 3.6 as closely as possible. For convenience, the latter set of values (“YBCO7 ( $A_i$ )”) is listed in Table 4.1.

A “trial” set of HF coefficients can be defined from the data in Table 4.1 using the relation from (3.3.4)

$$\mathcal{A}_i = N_A \mu_B K_i / z_i \chi_{si}, \quad (4.1.2)$$

where  $K_i$  are the “300K” values from the table,  $z_i$  are the numbers of Cu(2) neighbors, and  $\chi_{si}$  is the appropriate susceptibility estimate from the same

**Table 4.1.** The NMR shift tensors for  $^{17}\text{O}(2,3)$  and  $^{89}\text{Y}$  in YBCO6.63 at 300 K [9, 10] are listed in the top line, then the corresponding HF coefficients are stated for YBCO7 from Tables 3.4 and 3.6, below which the scaled coefficient values for YBCO6.63 derived from the stated shift values are listed for comparison. The scaling procedure is described in the text, wherein the weighted sum of fractional errors defined by (4.1.3) is minimized. Weighting factors  $w_i$  are designed to give each species the statistical weight it has in the unit cell. NMR shift values are given in %, the spin HF coefficients in  $\text{kOe}/\mu_B$ , and susceptibilities in  $10^{-6} \text{ emu}/\text{Cu}(2)$

| Shift Comp.     | $^{63}K_{s,ab}$ | $^{17}K_{s,a}$ | $^{17}K_{s,b}$ | $^{17}K_{s,c}$ | $^{89}K_{s,ab}$ | $^{89}K_{s,c}$ | $\chi_{s\perp}(300\text{ K})$ | $\chi_{s\parallel}(300\text{ K})$ |
|-----------------|-----------------|----------------|----------------|----------------|-----------------|----------------|-------------------------------|-----------------------------------|
| 300K Values     | 0.218           | 0.205          | 0.124          | 0.143          | 0.0173          | 0.0255         | 58                            | 72                                |
| Spin HF Coef.   | $A_{ab}^{(2)}$  | $C'_a$         | $C'_b$         | $C'_c$         | $D'_{ab}$       | $D'_c$         |                               |                                   |
| YBCO7 ( $A_i$ ) | 155             | 72             | 44             | 38             | 1.71            | 1.86           |                               |                                   |
| YBCO6.63        | 152             | 71.4           | 43.2           | 40.0           | 1.51            | 1.87           | 80                            | 100                               |
| $R_i$           | 1.370           | 1.386          | 1.372          | 1.470          | 1.231           | 1.338          |                               |                                   |
| $w_i$           | 4               | 8/3            | 8/3            | 8/3            | 1               | 1              |                               |                                   |

line of the table. The  $\mathcal{A}_i$  are multiplied by a scaler  $S$ , which is then adjusted to minimize a weighted total fractional squared error defined by

$$\mathcal{ERR} = \sum_i \frac{w_i [S\mathcal{A}_i - A_i]^2}{A_i^2} = \sum_i w_i [1 - SR_i]^2, \quad (4.1.3)$$

where the YBCO7 coefficients are labelled  $A_i$ , and  $R_i = \mathcal{A}_i/A_i$ . This procedure will also yield a new estimate of the susceptibility tensor, from (4.1.2), of  $\chi_{si}/S$ . The ratios  $R_i$  are listed in Table 4.1, and are seen to be grouped closely around a value  $\simeq 1.36$ .

It is easy to show that the errors are minimized when

$$S = \frac{\sum_i w_i R_i}{\sum_i w_i R_i^2} = 0.723. \quad (4.1.4)$$

The optimally scaled coefficients obtained are stated in Table 4.1 (“YBCO6.63”). Correspondence with the YBCO7 values is seen to be quite satisfactory. The resulting (scaled) susceptibility components are also given. They are somewhat larger than the values from Fig. 4.4, but are  $\sim 80\%$  of the corresponding values in Table 3.4, in reasonable agreement with the relative values shown by experimental data given by Takigawa et al. in [9].

One important consequence of this fitting procedure is that the reduction factor 0.70 used to estimate the HF coefficients in Table 3.4 is corroborated by the YBCO6.63 shift scaling (Fig. 4.4) results. These results strongly suggest that the composite Cu(2) shift coefficient, for which we find the value  $A_{ab}^{(2)} \simeq 155 \text{ kOe}/\mu_B$  (Table 4.1), must, in fact, be rather smaller than the value  $\simeq 198 \text{ kOe}/\mu_B$  given by Monien et al. [13].

Next, we consider the anisotropy of the  $^{17}\text{O}(2,3)$  and  $^{89}\text{Y}$  HF coefficients  $C'_\alpha$  and  $D'_\alpha$ , respectively. Not surprisingly, the  $C'_\alpha$  have a strong axial component along the Cu(2)-Cu(2) bond axis owing to the  $2p_\sigma$  hybridization. The observed  $c/a$  axis anisotropy is, however, mainly a  $g$ -factor effect. The constants  $C_\alpha$  to be used in the main Hamiltonian (3.3.4) are proportional to  $g_\alpha C'_\alpha$ , which differs by only a few percent between the  $b$  and  $c$  axes. This is within the expected errors. The  $D'_\alpha$  values, however, display a clear anisotropy if we consider the quantities  $g_\parallel D'_c$  vs.  $g_\perp D'_{ab}$ , where the former is  $\sim 30\%$  larger. The origin of this effect is not clear, but the  $Y^{3+}$  HF response is clearly more than simply the isotropic core polarization HF field, as noted in [9].

### *Dipolar Contribution to $^{89}\text{Y}$ HF Coupling.*

One candidate effect for the  $D_\alpha$  anisotropy is direct dipolar coupling from the  $\text{Cu}^{2+}$  moments, which has been considered by Takigawa et al. [10]. Since the  $^{89}\text{Y}$  HF couplings are rather small for YBCO, one must consider the possibility that the dipolar interaction between any  $\text{Cu}^{2+}$  moment  $-\sum_\alpha g_\alpha \mu_B S_\alpha \hat{u}_\alpha$ , where  $\hat{u}_\alpha$  is a cartesian unit vector, and a  $^{89}\text{Y}$  nuclear spin moment  $^{89}\mathbf{I}$ ,

$$\mathcal{H}_{dip}^{(89)} = -\frac{\gamma_{89}\hbar\mu_B}{r^3} \left[ \sum_\alpha g_\alpha S_\alpha {}^{89}I_\alpha - 3 \frac{({}^{89}\mathbf{I} \cdot \mathbf{r}) \sum_\alpha g_\alpha S_\alpha r_\alpha}{r^2} \right] \quad (4.1.5)$$

is a significant HF energy. The importance of this is that (4.1.5) does not have the simple diagonal form of (3.3.2), thereby changing the nature of the dynamical calculations if it is an important effect.

To consider the direct dipolar HF coupling with the  $^{89}\text{Y}$ , we note that owing to hybridization, the  $\text{Cu}^{2+}$  moment at the origin (Fig. 2.1(b)) actually consists of a fraction  $1 - 4\delta$  on the Cu(2) site and fractions  $\delta$  located on the four  $nn$  O(2,3) sites. At the hybridization level  $\delta \simeq 0.08$ , the two O(2,3) sites nearest the  $^{89}\text{Y}$  are quite significant, since they are rather closer to the  $Y^{3+}$  than the Cu(2). We ignore the two more distant O(2,3) sites in this estimate. The positions of various ions in the crystal (Fig. 3.1) are such that the Cu(2)-O(2,3) horizontal distance is  $d = 1.95 \text{ \AA}$ , and the vertical distances between  $^{89}\text{Y}$  and Cu(2) and O(2,3) are  $\Delta c1 = 1.65 \text{ \AA}$  and  $\Delta c2 = 1.42 \text{ \AA}$ , respectively. Using (4.1.5) we then find for the total contribution to the HF coefficients

$$\Delta D'_{dip,ab} = -8\mu_B \left[ \frac{1-4\delta}{r_{Cu}^3} \left( 1 - 3 \frac{d^2}{r_{Cu}^2} \right) + \frac{\delta}{r_O^3} \left( 2 - 3 \frac{d^2}{r_O^2} \right) \right] \quad (4.1.6a)$$

$$\Delta D'_{dip,c} = -8\mu_B \left[ \frac{1-4\delta}{r_{Cu}^3} \left( 1 - 3 \frac{\Delta c1^2}{r_{Cu}^2} \right) + \frac{2\delta}{r_O^3} \left( 1 - 3 \frac{\Delta c2^2}{r_O^2} \right) \right] \quad (4.1.6b)$$

where  $\mathbf{r}_{Cu} = \hat{i}d + \hat{j}d + \hat{k}\Delta c1$  and  $\mathbf{r}_O = \hat{i}d + \hat{k}\Delta c2$ . Inserting the foregoing numbers into these equations, we find  $\Delta D_{dip,ab} = 0.14 \text{ kOe}/\mu_B$  and  $\Delta D_{dip,c} = -0.28 \text{ kOe}/\mu_B$ . These are of the order of 20-30% of  $D'_\alpha$  and so they are quite appreciable as suggested in [9]. However, since they have the opposite sign of

the observed anisotropy, it is clear that there is another source of anisotropy which is twice as large.<sup>3</sup>

The other noteworthy point is that there are a number of dipolar terms which are effective for the  $T_1$  process but which have an angular dependence which does not vanish at the “magic angle” and therefore may be considerably larger than the shift coefficients estimated above. Thus, one may not find that  $T_1$  for  $^{89}\text{Y}$  exhibits the expected anisotropy from the measured  $D_\alpha$  coefficients. The dipolar effects for the  $^{89}\text{Y}$  were also discussed in detail by Auler et al. [15].

We shall address this matter further in the next subsection.

### 4.1.2 A Simple Model Theory of Spin Dynamics for YBCO6.63

The Spin-Hamiltonian formulation of HF coupling at the  $\text{Cu}^{2+}$  sites combined with the Mila-Rice-Shastry [12, 16] picture of transferred HF couplings from the  $\text{Cu}^{2+}$  moments to the Y and O(2,3) sites provides a definite basis for discussing electron spin-based static and dynamic NMR properties. In the last subsection we saw that one finds a consistent picture of HF couplings from NMR shift data, which apply to both YBCO7 and YBCO6.63. The coupling constants we refer to here are found in Tables 3.4, 3.6, 4.1. They were used in the Mila-Rice discussion of  $T_1$  in Chap. 3.

Meanwhile, here we consider the relaxation properties of YBCO6.63, where spin-spin correlations will be used to discuss comparative temperature variations of  $T_1$  in terms of dynamical spin fluctuations. As was noted in Sect. 3.3.3, dynamical spin correlations are the apparent cause of the T-varying  $^{63}\text{Cu}(2)$   $T_1$  anisotropy for YBCO7 [17]. Although a comparable data set is not available for YBCO6.63, we shall find application in this case for similar formulations of the  $^{89}\text{Y}$  and  $^{17}\text{O}(2,3)$  relaxation properties as well as the  $^{63}\text{Cu}(2)$ .

Let us anticipate some of the themes as well as stumbling blocks which arise in the course of trying to account for the relaxation behavior of the YBCO6.63 (60 K) phase. First, we note the pervasive characteristic temperature variation  $1/T_1T \propto K_s(T)$ , which arose in an empirical way, but then found a measure of theoretical justification [18]. Secondly, the case of  $^{89}\text{Y}$  has two special problems, which have been discussed by Takigawa et al. [10]: (i) The direct dipolar interaction is large enough to make an important contribution to the overall HF coupling, as we saw in the previous subsection. Thus, the HF coupling Hamiltonian does not have the simple form of (3.3.2). This complicates the relaxation calculations. (ii) The  $^{89}\text{Y}$  relaxation is driven by  $\text{Cu}^{2+}$  spin moments in neighboring  $\text{CuO}_2$  planes (see Fig. 3.1), so the question of interplanar spin correlations is an important one for  $T_1$ . As there is neutron-scattering evidence for such correlations [19], the  $^{89}\text{Y}$   $T_1$  phenomena are more complex on that account.

<sup>3</sup> A simple sign check is the following: For the c-axis case,  $\Delta D'_{\text{dip},c}$  has the same sign as for the limit  $\Delta c1, 2 \rightarrow 0$ . In the latter case, “up” moments on the  $\text{Cu}(2)$  or  $\text{O}(2,3)$  sites would clearly give “down” (i.e. negative) HF fields at the  $^{89}\text{Y}$  sites, in accord with the calculated result.

### ***T<sub>1</sub> Enhancement and a Model Susceptibility for Underdoped Cuprates.***

It was first noted empirically that the quantity  $(T_1 T K_s(T))^{-1}$  is *approximately constant* for  $^{89}\text{Y}$  and  $^{17}\text{O}(2,3)$  in both the YBCO7 and YBCO6.63 phases [8]. Moreover, the same quantity for the  $^{63}\text{Cu}(2)$  no longer exhibits a peak around 150 K, but executes a roughly power-law rise as  $T$  approaches  $T_c$  in the normal state. These behaviors are shown in Fig. 4.6 using data from various sources (see figure caption). Interestingly, the  $^{63}\text{Cu}(2)$  data for YBCO7 show a similar temperature characteristic. The  $^{89}\text{Y}$  and  $^{17}\text{O}(2,3)$  shown indicate very little change with  $T$ , i.e.  $1/T_1 T \propto \chi_s(T)$ . Later, more complete data, however, deviated from this simple picture.

The data plotted in Fig. 4.6 are scaled as  $[T_1(Korr.)/T_1(T)][K_s(300\text{K})/K_s(T)]$ , where

$$T_1(Korr.) = N_s \gamma_e^2 \hbar / (4\pi k_B T \gamma_n^2 K_s^2), \quad (4.1.7)$$

which is the usual Korringa expression with a factor  $N_s$  to account for multiple sources of HF fluctuations. Here,  $N_s = 4, 2$ , and  $8$  for  $\text{Cu}(2)$ ,  $\text{O}(2,3)$  and  $\text{Y}$ , respectively. Note that  $N_s = 4$  for the  $c$ -axis  $\text{Cu}(2)$   $T_1$  process, which is dominated by the four  $nn$  couplings. The shift has also been normalized arbitrarily to its room-temperature value, so that the absolute values plotted are only a relative indication of fluctuation enhancement levels. Clearly, for  $\text{Cu}(2)$  the YBCO6.63 case is smartly enhanced over the YBCO7, and both of these by a considerable margin over the ligands. These effects are attributed to AFM fluctuations, which barely touch the ligands, but strongly enhance the  $\text{Cu}(2)$  relaxation and increase quickly with carrier dilution.

The proportionality between  $1/T_1 T$  and  $K_s(T)$  is suggested by the model form [8, 22]

$$\chi''(\mathbf{q}, \omega) = \frac{\pi \chi_0 \omega}{\Gamma} G(\mathbf{q}) \quad (4.1.8)$$

for the low-frequency dynamics ( $\omega \ll \Gamma$ ) of the quasiparticles, where  $\chi_0$  is interpreted as an estimate of the static susceptibility, and the factor  $G(\mathbf{q})$  embodies any  $\mathbf{q}$ -dependent enhancement effects which occur. Since  $1/T_1 T \propto \sum_{\mathbf{q}} G(\mathbf{q})$ , this form suggests that  $1/T_1 T \propto \chi_0$ . To use this form even when  $\chi_0$  has the gapped temperature characteristic of an underdoped cuprate is to go beyond the usual mean-field theory interpretation of (4.1.8). Nonetheless, this procedure has been adopted in order to treat  $T_1$  phenomena in spin-gapped superconductors [23].

However, not long after the latter work appeared, a theoretical model was developed which actually exhibited such behavior. This was the “attractive” (i.e. negative- $U$ ) Hubbard model of Randini and Trivedi, which was studied using QMC techniques [18]. The authors only studied local,  $\mathbf{q}$ -independent HF couplings, and emphasized that this was not a suitable model for cuprate physics in other ways. Nonetheless, their results for the gapped behavior of both susceptibility and  $1/T_1 T$ , shown in Fig. 4.7, give a remarkably realistic version of the effects seen in Fig. 4.6 for, e.g. the  $^{89}\text{Y}$  and  $^{17}\text{O}(2,3)$  sites.

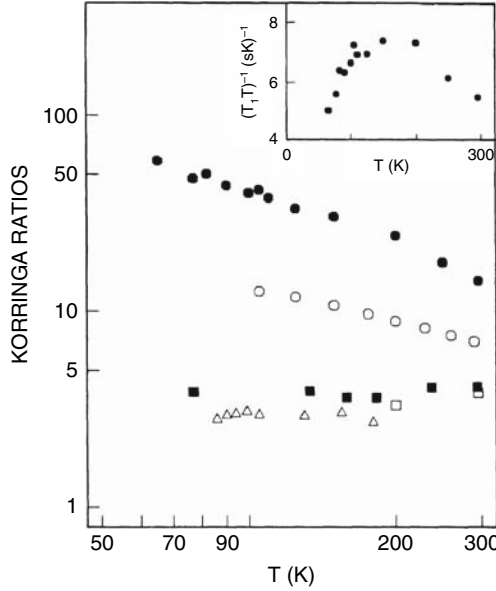


**Fig. 4.6.** The quantity  $[T_1(Korr.)/T_1][K_s(300\text{ K})/K_s(T)]$  is plotted vs.  $T$  in a log-log plot over the range  $50\text{ K} \leq T \leq 300\text{ K}$  for a series of cases as follows: Open and closed circles are for  $^{63}\text{Cu}(2)$  in YBCO6.63 [8] and YBCO7 [17], respectively. Closed squares are  $^{89}\text{Y}$  data from Alloul et al. [2] using, however, an independently determined value for the  $^{89}\text{Y}$  chemical shift [8]. (A similar value was reported later by Alloul et al. [5].) The open squares are data for YBCO7 from [20] using the same chemical shift. Finally, the open triangles represent  $^{17}\text{O}(2,3)$  data on YBCO7 from [21]. See text for a definition of  $T_1(Korr.)$  Figure reprinted from R.E. Walstedt, W.W. Warren, Jr., et al., Phys. Rev. B **41**, 9574 (1990). Copyright 1990 American Physical Society

To account for the Cu(2) data would require inclusion of  $\mathbf{q}$ -dependent enhancement effects in the negative-U Hubbard model, which has not, to our knowledge, been done. In any case, the results of Fig. 4.7 offer some support for the phenomenological treatment based on (4.1.8) with  $\chi_0 = \chi_s(T)$ .

#### 4.1.3 INS Data for the Pseudogap of Underdoped YBCO

Before we attempt to interpret  $T_1$  data for YBCO6.63 it is also important to discuss some neutron-scattering studies which are related to the low-frequency dynamical behavior. Several groups have reported spin correlations as well as AFM fluctuation peaks in  $\chi''(\mathbf{q}, \omega)$  for this compound [19, 24, 25]. INS data for a YBCO6.6 sample with  $T_c = 53\text{ K}$  are shown in Fig. 4.8 [19].

At  $\hbar\omega = 15\text{ meV}$ ,  $\mathbf{q}$ -scans through the AFM point  $[\mathbf{h}(1 + \delta), \mathbf{h}(1 - \delta), -1.8]$ , for two values of  $\delta$  and  $\mathbf{h} = 0.5$ , record the flat-topped AF peaks in  $\chi''(\mathbf{q}, \omega)$  at  $T = 10\text{ K}$  shown in Fig. 4.8(a) and (b) [19]. This appears to be a superposition

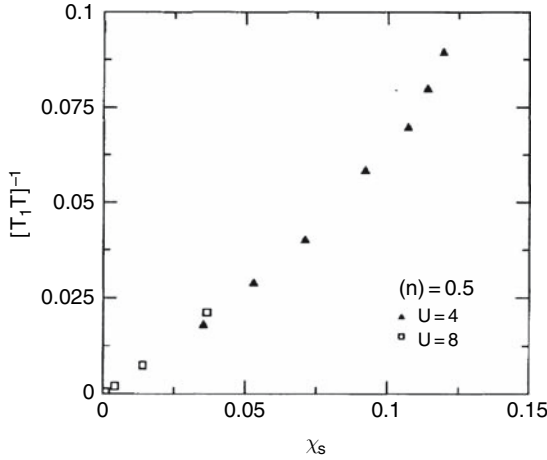


**Fig. 4.7.** The variation of  $1/T_1 T$  vs.  $\chi_s$ , with  $T$  as an implicit parameter, for the attractive- $U$  Hubbard model calculations of [18]. Over the lower 40% of the variation of  $1/T_1 T$ , this quantity shows a very clear linearity with the spin susceptibility, with a constant of proportionality which is essentially independent of the value of  $U$ . Figure reprinted from M. Randeria, N. Trivedi, A. Moreo, R.T. Scalettar, Phys. Rev. Lett. **69**, 2001 (1992). Copyright 1992 American Physical Society

of incommensurate peaks, but in any case it is a sign of strong in-plane AFM correlations. The authors suggest that this is strong enough to account for any observed enhancement of the Cu(2) relaxation. The temperature dependence of the integrated area under the AFM peak in  $\chi''(\mathbf{q}, \omega)$  ( $\mathbf{q} \sim \mathbf{Q}_{AF}$ ) shows an energy-gap behavior with a gap value given as  $9 \text{ meV} \simeq 104 \text{ K}$  [19]. This is the same gap energy as was derived from the static susceptibility data with an Arrhenius plot (Fig. 4.4, inset) for YBCO6.63. It seems that  $\chi_s(T)$  (i.e.  $\mathbf{q} = 0$ ) and  $\chi''(\mathbf{q}, \omega)$ ,  $\mathbf{q} \sim \mathbf{Q}_{AF}$  (for YBCO6.60) exhibit the same gap energy. Such a result is implied by the dynamic susceptibility model (4.1.8) and is therefore supportive of such a model.

Finally, a very substantial neutron intensity modulation has been observed in scanning  $\mathbf{q}$  along the  $c$  axis. The scan of  $(0.5, 0.5, l)$  for  $-3.5 \leq l \leq 3.5$  is shown in Fig. 4.8(c), where a modulation amplitude approaching 50% is seen to occur at  $T = 100 \text{ K}$ . Since the in-plane correlation length is only a few lattice spaces at most, the  $c$ -axis modulation reflects a larger exchange coupling between layers than one can easily account for. As was emphasized in [10], such an intensity modulation implies relatively strong interplanar spin correlations which cannot be ignored when we estimate the  $^{89}\text{Y}$  relaxation rate. However, it is possible that the  $c$ -axis correlation effect could diminish rapidly with increased doping level, and thus be smaller for YBCO6.63. Such a measurement needs to be compared with NMR data on the same sample material.

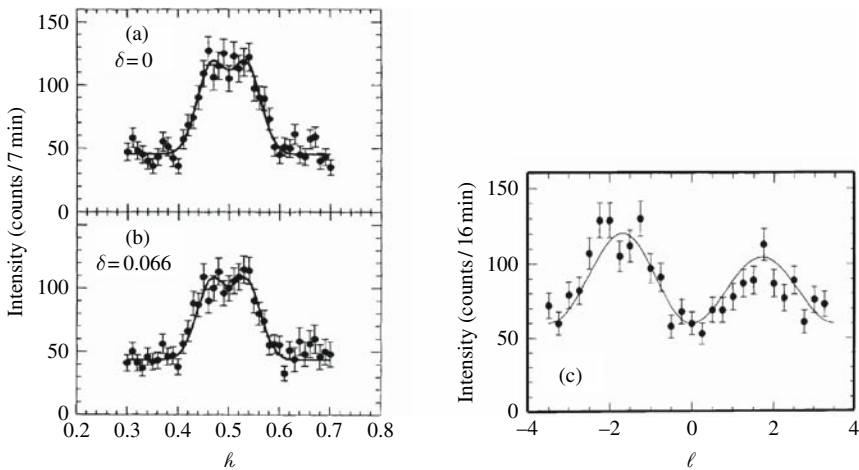


**Fig. 4.8.** (a) Neutron scattering intensity is shown for two scans in the vicinity of the AFM point along the diagonal (see text for details). These steep-sided peaks show signs of an incommensurability. They have been fitted with a pair of Gaussians as shown. (b) A scan along  $(0.5, 0.5, l)$  is recorded for an energy transfer of 9 meV at  $T = 100$  K on a crystal of YBCO $7-x$ , with  $x = 0.55$  and  $T_c \simeq 45$  K. The solid line is a resolution-corrected calculation of the inelastic structure factor from [19]. The variation of modulation amplitude with  $x$  is not known. Figure reprinted from J.M. Tranquada, et al., Phys. Rev. B **46**, 5561 (1992). Copyright 1992 American Physical Society

#### 4.1.4 A Comprehensive $T_1$ Data Set for YBCO6.63

We now consider the relaxation data for  $^{63}\text{Cu}(2)$ ,  $^{17}\text{O}(2,3)$ , and  $^{89}\text{Y}$  corresponding to the NMR shift and spin susceptibility results of Figs. 4.4 and 4.5.

In Fig. 4.9 are displayed the high-quality  $T_1$  data for  $^{63}\text{Cu}(2)$  and  $^{17}\text{O}(2,3)$  in YBCO7 (“y = 0”) and YBCO6.63 (“y = 0.37”) from Takigawa et al. [9]. The  $T_c$  points indicated refer to YBCO6.63, where  $T_c \simeq 64$  K. For the case of YBCO7 (open circles) the data for both  $^{17}\text{O}(2,3)$  and  $^{63}\text{Cu}(2)$  show very similar sharp declines at  $T_c \simeq 92$  K. For YBCO6.63 (closed circles), however, the overall curves are very different, and neither data plot shows any visible feature at  $T_c$  (indicated by arrows), where both curves are smooth and continuous. As shown in the inset to Fig. 4.1(a), however, the resistive superconducting transition remains as sharp as ever. As with  $\chi_s(T)$  (Fig. 4.4), then, the low-frequency spin dynamics show only a smooth decline in the vicinity of  $T_c$ . *This behavior shows that the pseudogap merges smoothly into the superconducting gap which presumably forms below  $T_c$ .*

Considering the  $^{63}\text{Cu}(2)$   $T_1$  data in Fig. 4.9(b), a plot of these data similar to Fig. 4.6 yields essentially the same result<sup>4</sup>. However, in spite of the

<sup>4</sup> As an example we consider the value of  $[T_1(Korr.)/T_1][K_s(T)/K_s(300)]$  at  $T = 100$  K. Using (4.1.7) with  $N_s = 4$ , we take  $1/T_1 \simeq 630 \text{ s}^{-1}$  from Fig. 4.9(b),

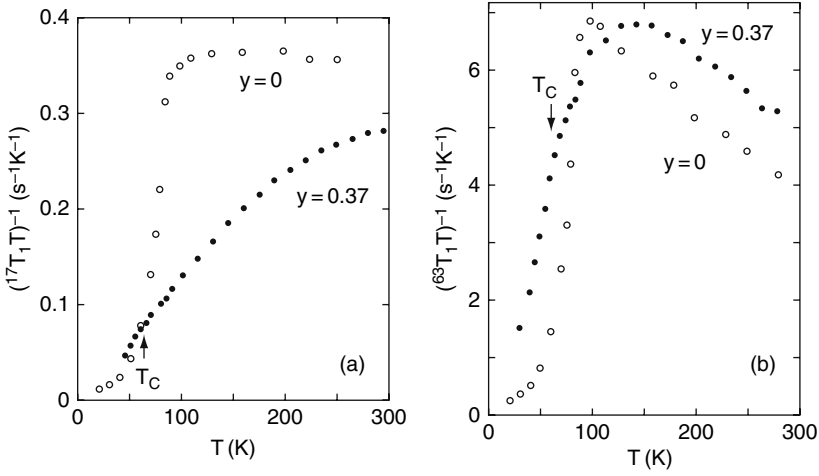


**Fig. 4.9.** (a) Data for  $1/T_1T$  for  $^{17}\text{O}(2,3)$  in both YBCO7 (“ $y = 0$ ”, open circles) and YBCO6.63 (“ $y = 0.37$ ”, closed circles) are plotted from 300 K down to well below  $T_c$  [9]. (b) With the same notation and symbols as in (a) the corresponding data for  $^{63}\text{Cu}(2)$  are shown. Figure reprinted from M. Takigawa, A.P. Reyes, P.C. Hammel, Phys. Rev. B **43**, 247 (1991). Copyright 1991 American Physical Society

large numbers one sees in Fig. 4.6, the actual enhancement of  $1/T_1T$  for Cu(2) is a relatively small number. From (3.3.14) one sees that  $1/T_{1c} \propto \chi_s(T)[1 + 0.29\mathcal{K}_{01} + 0.99(2\mathcal{K}_{12} + \mathcal{K}_{13})]$ . The  $\mathcal{K}_{ij}$ ’s presumably have small values above 300 K, and as  $T \rightarrow T_c$  could approach  $-1$  for  $\mathcal{K}_{01}$  and  $+1$  for  $\mathcal{K}_{12}$  and  $\mathcal{K}_{13}$ . Thus, the AFM exchange enhancement factor  $[\ ]$  varies from unity to a maximum  $[\ ] \simeq 3.68$ . Examination of the data plot in Fig. 4.9(b) shows that it changes substantially between 100 K and 300 K, but stays well within those limits.

Considering  $T_1$  data for  $^{17}\text{O}(2,3)$  in Fig. 4.9(a), we see that it very closely resembles the susceptibility curve in Fig. 4.4. A plot of  $(T_1TK_c(T))$  vs.  $T$  using data from the latter figures yields a curve varying by only a few percent between 100 K and 300 K [9]. The simple model form (4.1.8) for  $\chi''(\mathbf{q}, \omega)$  now leads us, however, into some difficulty. The correlation factor for  $^{17}\text{O}(2,3)$  is simply  $[1 + \mathcal{K}_{01}]$ , where the remainder of the expression  $\propto \sum_{\mathbf{q}} \chi''(\mathbf{q}, \omega)/\omega$ , has been shown by neutron studies to vary with temperature in the same energy-gapped fashion as  $\chi_s(T)$ . Thus,  $(T_1TK_s(T))^{-1} \simeq \text{constant}$  for the  $^{17}\text{O}(2,3)$  means  $[1 + \mathcal{K}_{01}] \simeq \text{constant}$ , which is not consistent with the “substantial” change in the correlations required by the  $^{63}\text{Cu}(2)$  above.

We shall now see that the  $^{89}\text{Y}$  data lead to further difficulties with the model susceptibility (4.1.8).

---

$K_s(100\text{ K}) \simeq 0.11\%$ , and  $[K_s(T)/K_s(300)] \simeq 0.5$ . Inserting these parameter values, one finds  $[T_1(Korr.)/T_1][K_s(100)/K_s(300)] \simeq 39$ , which lies among the closed circle points in Fig. 4.6.

***The Problem of  $^{89}\text{Y}$   $T_1$  Behavior in YBCO6.63.***

In Fig. 4.6  $^{89}\text{Y}$   $T_1$  data are plotted so as to test the pseudogap scaling with  $\chi_s(T)$ . The result is a very flat curve, based on data from [2]. However, there are two more recent sets of  $T_1$  measurements, by Takigawa et al. [10] and by Alloul et al. [5], neither of which agree with the previous conclusion. Data plots from [10] are shown in Fig. 4.10. In Fig. 4.10(a) are plotted  $1/T_1T$  for  $^{89}\text{Y}$  in YBCO6.63 with both field orientations as a companion to the NMR shift measurements in Fig. 4.5 on the same sample, as well as the  $^{17}\text{O}(2,3)$  relaxation data from Fig. 4.9 for comparison. It is clear that  $1/T_1T$  for the oxygen declines rather less at low temperatures than either  $^{89}\text{Y}$  measurement. This point is illustrated further in Fig. 4.10(b), where  $^{17}T_{1c}/^{89}T_{1c}$  is plotted for  $100\text{ K} \leq T \leq 300\text{ K}$ . At 100 K this ratio is seen to have increased by more than 20% over its value at 300 K. Similar data are given in [5] for both  $K_s(T)$  and  $1/T_1T$  for  $^{89}\text{Y}$  in YBCO6.64. Although the latter data have somewhat larger error bars, they are consistent with the data shown in Fig. 4.10. Since these more recent data are much more complete than those shown in Fig. 4.6, we conclude that  $(T_1TK_s(T))^{-1}$  for  $^{89}\text{Y}$  is not constant in this composition, in contrast with the  $^{17}\text{O}(2,3)$  data in Fig. 4.9.

We discuss the data in Fig. 4.10 further by means of the general  $T_1$  formulas (3.5.22) and (3.5.21). Taking the ratio of these equations, we find

$$\frac{{}^{89}T_{1ab}}{{}^{17}T_{1c}} = \frac{\gamma_{17}^2 [C_a^2 + C_b^2]}{\gamma_{89}^2 [D_{ab}^2 + D_c^2]} \frac{[1 + \mathcal{K}_{01}]}{[1 + 2\mathcal{K}_{01} + \mathcal{K}_{12} + \mathcal{K}^{IC}]} \quad (4.1.9)$$

where we have added an interplanar correlation coefficient  $\mathcal{K}^{IC}$  to take account roughly of that possibility for the  $^{89}\text{Y}$ . In the high temperature limit where  $\mathcal{K}_{ij} \ll 1$ , one would expect  ${}^{89}T_{1ab}/{}^{17}T_{1c} \rightarrow \gamma_{17}^2[C_a^2 + C_b^2]/\gamma_{89}^2[D_{ab}^2 + D_c^2]$ . Inserting parameter values from Table 4.1, we find a limiting ratio of 2360, as compared with the experimental ratio of 1305 at  $T = 300\text{ K}$  (Fig. 4.10) [10]. It seems, then, that the estimated rate  $1/{}^{89}T_1$  is too small by as much as a factor  $\sim 2$  when analyzed on the same basis as the  $^{17}\text{O}(2,3)$ .

On the other hand, this analysis has some positive points. First, the anisotropy of  ${}^{89}T_1$  according to the model (3.5.22) is given by  ${}^{89}T_{1c}/{}^{89}T_{1ab} = [D_{ab}^2 + D_c^2]/[2D_{ab}^2] \simeq 1.17$  by the data in Table 4.1. With modest error bars on that value, the data in Fig. 4.10 are in reasonable agreement with the latter estimate for both YBCO7 and YBCO6.63 and at all temperatures shown. Furthermore, when correlations become important at low temperatures, one would certainly expect that

$$[1 + 2\mathcal{K}_{01} + \mathcal{K}_{12} + \mathcal{K}^{IC}] < [1 + \mathcal{K}_{01}]. \quad (4.1.10)$$

One would therefore expect  ${}^{89}T_{1\alpha}/{}^{17}T_{1\alpha}$  to increase at low  $T$ , as it does in Fig. 4.10(b).

If we examine the effects of dipolar terms, in the case of negligible correlations they add less than 10% to the estimated rates. The case of dipolar

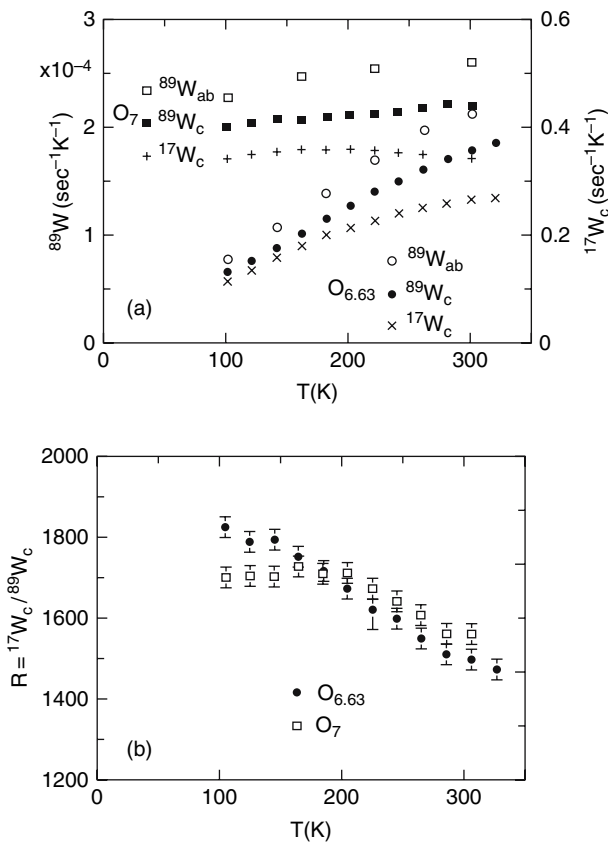


**Fig. 4.10.** (a) Data for  $1/T_1T$  for  $^{89}\text{Y}$  ( $^{89}\text{W}_{ab,c}$ ) in both YBCO7 ( $\text{O}_7$ ) and YBCO6.63 ( $\text{O}_{6.63}$ ) and for both “ab” and “c” axis field orientations are plotted from 100 K to above 300 K [10]. For comparison,  $1/T_1T$  for  $^{17}\text{O}(2,3)$  ( $^{17}\text{W}_c$ ), measured on the same samples, is also plotted. (b) With the same notation as in (a) the ratios  $R = ^{17}\text{W}_c / ^{89}\text{W}_c$  are plotted for both compositions and the same temperature range. Figures reprinted from M. Takigawa, W.L. Hults, J.L. Smith, Phys. Rev. Lett. **71**, 2650 (1993). Copyright 1993 American Physical Society

terms in the presence of intraplanar and interplanar correlations has been discussed in detail by Takigawa et al. [10]. While they could become significant in such a case, they have the opposite anisotropy to the  $D_\alpha$ 's, which is a serious drawback. One cannot see how a calculation based entirely on the model Hamiltonian (3.3.2) can heal the disparity in the estimated  $T_1$  for  $^{89}\text{Y}$ . Additional calculations with the full dipolar Hamiltonian have been performed by Auler et al. [15], where a substantial dipolar contribution to the  $^{89}\text{Y}$  relaxation was estimated. These results are discussed in Sect. 5.3.

Another possible answer for the  $^{89}\text{Y}$   $T_1$  problem is that there may be enough Y(3d)-hole character hybridized into the  $\text{Cu}^{2+}$  spin states to generate

a significant orbital  $T_1$  effect. After all, the measured  $D'_\alpha$  coefficients in Table 4.1 are undoubtedly the result of such an hybridization, which has its main effect through the core-polarization term. The orbital HF effects are typically of the same order, but are probably more nearly isotropic. Since there is no Fermi-surface orbital shift effect related to the orbital  $T_1$  term, the latter would just appear as a “background” relaxation effect unrelated to the spin HF effects. There could also be a small Van Vleck orbital NMR shift as part of the positive, temperature-independent chemical shifts recorded for the  $^{89}\text{Y}$ .

We turn now to pseudogap phenomenology as seen with other probes.

## 4.2 Pseudogap Phenomenology with Other Probes

In this section we address briefly several topics relating to pseudogap effects in the cuprates, but not directly related to NMR. Thus, we are discussing “background material”, the point of which is to give a deeper context in which to present and discuss the NMR results. It is essential to point out that pseudogap effects have been observed and studied in great detail with several other techniques. In particular, it is interesting to note that the presence of the pseudogap is felt in both spin and charge-based properties. One example is the in-plane conductivity  $\sigma_{ab}(T)$  of underdoped YBCO at  $250\text{ cm}^{-1}$ , which according to Rotter et al. [26] exhibits a gap-like feature at low temperatures very similar to  $1/T_1T$  for  $^{89}\text{Y}$  and  $^{17}\text{O}(2,3)$  for that case (see Figs. 4.1(b) and 4.9(a)). A clearly presented review of pseudogap effects has been given by Randeria [27].

### 4.2.1 Pseudogap Effects in the Electronic Specific Heat

We offer brief descriptions of experimental results which detect and elucidate the pseudogap effect in cuprates, the first of which is the electronic specific heat. By using a very precise differential technique, J.W. Loram and co-workers have produced an extraordinarily clear and detailed picture of the behavior of low-energy electronic states in the cuprates [28, 29, 30]. We review here a selection of their results on YBCO7- $\delta$ .

A sampling of specific heat results is shown in Fig. 4.11(a) and (b). In (a) one sees that, first, the peak in  $\gamma^{el}(T)$  ( $\equiv C_p(T)/T$ ) at  $T_c$  gradually vanishes as  $\delta$  is increased from 0, and simultaneously a pseudogap maximum appears at temperatures  $T \gg T_c$ , causing  $\gamma^{el}$  to decline as it approaches  $T_c$  from above. The peak at  $T_c$  makes a rather weak reappearance at  $T_c \sim 60\text{ K}$ , then declines further as superconductivity fades away at larger  $\delta$  values.

In Fig. 4.11(c) the entropy  $S^{el} = \int_0^T \gamma^{el}(T')dT'$  is plotted as  $S^{el}/T$  vs.  $T$ . Such a plot closely resembles  $\gamma^{el}(T)$ . The superconducting gap feature is very pronounced for  $\delta \ll 1$ , persisting up to  $\delta \sim 0.20$ . Then entropy loss at  $T > T_c$  becomes a major feature, namely the pseudogap, as  $\delta$  increases, while

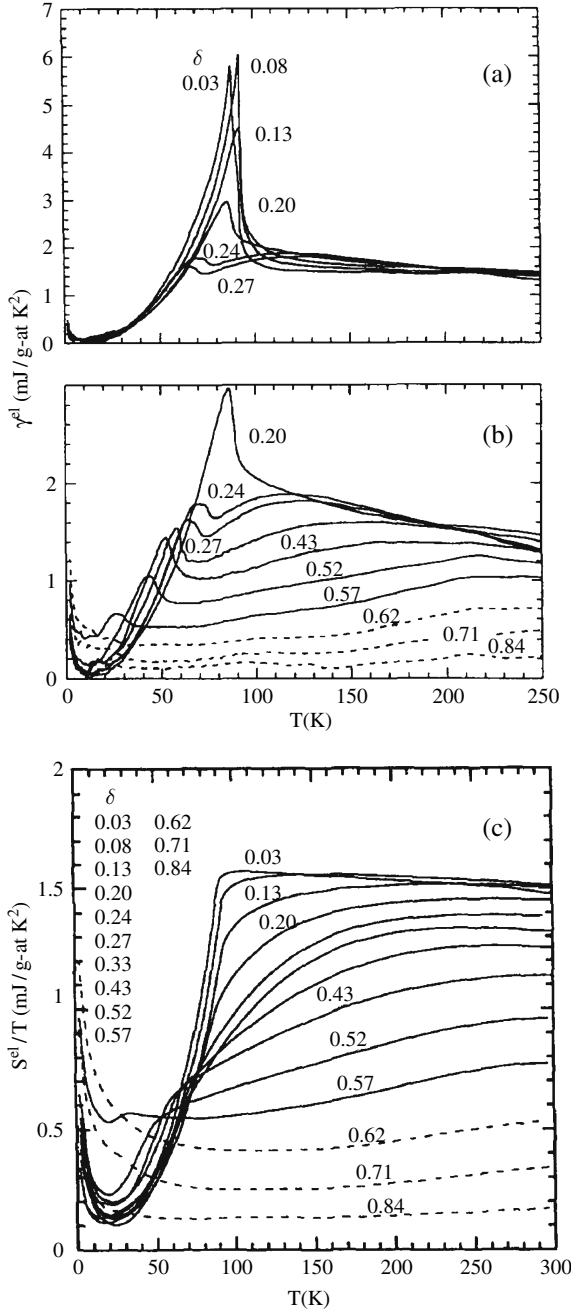


**Fig. 4.11.** (a) and (b) Data for the electronic specific heat coefficient  $\gamma^{el}$  of YBCO7- $\delta$ , obtained via differential measurements with YBCO6.0, are plotted for different doping levels  $\delta$  as a function of temperature up to 250 K [30]. In (b) there is clear

the decline in  $S^{el}/T$  begins at ever higher temperatures. Note, however, that a vestige of the superconducting gap feature beginning at  $T \sim T_c$  remains in place until superconductivity disappears altogether.

These effects on  $\gamma^{el}$  and  $S^{el}(T)$  seem to be entirely consistent with what one would expect based on the spin susceptibility and low-energy spin excitations reflected in the  $1/T_1T$  results given in Sect. 4.1. Loram et al. present a companion set of spin susceptibility curves [30] to confirm this point. There is a clear conclusion here of *non-separation of spin and charge behavior*, contrary to some of the early models of high- $T_c$  properties [31, 32].

#### 4.2.2 ARPES Studies of Pseudogapped Cuprates

Angle-resolved photoemission studies (ARPES) on cuprates exhibiting pseudogap effects have also given a great deal of insight into the microscopic physics of cuprate superconductors as well as the pseudogap phenomena per se. Since this method offers good resolution of energies as well as of  $\mathbf{k}$  values, one is able to study both gap energies and their anisotropy over the Fermi surface. Extensive investigations of the cuprate properties have been conducted. We shall briefly review studies of pseudogap effects in the Bi2212 family of superconductors by Harris, Shen et al. [33, 34, 35].

What ARPES reveals is not only that gaps appear anisotropically around the Fermi surface, but also that quasiparticle peaks in the normal state are greatly diminished. They appear mainly at temperatures below  $T_c$ . Gap energies are measured, then, as the distance between  $E_F$  and the “leading edge midpoint” of the photoemission intensity. The pseudogap is found to behave in similar fashion to a d-wave superconducting gap, namely to be at its maximum along the cut from  $(\pi, 0)$  to  $(\pi, \pi)$  and to vanish along the diagonal cut  $(0, 0)$  to  $(\pi, \pi)$ . With that in mind, we examine the temperature dependence of experimental gap data, which offers some insight into the relation between the pseudogap behavior and that of the superconducting gap which sets in below  $T_c$ .

Harris et al. reported a study of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Dy}_x\text{Cu}_2\text{O}_{8+\delta}$  untwinned thin-film crystals with variable doping controlled by the parameters  $x$  and  $\delta$  [33].



**Fig. 4.11.** (Continued) evidence for a pseudogap creating broad maxima in  $\gamma^{el}$  at progressively higher temperatures with increasing carrier dilution. (c) The quantity  $S^{el}/T$ , where  $S^{el}$  is the electronic entropy calculated from the data in (a) and (b), is plotted as a function of temperature up to 300 K. The superconducting gaps occurring at  $T_c$  as well as the pseudogap effects in these data are discussed in the text. Figure reprinted from W.Y. Liang, J.W. Loram, *Physica C* **263**, 277 (1996). Copyright 1996 Physica C

Their gap energy data scans extend over  $1/8$  of the (2D) Fermi surface.<sup>5</sup> Two separate doping levels yielded a sample with a “strong” pseudogap effect ( $T_c = 42$  K) and a second one with a much “weaker” pseudogap ( $T_c = 78$  K), where “strong” and “weak” are to be defined presently.

In Fig. 4.12(a) and (b) experimental gap energies are shown along an arc of the Fermi surface which extends from the diagonal  $(0.4, 0.4)\pi$  where the abscissa is zero to  $(1, 0.2)\pi$ , where it is nearly one. The abscissa is defined as  $0.5|\cos k_x a - \cos k_y a|$ , which would yield a linear variation of gap energy with a d-wave ( $d_{x^2-y^2}$ ) superconducting gap. For the data in Fig. 4.12(a), the superconducting state data (closed circles) show a nearly linear variation of gap energy along this path. In a conventional superconductor there would be no gap energy above  $T_c$ ; thus, the curve would remain flat. However, this  $T_c = 78$  K sample has a “weak” pseudogap, such that substantial gap energies occur

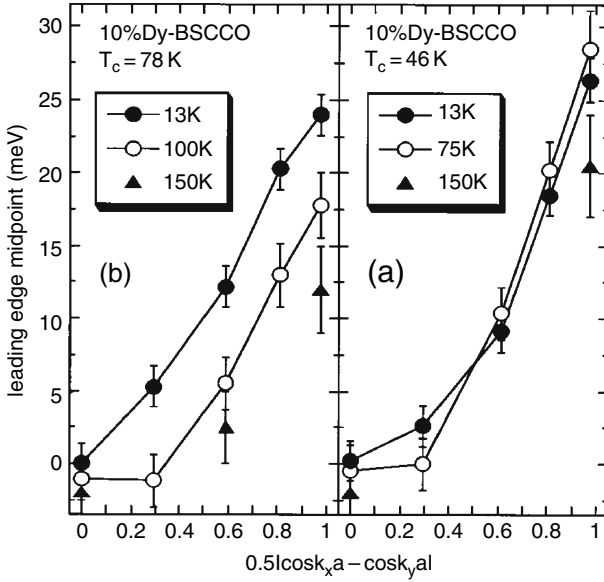


**Fig. 4.12.** ARPES measurements of gap energies, taken as described in the text on untwinned thin film crystals of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Dy}_x\text{Cu}_2\text{O}_{8+\delta}$ . In (a), gap variation results are shown along the Fermi surface at three temperatures for a “strong” pseudogap composition, and in (b) gap energies are shown at three temperatures for a “weak” pseudogap system, as described and discussed in the text. Figure reprinted from J.M. Harris, Z.-X. Shen, et al, Phys. Rev. B **54**, R15665 (1996). Copyright 1996 American Physical Society

<sup>5</sup> The region of  $\mathbf{k}$ -space considered is triangular, extending from  $(0,0)$  to  $(\pi,0)$ , then to  $(\pi,\pi)$  and back to  $(0,0)$ . The Fermi surface is an arc extending from  $\sim(0.4,0.4)\pi$  on the diagonal around to the point  $\sim(1,0.2)\pi$  on the  $(0,\pi) - (\pi,\pi)$  axis.

at 100 K and 150 K, but which behave only qualitatively like the superconducting gap.

On the other hand, the  $T_c = 46$  K sample exhibits a “strong” pseudogap, which means that the gap energy profile shown is the same both above and below  $T_c$ , exhibiting a flat region near the null (abscissa = 0) and rising to a maximum which is the same near the point  $(1,0.2)\pi$  both above and below  $T_c$ . At 150 K the gap energy shows a small decline. Thus, with a “strong” pseudogap, the gap energy profile in  $\mathbf{k}$ -space is very nearly the same above and below  $T_c$ . For either a weak or strong pseudogap, the gap energy behaves in  $\mathbf{k}$ -space in a very similar fashion to a superconducting gap, giving the impression that these effects are related.

At what temperature, then, does the energy gap finally collapse in an underdoped sample? An experimental answer to this question was given in [33], where measured gap energies at the maximum point were plotted vs. temperature up to  $T = 250$  K on a sample with  $T_c = 85$  K. Over this range of  $T$  the pseudogap declines completely to zero, beginning somewhere below  $T_c$ .

The anisotropic gap behavior found in this system and presumably occurring widely in the cuprates would have interesting consequences for the behavior of  $\chi''(\mathbf{q}, \omega)$  and therefore for  $T_1$  measurements of pseudogap systems. Although to our knowledge no such calculation has been reported, it seems very likely that the observed anisotropy of gap effects over  $\mathbf{k}$  space would result in some distribution of gapping effects in  $\mathbf{q}$  space as well. Speculating about the consequences of this, it seems likely that nuclei such as  $^{89}\text{Y}$  and  $^{17}\text{O}(2,3)$  in YBCO, which depend for relaxation on  $\mathbf{q}$  values over the entire zone except near the  $(0, \pi)$  axes would therefore always be subject to pseudogap effects. On the other hand, the pseudogap anisotropy may allow situations where the fluctuations peak strongly at  $(\pi, \pi)$  and are driven by  $\mathbf{k}$  vectors on or near the diagonals. Such behavior could tend to dominate the planar  $^{63}\text{Cu}$   $T_1$  process, which would not then be strongly affected by the pseudogap behavior. Such a case is found for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , as will be discussed in Sect. 4.4.

### 4.3 Pseudogap Behavior of $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y248)

Another pseudogap system which has been studied intensively is Y248, a superconductor which is unique among the cuprates in having a *fixed, stoichiometric carrier doping level*, which pegs it as slightly underdoped. It appears to have a pseudogap not unlike that of YBCO6.63 presented in Sect. 4.1. The structure of Y248 is closely related to YBCO7, except that there are two oxygenated chain layers between the pairs of  $\text{CuO}_2$  planes instead of one.  $\text{Cu}(1)$  sites in the chain layers are staggered along the  $b$  (chain) axis, so that the  $b$ -axis oxygen sites  $\text{O}(4)$  for one chain are apical oxygens for  $\text{Cu}(1)$  sites in the neighboring chain. Thus, planar arrays separated by a double chain layer

are also staggered, making the unit cell  $\sim 27\text{\AA}$  high [36]. This structure of chains is unusually stable, as the chain oxygens remain bound in the crystal up to temperatures beyond 700 K.

Thus, Y248 is a nearly ideal cuprate on which to conduct high-temperature studies. The equilibrium stoichiometric structure of Y248 also yields unusually narrow NMR lines, offering the possibility of high-precision NMR studies. We shall see some examples of this in Sect. 4.3.2.

It is very difficult to measure the ratio of mobile holes which occupy the Cu(1) and Cu(2) regions of the Y248 structure. It is, however, useful to estimate the doping level with the simple valence method. Assigning the usual valences, there is a single mobile hole per formula unit of  $\text{YBa}_2\text{Cu}_4\text{O}_8$ , which gives 0.25 carrier holes per Cu ion. With YBCO6.63, by comparison, the situation is more complicated in that 63% of the chain sites are oxygenated  $\text{Cu}^{2+}$  and 37% are two-fold coordinated  $\text{Cu}^+$  ions. On that basis one calculates 0.24 mobile holes per  $\text{Cu}^{2+}$  ion, giving very nearly equal doping for these two systems. There are marked differences in  $T_c$ , however, which is  $\sim 81\text{ K}$  for the “best” samples of Y248, but only 60-65 K for YBCO6.63. As we shall see, there are other important differences as well.

#### 4.3.1 NMR Shift and Relaxation Behavior in Y248

It is both interesting and informative to compare the pseudogap character of Y248 with that of YBCO6.63 and other systems. Owing to the simple and seemingly immutable character of this compound, a large responsibility seems to have been placed upon it and a great deal expected of it. Here we examine the general behavior of the pseudogap effect as reflected in NMR shift (i.e. susceptibility) and relaxation data. Our point of reference will be the simple behavior found for YBCO6.63 as reflected by the data in Figs. 4.4 and 4.9. As concerns the immutability issue, we shall consider the reproducibility of experimental measurements in data from several research groups.

Let us first look at the overall relaxation behavior in Fig. 4.13. The log scales give a broad overview of the Cu(1,2) sites both above and below  $T_c$  [37]. The Cu(1) relaxation rate crosses through  $T_c$  looking Korringa-like, much as it did in YBCO7. For the Cu(2) there is a near discontinuity of slope at  $T_c$  which is much more pronounced than in the YBCO6.63 data of Fig. 4.9. Below  $T_c$  there is a steep drop into a very brief  $T^3$  region, which then flattens into a presumably disorder-related (i.e. states in the gap) Korringa runout below  $\sim 20\text{ K}$ . Above  $T_c$  there is a near-Korringa stretch which flattens into a very gradual increase above  $\sim 200\text{ K}$ . Similar data have been given by Zimmerman et al. [38]. Apart from the pseudogap onset point around  $\sim 200\text{ K}$ , the normal state behavior is quite featureless. Nonetheless, it is useful to have data extending as high as 700 K. For another view of  $^{63}\text{Cu}(2)$  data for Y248 see the presentation by Yasuoka [39].

In Fig. 4.14 similar data for  $^{63}\text{Cu}(2)$  are plotted as  $1/T_1T$  vs.  $T$  [40]. These data were also taken with NQR, but on a different sample, and are

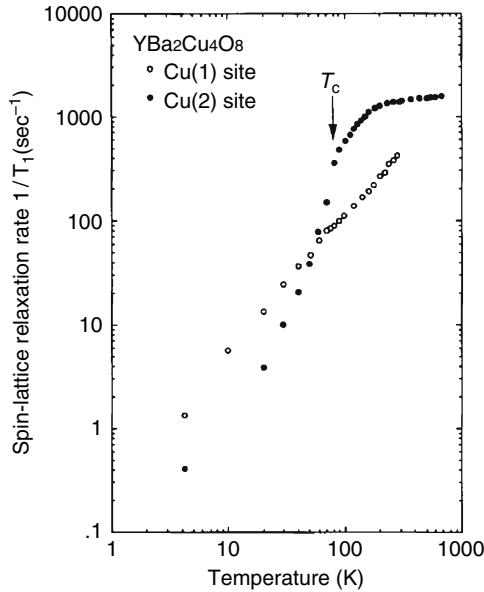


**Fig. 4.13.** NQR results for  $1/T_1$  vs.  $T$  are shown for the  $^{63}\text{Cu}(1)$  and  $^{63}\text{Cu}(2)$  sites in Y248 and for temperatures ranging from 4.2 K up to 700 K [37]. The log-log plot emphasizes major features in the data. See text for detailed discussion. Figure reprinted from T. Machi, I. Tomeno, et al, *Physica C***173**, 32 (1991). Copyright 1991 Physica C

in good agreement with Fig. 4.13. In Fig. 4.14, data for the  $^{17}\text{O}(2,3)$  are compared with those for  $^{63}\text{Cu}(2)$  up to 250 K. The  $^{17}\text{O}(2,3)$  data also show a very definite kink at  $T_c$ , below which they fall well below the corresponding curve for YBCO6.63. Recall that the latter  $^{17}\text{O}(2,3)$   $T_1$  data in Fig. 4.9(a) show no feature whatever at  $T_c$ . The pseudogap effect in Y248 is therefore somewhat like the  $T_c = 78$  K BSCCO sample in Fig. 4.12(b) for which the superconducting gap has its own distinct character, while YBCO6.63 is like the  $T_c = 46$  K (a) sample in that same figure, where the SC gap is completely merged into the pseudogap.

In contrast with  $T_1$  data, neither the Cu(2) NMR shift [37] nor that of the  $^{17}\text{O}(2,3)$  shown any abrupt change at  $T_c$ . The latter shift data  $^{17}K_{i,c}(T)$ ,  $i = 2$  and  $3$ , are shown in Fig. 4.15 where, unlike the case of YBCO6.63, they are resolved and separately measurable. The latter data presumably offer a reasonable measure of the pseudogap, but unfortunately these data have a very large, negative intercept at  $T = 0$ , and no value of the zero shift has been given for either site. We shall make some guesses about the  $T = 0$  shifts and diamagnetic corrections in our analysis below.

Another peculiar feature of the latter  $^{17}\text{O}(2,3)$  NMR shift data is the fact that these two sites have distinct and well-resolved  $T = 0$  shift values, but as

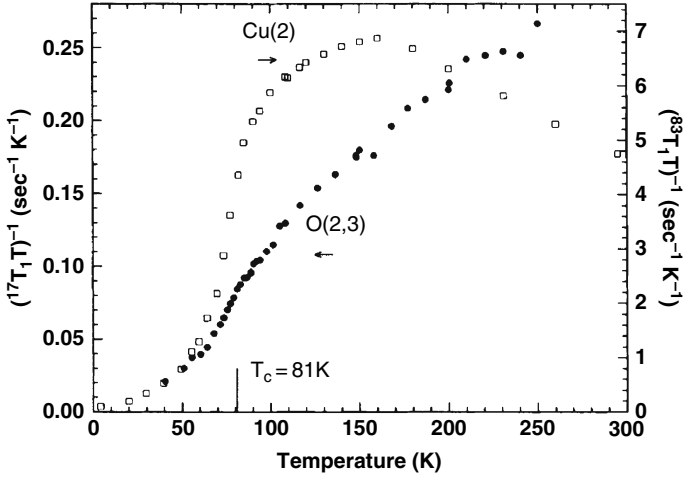


**Fig. 4.14.** Relaxation data for both  $^{63}\text{Cu}(2)$  and  $^{17}\text{O}(2,3)$  in Y248 are plotted as  $1/T_1 T$  vs.  $T$ , showing detailed behavior near  $T_c$ . Like the  $^{63}\text{Cu}(2)$  plot in Fig. 4.13, the planar  $^{17}\text{O}$  show a visible break in slope at  $T_c$ . Figure reprinted from I. Tomeno, T. Machi, et al., Phys. Rev. B **49**, 15327 (1994). Copyright 1994 American Physical Society

the temperature rises above  $T_c$  the two lines gradually merge together. This could be entirely coincidental, resulting from slightly different HF coefficients. Alternatively, there could be chemical migration of  $\text{O}^{2-}$  ions in the  $\text{CuO}_2$  planes at a rate  $\tau_{cm}^{-1}$  which increases with temperature and eventually becomes fast enough

$$\gamma_{17} H \Delta K_{2,3} \tau_{cm} \ll 1, \quad (4.3.1)$$

so that the two NMR lines merge into one. The latter possibility seems a bit remarkable, but would avoid an even more remarkable coincidence with the HF coefficients. It would be easy to test the chemical migration hypothesis with selective saturation techniques. As far as we know this has not been done.

We now inquire as to whether the Y248 NMR shift data can provide a simple measure of the pseudogap energy, as they did for YBCO6.63 (see the inset to Fig. 4.4). Accordingly, several NMR shift data sets are plotted as  $\ln(K(T))$  vs.  $1000/T$  in Fig. 4.16 for temperatures down to  $T_c$ . The linear slope of such a plot gives one measure of the pseudogap energy. The data shown here have been scaled up and down for display purposes. At the top we see data set (i),  $^{17}K_{c,ab}(T)$  and  $^{65}K_{ab}(T)$  (triangles, diamonds and circles) from Bankay et al. [41]. The straight line drawn through these points defines a gap energy  $T_G \simeq 84 \text{ K}$ , which is  $\sim 20\%$  smaller than that of YBCO6.63. The open and filled squares are both plots of the data for  $^{17}\text{O}(3)$  from Fig. 4.15, with two different assumptions regarding  $^{17}K_{3,c}(0)$ . In (ii)  $^{17}K_{3,c}(0)$  is assumed to be  $-0.04\%$ , with a diamagnetic correction of  $-0.005\%$ , while in (iii) it is assumed to be  $-0.02\%$  with a diamagnetic correction of  $-0.025\%$ . Both assumptions

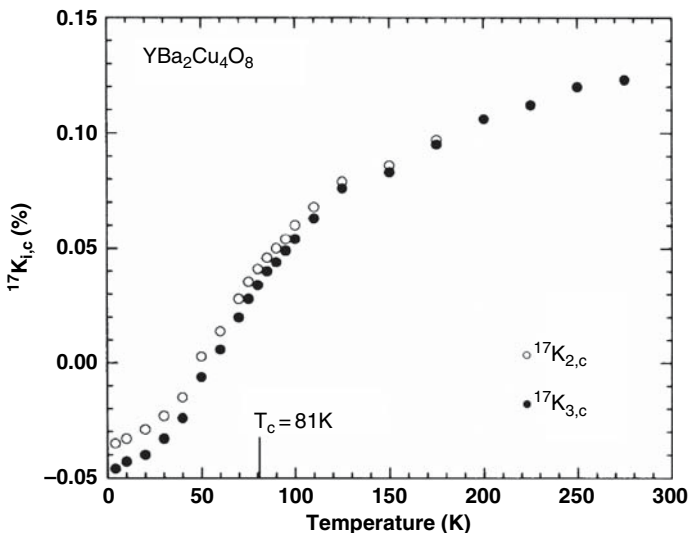


**Fig. 4.15.**  $^{17}\text{O}(2,3)$  NMR shift data for Y248 are plotted vs.  $T$  for temperatures up to 300 K [37]. Note that the O(2) and O(3) NMR lines are resolved below  $T \sim 150$  K, but merge above that point. See text for discussion and possible interpretation. Figure reprinted from T. Machi, I. Tomeno, et al, *Physica C* **173**, 32 (1991). Copyright 1991 Physica C

lead to a reasonable straight line, with  $T_G \simeq 96$  K and 106 K for (ii) and (iii), respectively. Option (ii) probably makes better physical sense and gives a gap energy closer to that of data set (i). Our main conclusion from plots (i)-(iii) is that Y248 NMR shifts show Arrhenius-type behavior with pseudogap energies 10-20% smaller than YBCO6.63.

Data plot (iv) in Fig. 4.16 shows the  $^{89}\text{Y}$  NMR shift data by Williams et al. [42], which the authors presented in a proposed test of the pseudogap isotope effect. The undifferentiated data points shown are for both  $^{16}\text{O}$  and  $^{18}\text{O}$ -doped samples, which gave indistinguishable behavior over the range of temperatures (131 K - 370 K) shown. The data are very precisely measured as one can see from the small scatter of the points, but the most striking thing is, first, how differently these  $^{89}\text{Y}$  data points behave compared with the other two data sets, and secondly, that they do not appear to correspond to a well-defined gap energy in this kind of plot. Noting that in a stoichiometric sample of Y248 with low disorder one would expect NMR shifts of the  $^{89}\text{Y}$ ,  $^{17}\text{O}(2,3)$ , and  $^{63,65}\text{Cu}(2)$  to follow a common temperature dependence as they did in YBCO6.63 (Fig. 4.4), the results shown suggest that the sample material used for data set (iv) is somewhat different from that used for data sets (i)-(iii).

In the following subsection we review efforts which have been reported to measure the pseudogap isotope effect in Y248.

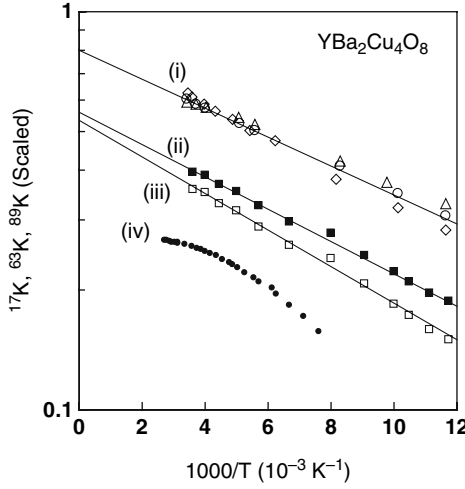


**Fig. 4.16.** An Arrhenius plot of several sets of NMR shift data for Y248 is presented to make estimates of the pseudogap energy for the density of states. The data are scaled to arbitrary positions along the vertical axis for display purposes. The data shown are, set (i):  $^{17}\text{K}_{ab}(T)$  (triangles),  $^{17}\text{K}_c(T)$  (diamonds),  $^{65}\text{K}_{ab}(T)$  (circles) from [41]; set (ii) and (iii) (same data, see text)  $^{17}\text{K}_c(T)$  (open and closed squares) from [40]; and set (iv)  $^{89}\text{K}_c(T)$  (dots) from [42]. The lines drawn are approximate fits to the data for the purpose of extracting pseudogap energies from the slopes

#### 4.3.2 Measuring the Pseudogap Isotope Effect in Y248 with NMR

The  $^{89}\text{Y}$  data set (iv) in Fig. 4.16 were reported as part of an effort to evaluate the isotope effect, if any, on the pseudogap and on  $T_c$  in Y248 [42]. The samples employed for that purpose were annealed with  $^{16}\text{O}$  and with  $^{18}\text{O}$ , respectively, and were found to have  $T_c(^{16}\text{O}) - T_c(^{18}\text{O}) \simeq 0.65\text{ K}$ , in reasonable agreement with previous work [43]. The shift data, as noted in the previous subsection, show no isotope effect to the unaided eye for  $T > 130\text{ K}$ , while undergoing a pseudogap-related decrease of  $\sim 40\%$  from their peak values at  $370\text{ K}$ . It is interesting at this point to inquire as to how large a change in the NMR shift curve is expected if the isotope effect on the pseudogap temperature  $T_g$  is the same as that on  $T_c$ .

First, let us define  $\alpha_{g,c} = d\ln(T_{g,c})/d\ln(M)$ , where  $M$  is the oxygen atomic weight. Note that if  $\alpha_c = \alpha_g$ , then  $\Delta T_g/T_g = \Delta T_c/T_c$ . We shall now use this in a very simple way to estimate the change which might be expected in the  $^{89}\text{Y}$  NMR shift curve. If we consider the gap function  $K(T) = K_0 \exp(-T_g/T)$  (or any function purely of  $T_g/T$ ), then the temperature interval  $\Delta T$  between equal values of shift for the two curves is  $|\Delta T/T| = |\Delta T_g/T_g|$ . The fits to shift data in Fig. 4.16 gave  $T_g \sim 90\text{ K}$ ; at  $T = 130\text{ K}$ , then, we expect curves

shifted by  $\Delta T \sim 1.1 \text{ K}$ .<sup>6</sup> At the lower end of the data curve the slope is  $\sim 1 \text{ ppm}/K$ , leading one to expect deviations with the foregoing temperature shift of  $\sim 1 \text{ ppm}$ . As the inset shows, there are deviations of that order, but the fluctuations are large. To resolve such an effect would require a very precise fitting curve and a large number of data points. In the light of the analysis given below for a different experimental effort to achieve the same end, we suggest that the  $^{89}\text{Y}$  NMR shift data given were excellent, but the foregoing analysis in the present case does not quite rule out the possibility of a pseudogap isotope effect.

A second effort to measure the pseudogap isotope effect was made via NQR studies of the  $^{63}\text{Cu}(2)$  relaxation curve for Y124, with the basic data plot of  $1/T_1T$  vs.  $T$  shown in Fig. 4.18(b) [44]. The data shown are for two samples, one with  $^{16}\text{O}$  and one with  $\sim 90\%^{18}\text{O}$ , as in the previous case. The peaks in the two curves are seen to occur at  $T \sim 150 \text{ K}$ , where there is a razor-thin margin between the curves fitted to the two sets of data. The measured difference in  $T_c$  values  $\sim 0.47 \text{ K}$  for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples is slightly smaller than in the previous case. The key to analyzing the isotope effect here is to find a precise functional fit to the data curves. For this purpose the authors have used

$$\frac{1}{^{63}T_1T} = \frac{C}{T^a} \left[ 1 - \tanh^2 \left[ \frac{\Delta}{2k_B T} \right] \right], \quad (4.3.2)$$

where the factor  $T^{-a}$ ,  $a \sim 1$ , fits the Curie-like decline of  $1/T_1T$  at high temperatures, and  $\Delta = k_B T^*$  acts as the spin pseudogap energy - see discussion below. The data are a good fit to (4.3.2), but the deviations were not quite random. The authors have therefore tinkered with the temperature scale a bit [44] and thus achieved the high-quality fit to the data shown in Fig. 4.18. This fit gives a shift in  $T^*$  for the two samples tested of  $0.96 \text{ K}$ . It is interesting that this temperature shift is less than was predicted for the  $^{89}\text{Y}$  NMR shift curves in Fig. 4.17, but was resolved using a precisely fitting function and a large number of data points.

The pseudogap energy value turned out to be  $T^* = 246.9 \text{ K}$  for the  $1/T_1T$  curves [44]. This is more than twice the values found with the Arrhenius plots in Fig. 4.16. Further, although (4.3.2) is just a fitting function,  $T^*$  really serves as an energy gap, since the asymptotic form of (4.3.2) is  $1/T_1T \propto T^{-a} \exp(-T^*/T)$  for  $T^*/T \gg 1$ . Note, however, that the NMR shifts represent the residual density of states, whereas  $T^*$  may represent the DOS squared. The appropriate comparison would then be between  $T^*/2$  and  $T_g \sim 90 \text{ K}$  from the NMR shift results. This point of view does not appear, however, to be supported by pseudogap theory [45] (see the following subsection).

It seems, then, at least for the dynamics that there is a pseudogap isotope effect which is similar to that of  $T_c$ . As far as we are aware, there is no

---

<sup>6</sup> This estimate is somewhat smaller than that of the authors [42], which is not stated explicitly.

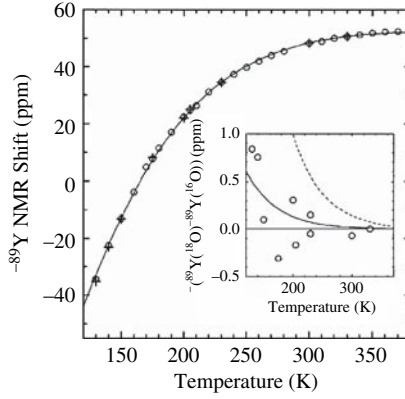


**Fig. 4.17.**  $^{89}\text{Y}$  NMR shift data measured on two samples of Y124, one with nearly 100%  $^{16}\text{O}$  (+ symbols) and the other with  $\simeq 94\%$   $^{18}\text{O}$  (circles) [42]. The difference between these data plots is clearly smaller than the plotting symbols. Inset: Plot of the differences along with calculated difference curves. See text for discussion. Figure reprinted from G.V.M. Williams, et al., Phys. Rev. Lett. **80**, 377 (1998). Copyright 1998 American Physical Society

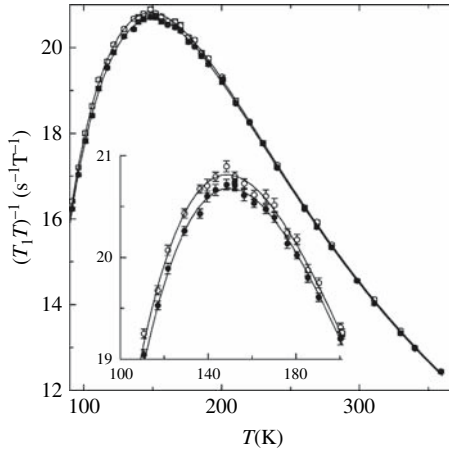


**Fig. 4.18.**  $T_1$  data are plotted as  $1/T_1T$  vs.  $T$  for two samples of Y124, one with  $^{16}\text{O}$  and the other with  $\sim 88\%$   $^{18}\text{O}$  [44]. Using the functional fit shown (see text) the difference in these two relaxation curves near their peak at  $T \sim 150\text{ K}$  is analyzed to find a difference in the pseudogaps roughly equal to that found for  $T_c$ . See text for detailed discussion. Inset: Detailed view of the peak vicinity. Figure reprinted from F. Raffa, T. Ohno, et al., Phys. Rev. Lett. **81**, 5192 (1998). Copyright 1998 American Physical Society

theoretical prediction available for the variation of the pseudogap with the atomic weight of the oxygen.

#### 4.3.3 Theory of the Pseudogap by Varma.

The only successful theory of the pseudogap which we are aware of is that by Varma [45]. Varma has constructed a theory of cuprate superconductivity and ancillary properties, based on the existence of a *quantum critical point* (QCP) at the center of the *superconducting dome* of the phase diagram shown in Fig. 4.19, where the abscissa is the doping level or carrier concentration in the  $\text{CuO}_2$  planes. Region I is the marginal Fermi liquid regime proposed and expounded in [46]. The pseudogap effects occur in Region II below the line  $T_p(x)$  [45]. In Region II there is a broken symmetry based on time-reversal violating (TRV) states in which fluctuating currents flow in the  $\text{CuO}_2$  plane. The existence of such currents has been verified experimentally via neutron-scattering experiments [47].

The aforesaid theory also predicts anisotropic gapping in  $\mathbf{k}$ -space near the chemical potential in Region II of the phase diagram, as was depicted by the gapping curves in Sect. 4.2.2. Corresponding calculations of the density of states in the pseudogap regime have been presented for comparison with experimental data on Y248. In Fig. 4.20 the  $^{89}\text{Y}$  NMR shift data from [42] (see

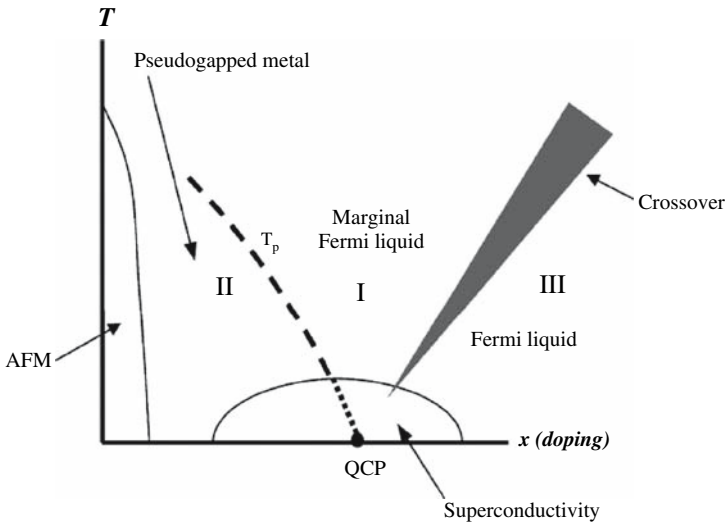


**Fig. 4.19.** Phase diagram of doped cuprates showing the putative quantum critical point at the center of the superconducting dome [45]. From normal metal behavior at high doping levels (III), there is a crossover to the marginal Fermi liquid behavior in (I) followed by pseudogap behavior below the line  $T_p(x)$  emanating from the QCP. The calculations presented in [45] are for Region II. Figure reprinted from C.M. Varma, Phys. Rev. B **73**, 155113 (2006). Copyright 2006 American Physical Society

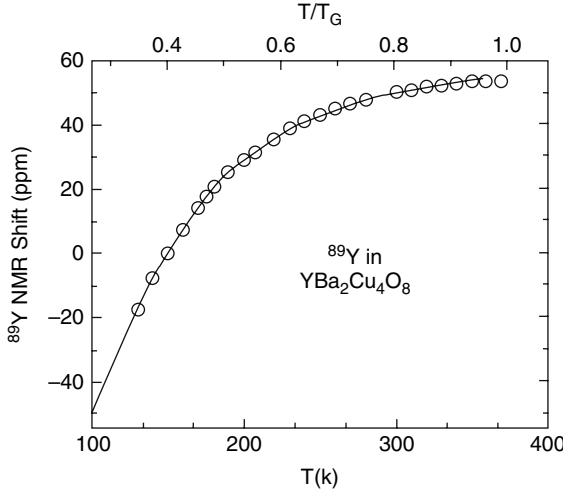


**Fig. 4.20.** The  $^{89}\text{Y}$  NMR shift data from Y248 (see Fig. 4.17) is shown here fitted by the pseudogap theory given by Varma [45] (solid line), yielding an excellent fit

Fig. 4.17) are compared with a calculated pseudogapped density of states from [45], where an excellent correspondence is seen to occur. It would, of course, be most interesting if more detailed calculations of, e.g.  $\chi''(\mathbf{q}, \omega)$  would be forthcoming, for comparison with the  $\mathbf{q}$ -dependent relaxation effects in these systems.

#### 4.3.4 Effect of Zn impurities on the Pseudogap in Y248

From early on it has been known that Zn impurities – thought to substitute for the  $\text{Cu}(2)$  – cause a dramatic reduction of  $T_c$  in high- $T_c$  cuprates [48]. Even though  $\text{Zn}^{2+}$  is a nonmagnetic ion core, its presence in the  $\text{CuO}_2$  plane (as well as  $\text{Li}^+$ ) is thought to cause potential scattering which destroys d-wave pairs, and it also causes the occurrence of a small localized magnetic moment in the same vicinity [49]. The latter is a very interesting effect in its own right, even exhibiting a Kondo effect [50, 51].

The strategy of Zn-doping to eliminate the effect of the SC transition on the pseudogap was adopted by Zheng et al. [52]. However, instead of the collapse of AFM spin fluctuations as found with YBCO7-x, the Zn-doped Y248 undergoes an enhancement of  $1/T_1$  for  $^{63,65}\text{Cu}$  similar to the "Curie-Weiss" behavior of  $T_1T$  in LSCO:x [53], as shown in Fig. 4.21. With 2% Zn substitution, the peak value of  $1/T_1T$  is almost three times the peak value of that quantity in the undoped case. Meanwhile, the NMR shift profile remains spin-gapped with effectively no change [52], in spite of a reduction of  $T_c$  by a factor  $\sim 3$ . The latter result suggests that the SC transition was already having very little effect on the shift profile in the undoped case.

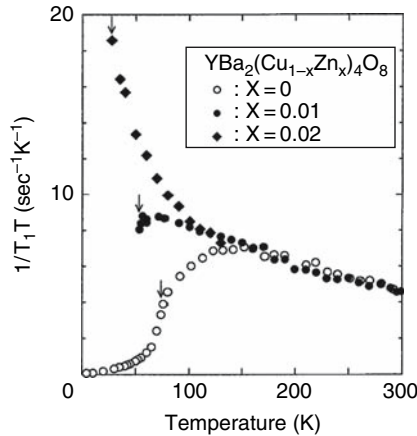


**Fig. 4.21.** A plot of data for  $1/T_1T$  for  $^{63}\text{Cu}(2)$  in Y248 made with samples which are undoped (*open circles*) and doped with 1% Zn (*closed circles*) and 2% Zn (*closed diamonds*), showing suppression of  $T_c$  from 74 K to 53 K and  $\sim 27$  K, respectively, combined with large progressive increases in the value of  $1/T_1T$  at  $T = T_c$  [52]. The corresponding change in the NMR shift curve is slight and barely resolvable. Figure reprinted from G.-Q. Zheng, T. Odaguchi, T. Mito, Y. Kitaoka et al: J. Phys. Soc. Japan **62**, 2591 (1993). Copyright 1993 Physical Society of Japan

The Zn impurities, while suppressing  $T_c$ , have the very specific effect of un-gapping the Fermi surface regions which contribute to  $\chi''(\mathbf{q}, \omega)$  near  $\mathbf{q} = (\pi, \pi)$ , or so it would appear. In connection with these remarkable data, the results of two additional relaxation measurements would be of great interest. First, a comparative plot of  $T_{2g}$  for the  $^{63}\text{Cu}(2)$  over the same temperature range would give a direct measure of the doping effect on  $\chi'(\mathbf{Q})$  (see Sect. 6.1). Second, the  $T_1$  behavior of either  $^{89}\text{Y}$  or of  $^{17}\text{O}(2,3)$  would test the effect of Zn doping on low-frequency fluctuations away from  $\mathbf{Q}$  as a corroboration of the unchanged NMR shift results. In other words, these measurements would further test the scenario where the Zn doping effect appears to be confined to the region of the AFM peak.

#### 4.4 “Pseudogap-like” Effects in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO:x)

Apart from introducing the LSCO structure in Sect. 3.1, there has been up to this point no discussion of LSCO. In spite of its rather low  $T_c$  relative to other cuprates, LSCO played a major role in high- $T_c$  physics research. This was because, (i) it was one of the first cuprate structures identified [54], (ii) it has a very interesting and accessible phase diagram similar to Fig. 1.1, and (iii) it is relatively easy to make large, homogeneous single crystals of LSCO:x. For the latter reason a great many neutron scattering measurements have been conducted on this system, making its dynamic susceptibility perhaps the best

characterized of all of the cuprates. This will be discussed extensively, along with NMR measurements, in Chap. 6.

From the standpoint of NMR technique, LSCO is a far simpler system to work with than YBCO. First, there are only one  $\text{Cu}^{2+}$  site and two  $\text{O}^{2-}$  sites, making spectra and relaxation studies generally easier to interpret. For the purposes of conducting  $^{17}\text{O}$  NMR studies in crystals, LSCO is also a favorable case, because it has very high oxygen mobility at relatively modest temperatures. Thus, it is easy to exchange  $^{17}\text{O}$  into a crystal and homogenize it with simple annealing procedures.

The foregoing circumstances notwithstanding, we shall see that the pseudogap effect in LSCO is not quite the same as in the other cuprates. One rarely even finds the word pseudogap applied to LSCO, so we refer here instead to “pseudogap-like” effects. While the NMR shift and susceptibility behavior is pseudogap-like (with important differences), the relaxation behavior of the  $^{63}\text{Cu}$  is quite different from that of YBCO6.63. On the other hand, the planar  $^{17}\text{O}$  shift and relaxation appear to follow the spin susceptibility rather like the  $^{17}\text{O}(2,3)$  data for YBCO6.63 in Fig. 4.9(a), making the overall picture pseudogap-like except for the  $^{63}\text{Cu}$   $T_1$  results. We now present a detailed account of these points.

#### 4.4.1 Spin Susceptibility Scaling for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ .

Around the time that the first studies of underdoped YBCO7-x appeared, it was revealed by D.C. Johnston that the susceptibility of LSCO:x obeys a simple scaling law over essentially the entire range of superconducting compositions [7],

$$\chi(x, T) = \chi_0(x) + \chi_{s, \max}(x) F_s(T/T_{\max}(x)) + C(x)/T, \quad (4.4.1)$$

where  $\chi_0(x)$  is a temperature-independent background susceptibility,  $\chi_{s, \max}$  is the maximum spin susceptibility for composition  $x$ , which occurs at  $T_{\max}(x)$ , and  $F_s(T/T_{\max}(x))$  is a scaling function valid for  $0.05 \leq x \leq 0.30$  [7].  $C(x)$  is a spurious Curie term which occurs at higher doping levels [55]. By definition,  $F_s(1) = 1$ . The term  $\chi_0(x)$  represents Van Vleck orbital and diamagnetic contributions (see Sect. 2.3.2). The function  $F_s(T/T_{\max}(x))$  is such that  $\chi(x, T)$  is qualitatively similar to the YBCO6.63 result in Fig. 4.4.

To illustrate the behavior of  $\chi(x, T)$  for LSCO:x we display the somewhat more complete data set reported later by Nakano et al. [55] in Fig. 4.22 for  $0.08 \leq x \leq 0.26$ , all superconducting samples. While the latter data extend up to  $\sim 550\text{ K}$ , data from another study extending up to  $\sim 1000\text{ K}$  show that  $\chi(x, T)$  for  $x \leq 0.09$  had no (accessible) maximum value, but all data plots for  $x > 0.09$  exhibited a maximum at some temperature [56]. *This Curie-Weiss-like rise in susceptibilities at low temperatures for the higher doping levels is one factor which sets LSCO:x apart from the pseudogap behavior of other cuprates.*

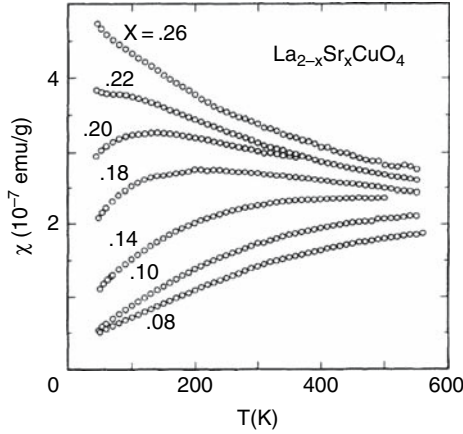


**Fig. 4.22.** Susceptibility data for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  are plotted as a function of temperature for a series of random powder samples with  $0.08 \leq x \leq 0.26$  [55]. These data are found to scale as described in the text and in Fig. 4.23. Figure reprinted from T. Nakano et al., Phys. Rev. B **49**, 16000 (1994). Copyright 1994 American Physical Society

Nonetheless, there is a clear gap feature in  $\chi(x, T)$ , which may be seen in Fig. 4.23, where  $\chi_s(T)/\chi_{s,max} = (\chi(x, T) - \chi_0)/\chi_{s,max}$  vs.  $T/T_{max}$  is plotted [55]. The data for the eleven compounds shown follow this scaling curve to a remarkable degree. It seems highly plausible that this behavior is related to the pseudogap effect identified in both YBCO6.63 and Y1248. This scaling of data may not reflect a simple energy gap parameter as in Fig. 4.4. The limiting, low- $T$  behavior  $\chi_s(T) \propto T^\beta$ ,  $\beta \sim 0.5$ , is actually one of the predictions of Varma's theory of the pseudogap [45], which was fitted to the data in Fig. 4.20.

It is interesting to examine the behavior of the other parameters in the fit to (4.4.1). The values obtained for  $T_{max}(x)$ ,  $\chi_0(x)$ , and  $C(x)$  are displayed as a function of  $x$  in Fig. 4.24(a). It is seen that there is a peculiar sort of transition point between data fits for  $0.10 \leq x < 0.20$  (Region I) and  $0.20 \leq x \leq 0.28$  (Region II). In Region I,  $T_{max}$  declines in a roughly linear fashion<sup>7</sup> from  $T_{max} \sim 700$  K for  $x = 0.10$  down to  $T_{max} \sim 100$  K at  $x = 0.20$ . In region II,  $T_{max} \sim 100$  K. In Region I,  $\chi_0$  rises from a slightly negative value at  $x = 0.10$  to  $\chi_0 \sim 1.8 \times 10^{-7}$  emu/g at  $x = 0.20$  and remains constant above that point. Finally,  $C(x) = 0$  in Region I, rising rapidly in Region II to where it becomes a major feature of the susceptibility data. Although there is no result given which identifies  $\chi_0(x)$  as the residual susceptibility at  $T \ll T_c$ , we regard  $\chi_s(T)$  as the spin susceptibility. The magnetic behavior then distinguishes Regions I and II very clearly as “underdoped” and “overdoped”, respectively. In a more speculative vein, one could term these *subcritical* and *supercritical* relative to a putative quantum critical point at  $x \simeq 0.20$ .

<sup>7</sup> There were no fits to data below  $x = 0.10$ .

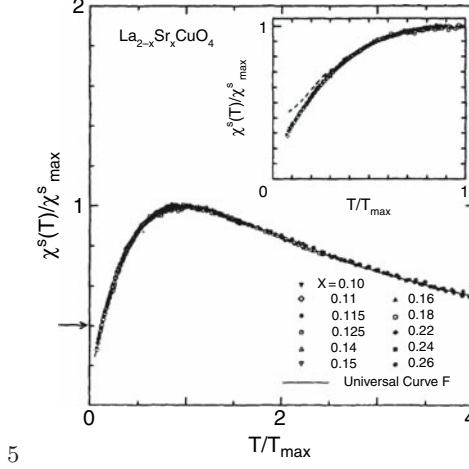


**Fig. 4.23.** The data from Fig. 4.22 are plotted as  $\chi_s(T)/\chi_{s,\max}$  vs.  $T/T_{\max}$  as defined in (4.4.1). The resulting scaling curve defines the function  $F_s(T/T_{\max}(x))$  from the latter equation as well, identified as “Universal Curve F” [55]. The inset shows that compared with previous scaling curves (e.g. [7]) represented by the dashed line, the present data decline more sharply as  $T \rightarrow 0$ . As noted in the text, the theory by Varma [45] predicts  $\chi_s(T) \propto T^{1/2}$  near  $T = 0$ , very near to what is observed

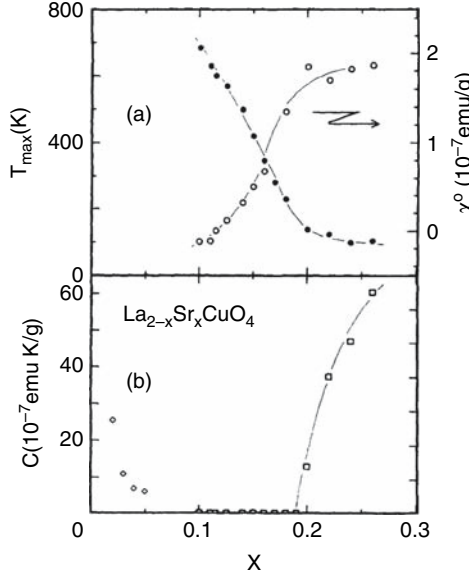


**Fig. 4.24.** (a) The fitting parameters  $T_{\max}(x)$  and  $\chi_0(x)$ , and (b)  $C(x)$  from (4.4.1) are plotted as a function of  $x$  for the series of fits shown in Fig. 4.23 [55]. The behavior of these parameters clearly divides this doping range into regions I and II, where  $x \simeq 0.20$  is the boundary line. See text for more discussion

#### 4.4.2 Behavior of the $^{17}\text{O}$ and $^{63}\text{Cu}$ NMR Shifts in $\text{LSCO:x}$ .

Scaled  $^{17}\text{O}$  NMR shift values are plotted as a function of temperature in Fig. 4.25 for  $x = 0.15$  and  $0.24$  [55]. The shift data used for these plots are from Ishida et al. for  $x = 0.15$  [57] and from Zheng et al. for  $x = 0.24$  [58]. The lines drawn represent susceptibility data from [55], but the shift scales have been omitted from the figure. We note that the original data reflects  $c$ -axis shift coefficients  $50 - 60 \text{ kOe}/\mu_B$ , which is somewhat larger than the values of  $C'_\alpha$  for YBCO6.63 in Table 4.1. In both cases, the scaled  $^{17}\text{O}$  shift values are a good quantitative match to the susceptibility data.

Data for the  $^{63}\text{Cu}$   $c$ -axis NMR shifts in  $\text{LSCO:x}$  (not shown) have been found to have the following features [59]. With field along the  $c$  axis, compositions in the superconducting range show a very nearly constant shift  $K_c \simeq 1.22\%$  independent of temperature. For fields in the  $ab$  plane, shift data appear to follow the same trends as the susceptibility data in Fig. 4.22. Although to our knowledge they have not been scaled with susceptibility data as in Fig. 4.25, a simple estimate of  $\Delta K_{ab}/\Delta\chi$  gives a value  $A_{ab} \simeq 149 \text{ kOe}/\mu_B$ , within 2-3% or so of the values given (Table 4.1) for the composite  $^{63}\text{Cu}(2)$  shift coefficients in YBCO. For the  $\text{Cu}^{2+}$  at least, the Mila-Rice HF Hamiltonian from Sect. 3.3.3 appears to have near universal validity in the cuprates.

The static spin-paramagnetic effects for  $\text{LSCO:x}$  therefore behave in an internally consistent fashion, exhibiting a gap-like decline at low temperatures which becomes more pronounced at lower doping levels. The gapping feature is, however, superimposed on a Curie-Weiss-like increase at low temperatures which is often found in itinerant antiferromagnets. There is also a weak maximum in the susceptibility of the  $\text{Cu}(2)$  sites in YBCO7. Since the overdoped region is inaccessible for YBCO, one cannot say whether or not Curie-Weiss

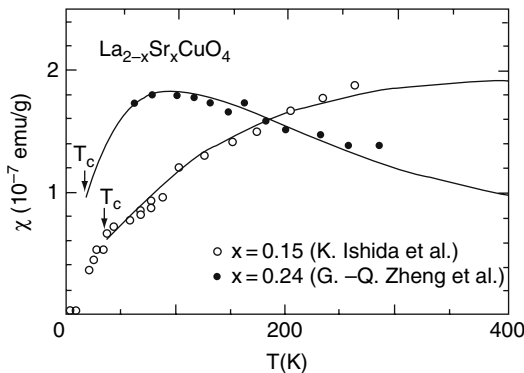


**Fig. 4.25.** The  $^{17}\text{O}$  NMR shifts measured for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  with  $x = 0.15$  [57] and  $0.24$  [58] are fitted to susceptibility curves such as those shown in Fig. 4.22 and plotted vs. temperature [55]. The scale of shift values is such that  $C'_c = 50\text{-}60 \text{ kOe}/\mu_B$

behavior is found there. Be that as it may, we shall now see that the Cu-site  $T_1$  behavior is distinctly different for these two systems.

#### 4.4.3 $^{63}\text{Cu}$ NQR spectra and Contrasting $T_1$ Behaviors in LSCO:x.

Whereas oxygen-deficient YBCO7-x shows line-broadening caused by crystalline disorder, LSCO:x has nearly resolved  $^{63}\text{Cu}$  NQR and NMR “impurity” lines attributable to sites neighboring the  $\text{Sr}^{2+}$  dopant ions. NQR spectra are shown in Fig. 4.26 for three  $\text{Sr}^{2+}$  doping levels [60]. The spectra have been analyzed into pairs of  $^{63,65}\text{Cu}$  NQR lines representing sites neighboring the impurities and “bulk”  $\text{Cu}^{2+}$  sites away from the  $\text{Sr}^{2+}$  sites. Since the charge environment near a dopant site is quite different from that of a bulk site, it is not surprising to find a different EFG at such sites. For a sample with  $x = 0.30$  there is a very high probability that a  $\text{Cu}^{2+}$  site will have a  $\text{Sr}^{2+}$  neighbor, and the corresponding impurity line is now larger than the bulk line (see Fig. 4.26). Perhaps it is because of this high level of impurity-induced disorder in LSCO:x that  $T_c$  peaks at  $\sim 1/2$  the peak value for YBCO7-x.

##### $T_1$ Results for $^{63}\text{Cu}$ .

As noted earlier, the peak  $T_c$  value in LSCO:x also occurs in samples ( $x \simeq 0.15$ ) with quite a pronounced pseudogap feature in the susceptibility. However, the  $T_1$  curve for  $^{63}\text{Cu}$  in such a sample is shown in Fig. 4.27 is not unlike what is found for YBCO7, although the relaxation rate is nearly three times as great. There is a flatter-than-linear characteristic in the normal state and a pronounced  $T^3$  region in the superconducting state just below a region which is somewhat steeper than that. These measurements have been taken both on the bulk and impurity-neighbor NQR lines, with very similar results for both sites [60]. There is little indication of the spin-gapped nature of the susceptibility data in the behavior of  $T_1$  for this composition. Apart from the fact that the LSCO relaxation is  $\sim 3$  times faster, the results in Fig. 4.27 bear a strong resemblance to the YBCO7 results in Fig. 3.11.

##### $T_1$ and NMR Shift Results for $^{17}\text{O}$ .

The dynamic susceptibility  $\chi''(\mathbf{q}, \omega)$  for underdoped LSCO:x near  $\mathbf{q} \sim \mathbf{Q}_{AF} = (\pi/a, \pi/a)$  is therefore not affected by the static, uniform pseudogap effect noted earlier. For the behavior of low-frequency excitations over the rest of the zone we look at  $T_1$  behavior of the planar  $^{17}\text{O}$  nuclear spins. A plot of  $1/T_1T$  for the planar  $^{17}\text{O}$  in LSCO:0.15 is shown in Fig. 4.28, along with NMR shift data on the same system [61]. The  $^{17}\text{O}$  data stand in sharp contrast with the  $^{63}\text{Cu}$  results, where they are seen to follow the shift data,  $1/T_1T \propto K_s(T)$ . This is similar behavior to the  $^{17}\text{O}(2,3)$  data for YBCO6.63 in Fig. 4.9(a), and therefore a “classic” pseudogap result. The  $^{17}\text{O}$  data suggest that gapped excitations similar to those at  $\mathbf{q} \sim 0$  occupy the bulk of the Brillouin zone, and only those near  $\mathbf{Q}_{AF}$  are immune to the gapping effect. The latter excitations

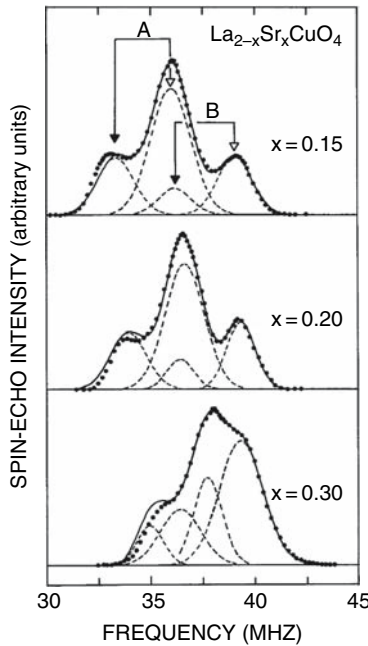


**Fig. 4.26.** NQR spectra for  $^{63,65}\text{Cu}$  in  $\text{LSCO}:x$  are shown for three typical values of  $x$ . the spectra have been analyzed into a pair of “A” lines, which represent bulk material away from the doping centers, and a pair of “B” lines representing sites which have at least one  $\text{Sr}^{2+}$  neighbor. For each case there are two lines representing the two isotopes with their roughly 7:3 ( $^{63}:\text{Cu}$ ) abundance ratio. For  $x = 0.30$  the B lines have well over half of the intensity. The dashed lines shown are Gaussian components in the spectrum which sum up to the solid lines drawn, giving a reasonable facsimile of the experimental spectra. Figure reprinted from K. Yoshimura, T. Imai, et al., J. Phys. Soc. Japan **58**, 3057 (1989). Copyright 1989 Physical Society of Japan

must be very strong, however, as they dominate the ultra-fast relaxation of the  $^{63}\text{Cu}$ .

The  $\text{LSCO}:x$  system therefore exhibits a mixture of pseudogap and non-pseudogap-like features. However, it seems quite clear that the pseudogap effect is present and well-defined for  $\text{LSCO}:x$ , for both static,  $\mathbf{q} = 0$  behavior, as well as for low-frequency quasiparticle excitations over the bulk of the Brillouin zone. However, the Fermi surface, which is known to be different from that of  $\text{YBCO7}$ , could very well be situated so that the dynamic susceptibility near  $(\pi, \pi)$  samples only the non-gapped regions (see discussion of this point in Sect. 4.2). Moreover, the AFM peak for  $\text{LSCO}:x=0.15$  must be so large that it completely dominates the  $^{63,65}\text{Cu}$  relaxation rate. The planar oxygen then evidently have a dramatically different relaxation character.

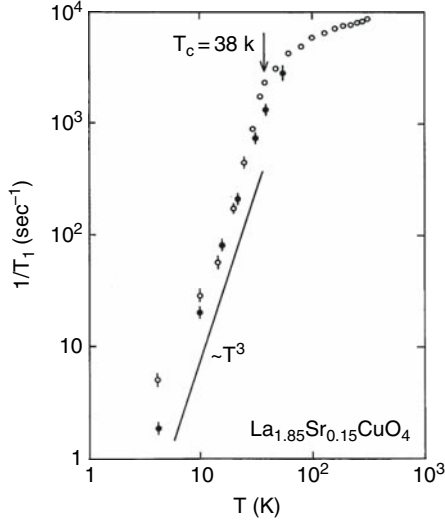


**Fig. 4.27.** Data are plotted for  $1/T_1$  as a function of temperature for both the A (open circles) and B (closed circles) sites identified in Fig. 4.26 in a sample with  $x = 0.15$ . The two data sets, where comparable, are quite similar in character. The A-site measurements show a typical flat region in the normal state, with a steep drop below  $T_c$ , then a  $T^3$  region [60]. Very little evidence is seen of the pseudogap feature found in the susceptibility for this composition

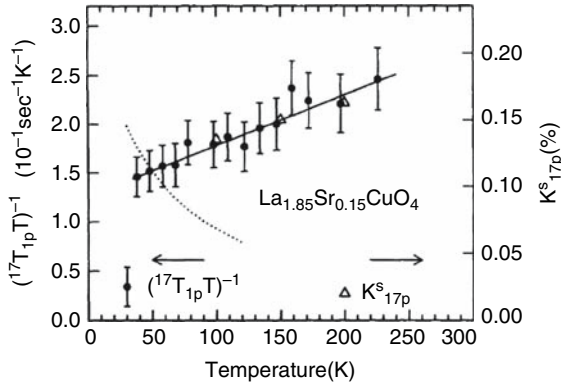


**Fig. 4.28.**  $1/T_1 T$  data for the planar  $^{17}\text{O}$  in the LSCO 0.15 system are plotted (solid circles, left axis) in comparison with scaled data on the same sample for  $K_s(T)$  (open triangles, right axis), showing that these two quantities are proportional over the range  $100 \text{ K} \leq T \leq 200 \text{ K}$  [61]. Note the sharp contrast in behavior between the  $^{63}\text{Cu}$  relaxation, represented by the dotted line, and the planar  $^{17}\text{O}$  in this system. Figure reprinted from R.E. Walstedt, B.S. Shastry, S.-W. Cheong, Phys. Rev. Lett. **72**, 3610 (1994). Copyright 1994 American Physical Society

There will be further discussion of relaxation effects in LSCO: $x$  in Chap. 6, where there is extensive discussion of INS results on this compound as well as of  $T_{2g}$  data in connection with the quantum critical scaling model of Pines and co-workers.

## References

1. W.W. Warren, Jr., R.E. Walstedt et al., Phys. Rev. Lett. **62**, 1193 (1989) 116, 120
2. H. Alloul, T. Ohno, P. Mendels, Phys. Rev. Lett. **63**, 1700 (1989) 116, 117, 118, 128, 132
3. M. Horvatić, P. Ségransan, C. Berthier, Y. Berthier et al., Phys. Rev. B **39**, 7332 (1989) 116
4. H. Yasuoka, T. Imai, T. Shimizu, In *Strong Correlations and Superconductivity*, ed H. Fukuyama, S. Maekawa, A.P. Malozemoff (Springer-Verlag, Berlin, 1989) See also H. Yasuoka, S. Kambe, et al., Physica B **199&200**, 278 (1994) 116
5. H. Alloul, A. Mahajan, H. Casalta, O. Klein, Phys. Rev. Lett. **70**, 1171 (1993) 117, 128, 132
6. J. Friedel, Physica C **153-155**, 1610 (1988) 117
7. D.C. Johnston, Phys. Rev. Lett. **62**, 957 (1989) 117, 149, 151
8. R.E. Walstedt, W.W. Warren, Jr., et al., Phys. Rev. B **41**, 9574 (1990) 118, 120, 127, 128
9. M. Takigawa, A.P. Reyes, P.C. Hammel, Phys. Rev. B **43**, 247 (1991) 118, 120, 121, 122, 124
10. M. Takigawa, W.L. Hults, J.L. Smith, Phys. Rev. Lett. **71**, 2650 (1993) 118, 122, 123, 124,
11. S.E. Barrett, D.J. Durand, et al., Phys. Rev. B **41**, 6283 (1990) 120
12. B.S. Shastry, Phys. Rev. Lett. **63**, 1288 (1989) 120, 126
13. H. Monien, D. Pines, M. Takigawa, Phys. Rev. B **43**, 258 (1991) 122, 124
14. A. Uldry and P.F. Meier, Phys. Rev. B **72**, 094508 (2005) 122
15. T. Auler, M. Horvatic et al., Physica C **313**, 255 (1999) 126, 133
16. F. Mila, T.M. Rice, Physica C **157**, 561 (1989) 126
17. R.E. Walstedt, W.W. Warren, Jr., et al., Phys. Rev. B **40**, 2572 (1989) 126, 128
18. M. Randeria, N. Trivedi, A. Moreo, R.T. Scalettar, Phys. Rev. Lett. **69**, 2001 (1992) 126, 127, 129
19. J.M. Tranquada et al., Phys. Rev. B **46**, 5561 (1992) 126, 128, 129, 130
20. G. Balakrishnan, R. Dupree et al., J. Phys. C: Solid State Phys. **21** L847 (1988) 128
21. M. Takigawa, P.C. Hammel, R.H. Heffner, Z. Fisk, Phys. Rev. B **39**, 7371 (1989) 128
22. A.J. Millis, H. Monien, D. Pines, Phys. Rev. B **42**, 167 (1990) 127
23. A.J. Millis, H. Monien, Phys. Rev. B **45**, 3059 (1992) 127
24. P.M. Gehring, J.M. Tranquada, et al., Phys. Rev. B **44**, 2811 (1991) 128
25. J. Rossat-Mignod, et al., Physica B **169**, 58 (1991) 128
26. L.D. Rotter et al., Phys. Rev. Lett. **67**, 2741 (1991) 134
27. M. Randeria, *Precursor Pairing Correlations and Pseudogaps*, [Varenna Lectures 1997]; cond-mat/9710223 134
28. J.W. Loram et al., Phys. Rev. Lett. **71**, 1740 (1993) 134
29. J.W. Loram et al., Physica C **135-140** 134 (1994) 134
30. W.Y. Liang, J.W. Loram, Physica C **263**, 277 (1996) 134, 135, 136
31. P.W. Anderson, Science **235**, 1196 (1987) 136
32. N. Nagaosa, P.A. Lee, Phys. Rev. B **45**, 966 (1992) 136

33. J.M. Harris, Z.-X. Shen et al., Phys. Rev. B**54**, R15665 (1996) 136
34. A.G. Loeser et al., Science **273**, 325 (1996) 136
35. H. Ding et al., Nature (London) **382**, 51 (1996) 136
36. R.M. Hazen, in *Physical Properties of High Temperature Superconductors*, ed D.M. Ginsburg (World Scientific, Singapore, 1990), Vol. II, p.121 139
37. T. Machi, I. Tomeno, et al., Physica C**173**, 32 (1991) 139, 140, 142
38. H. Zimmerman, et al., Physica C**159**, 681 (1989) 139
39. H. Yasuoka, Hyperf. Int. **105**, 27 (1997) 139
40. I. Tomeno, T. Machi et al., Phys. Rev. B**49**, 15327 (1994) 139, 143
41. M. Bankay, M. Mali, J. Roos, D. Brinkmann, Phys. Rev. B**50**, 6416 (1994) 141, 143
42. G.V. M. Williams et al., Phys. Rev. Lett. **80**, 377 (1998) 142, 143, 144, 145, 146
43. J.P. Franck, in *Physical Properties of High Temperature Superconductors*, ed D.M. Ginsburg (World Scientific, Singapore, 1994), Vol. IV, p.189 143
44. F. Raffa, T. Ohno et al., Phys. Rev. Lett. **81**, 5192 (1998) 144, 145
45. C.M. Varma, Phys. Rev. B**73**, 155113 (2006) 144, 146, 147, 150, 151
46. C.M. Varma, P. Littlewood et al., Phys. Rev. Lett. **63**, 1996 (1989) 146
47. B. Fauqué et al., Phys. Rev. Lett. **97**, 197001 (2006) 146
48. G. Xiao, M.Z. Cieplak et al., J. Phys. Soc. Japan **62**, 2591 (1993) 147
49. A.V. Mahajan, H. Alloul, G. Collin, J.F. Marucco, Phys. Rev. Lett. **72**, 3100 (1994) 147
50. J. Bobroff, W.H. MacFarlane, H. Alloul, P. Mendels et al., Phys. Rev. Lett. **83**, 4381 (1999) 147
51. W.H. MacFarlane, J. Bobroff, H. Alloul, P. Mendels, N. Blanchard, Phys. Rev. Lett. **85**, 1108 (2000) 147
52. G.-Q. Zheng, T. Odaguchi, T. Mito, Y. Kitaoka et al., J. Phys. Soc. Japan **62**, 2591 (1993) 147, 148
53. S. Ohsugi, Y. Kitaoka, K. Ishida, G.-q. Zheng, K. Asayama, J. Phys. Soc. Japan **63**, 700 (1994) 147
54. R.J. Cava, R.B. Van Dover, B. Batlogg, E.A. Rietman, Phys. Rev. Lett. **58**, 408 (1987) 148
55. T. Nakano et al., Phys. Rev. B**49**, 16000 (1994) 149, 150, 151, 152
56. R. Yoshizaki et al., Physica C **166**, 417 (1990) 149
57. K. Ishida et al., J. Phys. Soc. Japan **60**, 3516 (1991) 152
58. G.-q. Zheng, et al., Phys. Rev. Lett. **86**, 4664 (2001) 152
59. S. Ohsugi, Y. Kitaoka, K. Ishida, G.-Q. Zheng, K. Asayama, J. Phys. Soc. Japan **63**, 700 (1994) 152
60. K. Yoshimura, T. Imai et al., J. Phys. Soc. Japan **58**, 3057 (1989) 153, 155
61. R.E. Walstedt, B.S. Shastry, S.-W. Cheong, Phys. Rev. Lett. **72**, 3610 (1994) 153, 155

*This page intentionally blank*

## Relaxation Models for Cuprate NMR

From the very beginning of cuprate NMR studies, it was clear that understanding the relaxation properties for all sites with nuclear spin species would be a major challenge for theorists and experimentalists alike. In Chap. 3 the Mila-Rice-Shastry model [1, 2] was presented, including the quantum-chemical basis for transferred HF couplings and the spin Hamiltonian treatment of local spin and orbital HF effects at the  $\text{Cu}^{2+}$  sites. With the latter formulation a complete characterization of the NMR shift tensors for YBCO7 and YBCO6.63 has been carried out in Chaps. 3 and 4. Then, using general expressions for  $1/T_1$ , Mila and Rice discussed  $T_1$  anisotropy for  $^{63}\text{Cu}(2)$  in YBCO7 (Sect. 3.3.4). A simplified model given in Sect. 4.1.2 offered an interpretation of  $T_1$  anisotropies and spin correlation effects for the  $^{89}\text{Y}$  and  $^{17}\text{O}(2,3)$  sites. These developments set the stage for the most serious challenge, which is the locally-varying, overall temperature dependences of the  $T_1$  processes in these compounds. Such a panorama of complex relaxation behavior had never been encountered before the cuprates were discovered.

A variety of models treating the relaxation processes have been put forward in the literature. Here, we will review the results of several of these models in an effort to gauge the present status of our understanding of these matters. There have been phenomenological models put forward by Monien and Pines [3] and Millis, Monien, and Pines [4, 5], where the AFM fluctuations are taken into account by means of an RPA treatment of the AFM exchange interactions. Moreover, it is assumed and is consistent with experiment that the  $\text{Cu}^{2+}$  spin variables are itinerant and undergo pairing in the superconducting state. Similar modeling along these lines has also been put forward by Horvatić et al. [6].

These models were presented early on and gave a reasonable account of the data which were available at the time. In particular, they met the challenge of explaining the behavior of all measured relaxation processes with a single dynamical variable per Cu site, and did so using only HF couplings generated by the  $\text{Cu}^{2+}$  spin moments, in a picture consistent with the Mila-Rice model [1] of on-site spin-Hamiltonian and transferred HF couplings of the general

form  $\sum_{\alpha} A_{\alpha} S_{\alpha} I_{\alpha}$ . A possible deviation from this form may occur in the case of  $^{89}\text{Y}$  in YBCO compounds, where the transferred coupling is very weak and the dipolar interactions, which do not have the latter form, come into play.

A slightly different approach to modeling the dynamical susceptibility has been pursued by Auler et al., [7], where the basic form of the dynamic susceptibility was taken directly from INS data. This scenario had the unusual feature that the range of spin-spin correlations was fixed, although their strength certainly increased as temperature was lowered. These authors also made the unusual step of using spin-echo decay time ( $T_{2g}$ ) measurements to determine the strength of the AFM susceptibility peak. In reviewing the results of their analysis, we shall find that a satisfactory account of the data can be achieved in this fashion.

Beyond phenomenology, there have also been first-principles model calculations by Bulut and Scalapino [8] and by Si, Levin, and co-workers [9]. The latter are, of course, more difficult to formulate and execute, but these have yielded impressive insights. Finally, there has been a proposal by Varma which departs from the usual spin HF-only picture wherein an intersite orbital matrix element is suggested to make an important contribution to the Cu(2)-site relaxation process [10]. The essence of these various results will be summarized below.

This chapter will begin, however, with a discussion of the characterization of the cuprate relaxation properties developed quite recently by Uldry and Meier [11] (UM). This is a scheme of a fairly general nature for characterizing the spin dynamics and spin-spin correlations which determine the relaxation behavior in the  $\text{CuO}_2$  planes. It serves as a useful framework for evaluating almost any experimental data or theoretical model.

## 5.1 The Uldry-Meier Parameterization Model

The Uldry-Meier (UM) approach to the analysis of cuprate relaxation data relies only on a general formulation of spin-fluctuation  $T_1$  processes, which is characterized by just three elements, (i) the HF constants, (ii) real-space, dynamical spin-spin correlation coefficients, and (iii) an effective correlation time parameter in which the temperature variation of the spin dynamics is also implicit in a very general way. The HF parameters used are those derived from the Mila-Rice-Shastry model (3.3.2) for each site in and near the  $\text{CuO}_2$  planes.<sup>1</sup> The spin-spin correlations and correlation time which characterize the relaxation processes are assumed to apply to all nuclear species considered, e.g. the  $^{63}\text{Cu}(2)$ ,  $^{17}\text{O}(2,3)$ , and the  $^{89}\text{Y}$  in YBCO7 and YBCO6.63, etc. The spin-spin correlations are allowed to be anisotropic, but the correlation time variable is assumed to be isotropic and common to all spin fluctuation processes. After describing the UM analysis, the broader significance of this methodology will be discussed at the end of this section.

---

<sup>1</sup> The Cu(1) sites and environs in YBCO are set aside as a separate problem.

### 5.1.1 Basic Formulation of the UM Analysis

In the first step, UM define single-axis  $T_1$  components

$$\frac{1}{T_{1\alpha}} = U_\beta + U_\gamma, \quad (5.1.1)$$

where the subscripts are a permutation of the axes (a,b,c). Thus,  $U_\alpha$  is an axis-specific fluctuation term given by

$$U_\alpha = \frac{1}{4} \sum_{i,j} [A_{i\alpha} A_{j\alpha} \mathcal{K}_{ij}^\alpha] \tau_{eff}, \quad (5.1.2)$$

where  $A_{i\alpha}$  is the HF coefficient for the  $i_{th}$  neighbor spin  $\mathbf{S}_{i\alpha}$  (see (3.3.2)), and the  $\mathcal{K}_{ij}^\alpha$  are now defined as

$$\mathcal{K}_{ij}^\alpha = 4 \langle S_{i\alpha} S_{j\alpha} \rangle, \quad (5.1.3)$$

where the index  $\alpha$  allows the spin-spin correlations to be anisotropic. The only  $\mathcal{K}_{ij}^\alpha$ 's which will occur in the analysis are  $\mathcal{K}_{ii}^\alpha = 1$  and  $\mathcal{K}_{01}^\alpha$ ,  $\mathcal{K}_{12}^\alpha$ , and  $\mathcal{K}_{13}^\alpha$ , where the subscripts refer to the sites in Fig. 3.6.

These correlation factors, originally introduced by Mila and Rice [1] were defined and discussed in Sect. 3.3 and 3.5. In particular, they are easily expressed in terms of  $\chi''(\mathbf{q}, \omega)$  (see (3.5.17) and (3.5.18)). The parameter  $\tau_{eff}$  plays the role of a correlation time in (5.1.2), but also contains the effects of quasiparticle dynamics in the calculation. At low temperatures, for example,  $\tau_{eff} \propto T$ . In (3.5.17) a similar quantity  $\mathcal{X}_{at}$  was introduced, where we can make the identification  $\tau_{eff} = (k_B T / \hbar) \mathcal{X}_{at}$ . In fitting (5.1.2) to the experimental data, the principal assumption is the form of the HF coupling Hamiltonian (3.3.2), where it should be noted that deviations from this form (e.g. dipolar coupling) are not unusual. In Sect. 3.5 the  $\mathcal{K}_{ij}$ 's were also formulated in terms of  $\chi''(\mathbf{q}, \omega)$ , giving a firm theoretical foundation for (5.1.2) in terms of spin-fluctuation relaxation processes.

The determination of  $T_1$  for any nuclear spin site given  $\chi''(\mathbf{q}, \omega)$  and a set of HF tensors is clear enough in terms of the foregoing definitions. However, the innovative task performed by Uldry and Meier was to devise a scheme to extract the HF constants,  $\tau_{eff}$ , and the  $\mathcal{K}_{ij}$ 's, including temperature dependences, from a comprehensive body of relaxation data for a cuprate compound. We review their method here, using the example of YBCO7.

In order to fully characterize the relaxation process of a given nuclear site, it is necessary to have  $T_1$  data from all three axes, since from (5.1.1) we have  $U_\alpha = \frac{1}{2}[1/T_{1\beta} + 1/T_{1\gamma} - 1/T_{1\alpha}]$ . It simplifies, of course, if there is  $ab$  plane symmetry. Thus, it is necessary to have a full data set for all nuclear sites of interest in order to apply this scheme of analysis to any given cuprate. In Fig. 5.1(a)–(c), a 100 K - 300 K data set is shown for  $^{63}\text{Cu}(2)$  [12, 13],  $^{17}\text{O}(2,3)$  [14], and  $^{89}\text{Y}$ [15] in YBCO7, plotted as  $1/T_1 T$  vs.  $T$ . Using (5.1.1), the corresponding (interpolated) plots for  $^{63}U_\alpha$ ,  $^{17}U_\alpha$ , and  $^{89}U_\alpha$  are shown

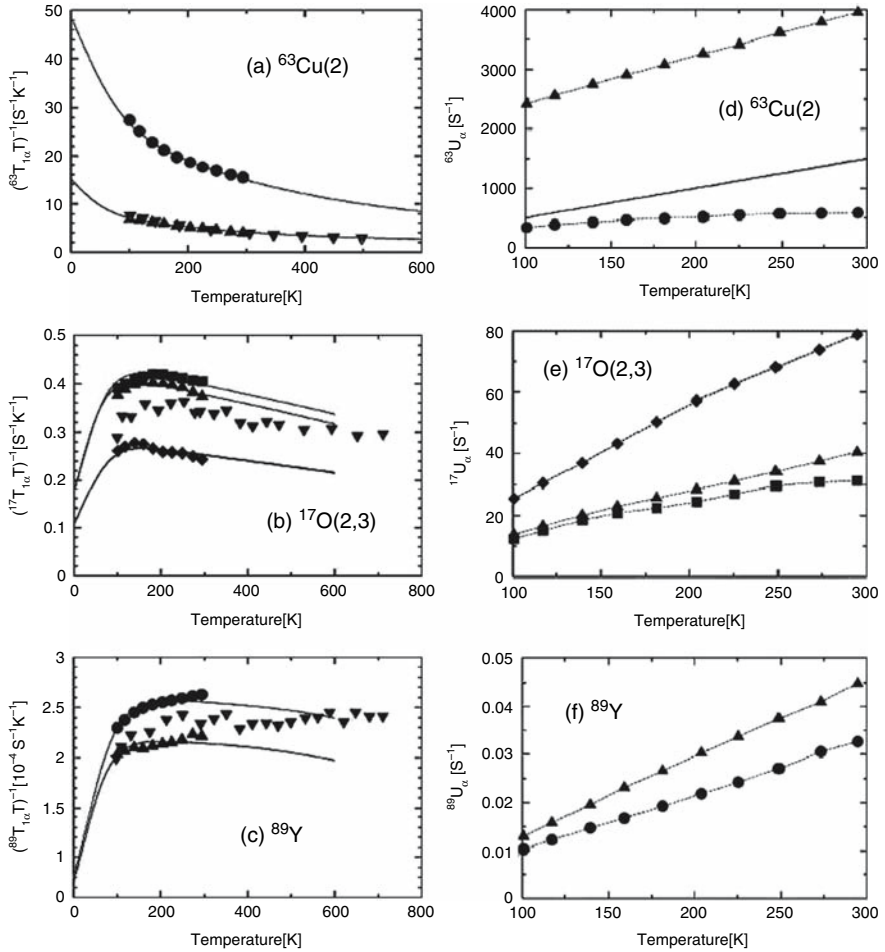


**Fig. 5.1.** (a)–(c) Relaxation data for YBCO7 plotted as circles, upward triangles, and diamonds from [12] ( $^{63}T_{1c}$ ), [13] ( $^{63}T_{1ab}$ ), [14] ( $^{17}T_{1\alpha}$ ), and [15] ( $^{89}T_{1\gamma}$ ) are plotted as  $1/T_1 T$  vs.  $T$ . Solid lines drawn are fitted curves derived from the UM model calculations (see text). The downward triangles are supplemental data included to illustrate high- $T$  behavior for the  $^{17}\text{O}(2,3)$  [16] and the  $^{89}\text{Y}$  [17], as discussed in the text. (d)–(f) Interpolated values of  $^k U_{\alpha}(T)$  derived from the data shown and described in (a)–(c), with which the actual fitting process was conducted. The solid lines drawn are guides for the eye. The straight line drawn in panel (d) shows  $1/^{63}T_1$  vs.  $T$  for Cu metal for comparison. Reprinted figures from A. Uldry and P. F. Meier, Phys. Rev. B **72**, 094508 (2005). Copyright 2005 American Physical Society

in Fig. 5.1(d)–(f). It is remarkable how similar the latter curves look when plotted as  $1/T_1$  rather than as  $1/T_1 T$ .

The next step was to make a simplifying approximation regarding the  $\mathcal{K}_{ij}$ ’s. Since the three described above correspond to spin sites separated by distances  $a/2$ ,  $a/\sqrt{2}$ , and  $a$ , respectively, UM have assumed that  $\mathcal{K}_{12}^\alpha = (\mathcal{K}_{01}^\alpha)^{\sqrt{2}}$ , and  $\mathcal{K}_{13}^\alpha = (\mathcal{K}_{01}^\alpha)^2$ , which is equivalent to the assumption of the form  $\mathcal{K}_{ij}^\alpha = \exp(-2r_{ij}/a\lambda_\alpha)$ . At each temperature, then, the fit procedure only has to determine the two values  $\lambda_{ab,c}$ , rather than six  $\mathcal{K}_{ij}^\alpha$ ’s. If this approach should prove unsatisfactory it could easily be modified.

It is also convenient to define, along with the  ${}^kU_\alpha$ ’s, a parallel set of coefficients  ${}^kV_\alpha$ , given by  ${}^kU_\alpha = {}^kV_\alpha \tau_{eff}$ . Then from (3.5.20), (3.5.21), and (3.5.22) we have

$${}^{63}V_\alpha(T) = \frac{1}{4}[A_\alpha^2 + 4B^2 + 8A_\alpha B \mathcal{K}_{01}^\alpha(T) + 8B^2 \mathcal{K}_{12}^\alpha(T) + 4B^2 \mathcal{K}_{13}^\alpha(T)] \quad (5.1.4a)$$

$${}^{17}V_\alpha(T) = \frac{1}{2}C_\alpha^2[1 + \mathcal{K}_{01}^\alpha(T)] \quad (5.1.4b)$$

$${}^{89}V_\alpha(T) = 2D_\alpha^2[1 + 2\mathcal{K}_{01}^\alpha(T) + \mathcal{K}_{12}^\alpha(T)], \quad (5.1.4c)$$

where superscripts are used to label the isotope concerned. Since the HF coefficients used here relate directly to (3.3.2), their anisotropies as well as those of the  $\lambda_\alpha$ ’s should stem directly from the data in a natural way.

### 5.1.2 The Uldry-Meier Analysis of YBCO7

The following procedure was used to apply the foregoing analytical scheme to the data in Fig. 5.1(d)–(f). Defining the six ratios,

$$r_1 = \frac{{}^{63}U_c}{{}^{17}U_c}; r_2 = \frac{{}^{63}U_{ab}}{{}^{17}U_a}; r_3 = \frac{{}^{63}U_{ab}}{{}^{17}U_b}; r_4 = \frac{{}^{17}U_b}{{}^{17}U_c}; r_5 = \frac{{}^{89}U_c}{{}^{89}U_{ab}}; r_6 = \frac{{}^{17}U_a}{{}^{89}U_c}, \quad (5.1.5)$$

the HF constants in (5.1.4) and the  $\lambda_\alpha$ ’s are then determined by minimizing the quantity

$$\chi^2 = \frac{1}{n_r} \sum_i^{n_r} \sum_j^{n_p} \frac{[r_i^{exp}(T_j) - r_i^{mod}(T_j)]^2}{r_i^{exp}(T_j)^2}, \quad (5.1.6)$$

where  $n_r$  and  $n_p$  are the numbers of ratios ( $= 6$ ) and the numbers of points ( $= 10$ ), respectively, and where the  $r_i^{mod}$  for the “model” are actually calculated from (5.1.4) in terms of the HF constants and the  $\lambda_\alpha$ ’s. Note that the  $r_i$ ’s do not involve the quantity  $\tau_{eff}$ . The HF parameters so obtained are listed in Table 5.1, where for comparison a “standard” set of parameter values from UM are given, as well as the YBCO parameters derived from NMR shift data in Chaps. 3 and 4. We consider these comparisons in detail below.

A plot of  $\tau_{eff}$  vs.  $T$  is then determined for each parameter  $U_\alpha$  via (5.1.2). The  $\lambda_\alpha$ ’s and the results for  $\tau_{eff}$  so determined are displayed in Fig. 5.2(a) and

**Table 5.1.** HF coefficients defined in (3.3.4) and derived from the UM fit procedure with the  $T = 100$  K relaxation data shown in Fig. 5.1, as described in the text, are listed and compared with data presented by Nandor et al., [17] as well as with data derived from NMR shift measurements as described and presented in Tables 3.4 and 3.6. HF coefficient values are given in units of  $10^{-6}eV$ . See text for discussion of these results

| HF Constant | $^{63}A_c$ | $^{63}A_{ab}$ | $B$   | $^{17}C_a$ | $^{17}C_b$ | $^{17}C_c$ | $-^{89}D_{ab}$ | $-^{89}D_c$ |
|-------------|------------|---------------|-------|------------|------------|------------|----------------|-------------|
| UM Fit      | -1.68      | 0.168         | 0.438 | 0.259      | 0.173      | 0.196      | 0.00280        | 0.00349     |
| Nandor      | -1.6       | 0.29          | 0.4   | 0.25       | 0.13       | 0.156      | 0.0048         | 0.0048      |
| Shift Coef. | -1.67      | 0.05          | 0.409 | 0.355      | 0.217      | 0.209      | 0.00286        | 0.00369     |

(b), respectively. The correlation lengths, which are of the order of the lattice constant, are seen to execute a smooth progression toward longer values as  $T$  decreases, a process which accelerates below 150 K. They also find consistent anisotropy of  $\sim 20\%$ , the stronger  $c$ -axis correlations suggesting the possibility of a corresponding exchange anisotropy between neighboring  $Cu^{2+}$  spins. Although the fitting scheme with the ratios  $r_i$  promotes consistency among  $\tau_{eff}$  values it is nonetheless remarkable how nicely they each describe a very similar arc with temperature. As we shall see below, some of the most subtle physics of the cuprate spin fluctuations is embodied in the behavior of  $\tau_{eff}$ , where even at this point a great deal remains to be understood.

The HF coefficients from the fit are compared with values from other sources in Table 5.1. The HF constants labelled “Nandor” [17] are actually mostly derived from Barzykin and Pines [18], and are seen to be in rough accord with the fit. The “Shift Coef.” values shown have been converted from the primed coefficients in Tables 3.4 and 3.6 using (3.3.4) so that  $g$ -factor anisotropy (3.3.7) comes into play. The value of  $B$  given, for example, comes from  $c$ -axis shift measurements. The value of  $^{63}A_{ab} = 0.05 \times 10^{-6}eV$  is obtained by subtraction of large values and is correspondingly unreliable. The agreement of the  $^{63}A_c$  and of the  $^{89}D_\alpha$  tensors is very good, indeed.

The fitted values of the  $^{17}C_\alpha$  are 10–20% below those derived from the NMR shifts. This is an interesting point, because the “ $T_1$  problem” for the  $^{89}Y$  discussed in Sect. 4.1.2 has been managed in the UM fit process not by enhancing the  $^{89}D_\alpha$  tensor coefficients, but by reducing the  $^{17}C_\alpha$  ones. Either way, there will be a discrepancy between shift coefficients and those derived from relaxation. We continue to believe that there is an additional  $^{89}Y$  relaxation process (orbital or dipolar), which is beyond the effects of the MR Hamiltonian (2.3.2). In spite of this effect, there is quite a good correspondence between HF constants derived from the UM fit and those from NMR shifts.

It is also noteworthy that the fitting procedure based on 5.1.5 is independent of scale. That is, all HF constants (e.g. the  $^kV_\alpha$ ’s in (5.1.4)) can be multiplied by a uniform scale factor and the results will not be affected. Thus,

any set of results for the HF constants needs to be keyed to some particularly reliable value. In Table 5.1 the results are, in effect, keyed to  $^{63}V_c$ .

The UM fitting procedure leads to temperature dependences for the correlation lengths  $\lambda_\alpha$  shown in Fig. 5.2(a) and to seven estimates (from the  $^kV_\alpha$ 's in (5.1.4)) for the correlation time curve  $\tau_{eff}(T)$ , which are summarized in a plot in Fig. 5.2(b). In the latter case the extrema of the bundle of seven curves are shown as dashed lines, where the circles are the average values. The dotted line is a functional fit described below. Considering the  $^{89}\text{Y}$  relaxation rate

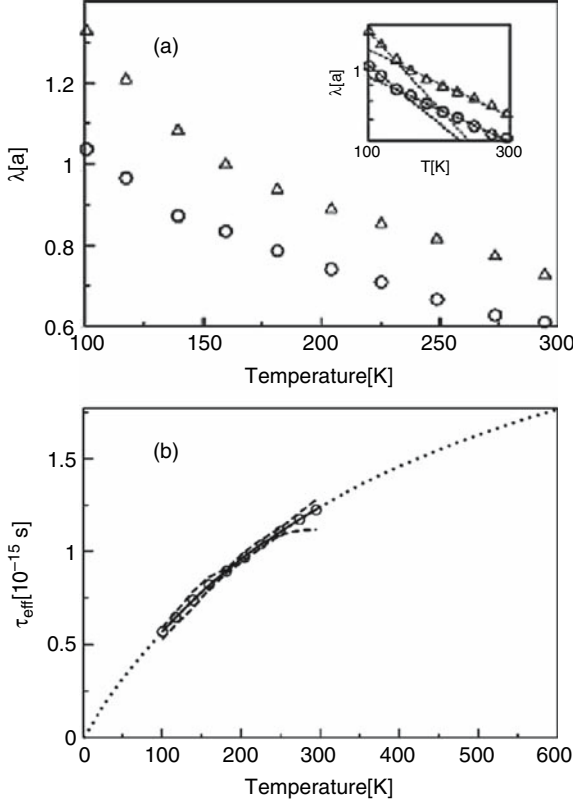


**Fig. 5.2.** (a) Correlation lengths  $\lambda_{ab}$  (circles) and  $\lambda_c$  (triangles) derived from the UM fit to YBCO7 are plotted vs.  $T$  over the range of the fit. Inset: Low and high- $T$  asymptotic behavior used to extrapolate the  $\lambda_\alpha$ 's is shown with dotted lines. (b) The average (circles) and extremal (dashed lines) values for the seven sets of  $\tau_{eff}$  parameters obtained from the  $T_1$  data fit for YBCO7 are plotted vs.  $T$ . The dotted line is a fit to these data which is extrapolated down to  $T = 0$  and upward to  $T = 600$  K. This fit and its interpretation are described in the text. Reprinted figures from A. Uldry and P.F. Meier, Phys. Rev. B **72**, 094508 (2005). Copyright 2005 American Physical Society

anomaly noted above and in Sect. 4.1.2, the degree of consistency among  $\tau_{eff}$  values is surprisingly good.

### *Extrapolation of the Fits to Higher Temperatures*

In Fig. 5.1(a)–(c) we see that the fits are generally very good over the fitting temperature range. However, UM went on to extrapolate their fits to higher temperatures with a fitting function *ansatz* as follows. The general behavior of  $\tau_{eff}(T)$  in Fig. 5.2(b) is one of downward curvature, but linear in  $T$  at the low- $T$  end. The latter feature is expected in metallic hosts, but the curving over is much greater than could be attributed to loss of Fermi-statistical degeneracy. They propose a fitting function wherein a Fermi-statistical term  $\tau_1 = aT$  is combined in an inverse fashion with a constant term  $\tau_2$  which dominates at high temperatures. Thus [11],

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_1} + \frac{1}{\tau_2} = \frac{1}{aT} + \frac{1}{\tau_2}, \quad (5.1.7)$$

where  $a = 7 \times 10^{-18} \text{ s/K}$  and  $\tau_2 = 3 \times 10^{-15} \text{ s}$ . The line representing this function is plotted in Fig. 5.2(b) as a dotted line up to 600 K. In Sect. 5.4 and 5.5 we shall look for the possible origin of this flattening effect in the Hubbard models. However, it does not appear to have been successfully identified yet.

The physics of the *ansatz* (5.1.7) is a bit unfamiliar, because normally when two rates combine inversely, it is the “faster” of the two which dominates. Here, however, at high temperatures when the Korringa  $T_1$  is very short, it is undercut by a weaker relaxation process. As for the form of  $\tau_1$ , Pines and Slichter [19] suggest a picture where  $\tau_1 = \tau_c T/T_F$  is made up of a correlation time factor  $\tau_c \sim \hbar/E_F$  representing the dwell time of a carrier in the unit cell, and  $T/T_F$  represents a Fermi-statistical scattering probability factor. Thus,  $a = \hbar/k_B T_F^2$ , from which UM estimated  $T_F \sim 1000 \text{ K}$ . Meanwhile,  $\tau_2$  appears to represent the behavior of the gas of quasiparticles when the degeneracy is completely lifted.

This extrapolation of the curve for  $\tau_{eff}(T)$  is also used to extrapolate the fit curves in Fig. 5.1(a)–(c). It is interesting to compare these extrapolations with high-temperature data by Nandor et al., [17] for  $^{17}\text{O}(2,3)$  and for  $^{89}\text{Y}$ , shown in panels (b) and (c) as downward triangles. The data for  $^{17}\text{O}(2,3)$  fall somewhat below the fitted data, but show a temperature dependence which is in general accord with the extrapolated model prediction. For the  $^{89}\text{Y}$ , however, contrary to the model the data are flat if not slightly rising with temperature. This behavior is consistent with the finding in Sect. 4.1.2 that there is an additional relaxation term for the  $^{89}\text{Y}$  beyond what is derived from (2.3.2). A possible orbital term was mentioned in Sect. 4.1.2. There are also dipolar terms which do not follow the spin-spin correlations [15]. The dipolar terms have also been calculated by Auler et al., [7] and are discussed further in Sect. 5.3.

### *The Spin Correlations and the “Basic” Relaxation Mechanism*

The fit to YBCO7 data illustrates rather dramatically the role played by antiferromagnetic (AFM) spin-spin correlations in the relaxation processes of all nuclei. It is interesting in this connection to examine the behavior of the  ${}^kV_\alpha(T)$ . According to the definitions (5.1.4), the  ${}^kV_\alpha(T)$  can vary from a high-temperature limit where  $\mathcal{K}_{ij} \rightarrow 0$ , to a fully correlated limit at low  $T$  where (in principle)  $\mathcal{K}_{01} \rightarrow -1$  and  $\mathcal{K}_{12}, \mathcal{K}_{13} \rightarrow 1$ . The  $T \rightarrow \infty$  limits for the  ${}^kV_\alpha(T)$  are defined to be  ${}^kV_\alpha^0$ , and are given by

$${}^{63}V_\alpha^0 = \frac{1}{4}(A_\alpha^2 + 4B^2) \quad (5.1.8a)$$

$${}^{17}V_\alpha^0 = \frac{1}{2}C_\alpha^2 \quad (5.1.8b)$$

$${}^{89}V_\alpha^0 = 2D_\alpha^2. \quad (5.1.8c)$$

The “basic” relaxation mechanism is what it would be in the absence of AFM correlations and is given by  $1/{}^kT_{1\alpha} = {}^kV_\alpha^0\tau_{eff}$ . Thus, apart from a scale factor, it is the same for all nuclei in the system.

The AFM correlation factors are the only thing which distinguishes the behavior of different nuclei. Fig. 5.3(a)–(c) illustrate this point by plotting the  ${}^kV_\alpha(T)$  vs.  $T$  for the YBCO7 fit. (Fig. 5.3(d)–(f) plot the same quantities for YBCO6.63 – see discussion below.) The high-temperature ( $\mathcal{K}_{ij} = 0$ ) limits are shown as solid bars on the right, and the low-temperature limits by solid bars on the left side of the figures. The  $T \rightarrow 0$  behaviors are estimated by extrapolating the correlation lengths in Fig. 5.2(a) by means of the dotted lines shown in the inset. The behavior seen in these plots shows (i) that the correlation causes the relaxation rates of the  ${}^{63}\text{Cu}(2)$  to increase and those of the  ${}^{17}\text{O}(2,3)$  and the  ${}^{89}\text{Y}$  to decrease, and (ii) that the behavior of all three nuclear species is changed by similar amounts as a result of the correlations. In this picture it is something of an accident that the  ${}^{17}\text{O}(2,3)$  and the  ${}^{89}\text{Y}$  relaxation processes appear to be Korringa-like in the normal state.

According to Fig. 5.3(a)–(c) the AFM correlations make sharp increases in the superconducting state. It must be emphasized that this is an extrapolation of normal-state behavior and is entirely hypothetical. As we shall see in Sect. 5.7, the actual behavior below  $T_c$  is quite different from what is shown here.

#### **5.1.3 The Uldry-Meier Analysis of YBCO6.63**

A very similar analysis to that described above was carried out by UM for YBCO6.63. The quality of the input data was perhaps not quite as good, and there were no data at all for  ${}^{63}T_{1ab}$ . The analysis was simplified a bit by adopting the HF tensor values shown in Table 5.1 for the YBCO6.63 analysis (recall that the values derived from NMR shifts in Chap. 4 were found to be nearly the same). The fitted curves (not shown) were only slightly less good, where, not surprisingly, the  ${}^{89}\text{Y}$  fits were noticeably worse than the others.

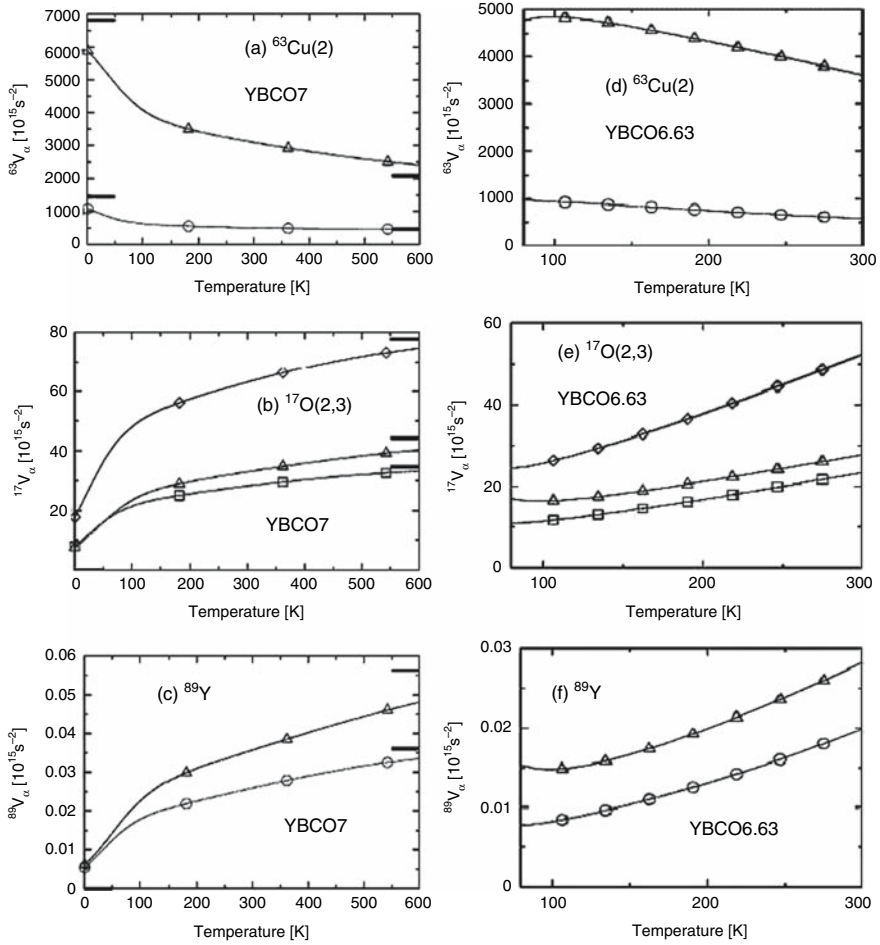


**Fig. 5.3.** (a)–(c) Curves are plotted representing  $^{63}V_\alpha(T)$ ,  $^{17}V_\alpha(T)$ , and  $^{89}V_\alpha(T)$  for the fit to YBCO7 in (a), (b), and (c), respectively. The solid bars on the right represent the values of  $^kV_\alpha^0$  corresponding to zero spin correlations, and the bars on the left represent maximum correlations as explained in the text. The data plotted are seen to run between these two limits. The zero-temperature points for these curves were obtained by extrapolating the variation of the  $\lambda_\alpha$ 's near 100 K to zero temperature. Such an extrapolation is entirely hypothetical. (d)–(f) Curves are plotted representing  $^{63}V_\alpha(T)$ ,  $^{17}V_\alpha(T)$ , and  $^{89}V_\alpha(T)$  for the fit to YBCO6.63 in (d), (e), and (f), respectively. These results are similar to those on the left, but AFM correlations show a wider range and reversed curvature as compared with YBCO7. Reprinted figures from A. Uldry and P. F. Meier, Phys. Rev. B **72**, 094508 (2005). Copyright 2005 American Physical Society

The results for  ${}^kV_\alpha(T)$  curves are shown in Fig. 5.3(d)–(f), where they are seen to be quite different from those for YBCO7. The correlation lengths for YBCO6.63 were longer than for YBCO7, reaching  $\sim 2.5a$  or so. As a result the range and magnitude of the correlation factors driving the  ${}^kV_\alpha(T)$  curves are considerably greater than for YBCO7. Another interesting feature is that the curvature of the  ${}^kV_\alpha(T)$  curves is in all cases the opposite in these two systems.

There was also slightly more scatter in the  $\tau_{eff}(T)$  curves for YBCO6.63, shown in Fig. 5.4(a), where they execute a considerably greater range than for YBCO7 (Fig. 5.2(b)). This, of course, results from the gapped nature of the static and dynamical properties of YBCO6.63. The average curve for  $\tau_{eff}$  (circles) was again fitted with the ansatz (5.1.7), except that a gap feature is introduced into the density of states with

$$\tau_1(T) = a T \exp(-T_g/T). \quad (5.1.9)$$

With that modification, (5.1.7) was fitted to the data in Fig. 5.4(a) and is shown as a dotted line extending from 0 K to 600 K. The fitting parameters are listed below in Table 5.2, where  $a$  and  $\tau_2$  are seen to be quite similar to those for YBCO7. The gap energy  $T_g = 94$  K is very close to that (104 K) derived from the susceptibility in Fig. 4.4, *rather than being twice that value* as we found for Y248 in Sect. 4.3. The slightly lower value for  $a$  suggests a somewhat lower degeneracy temperature for YBCO6.63 as shown in the table.

#### 5.1.4 The Uldry-Meier Analysis of $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y248)

The foregoing analytical scheme was also applied, in a somewhat restricted fashion, to the case of Y248, analyzing the same body of NQR data for  ${}^{63}\text{Cu}(2)$  as were discussed in Sect. 4.3. The method was restricted owing to a total lack of  $T_1$  data for other sites and orientations. As a consequence, the  ${}^{63}V_{ab}(T)$  curve for YBCO7 (see Fig. 5.3(a)) was adopted for the Y248 calculation, where

$$\frac{1}{{}^{63}T_{1c}} = 2 {}^{63}V_{ab}\tau_{eff}. \quad (5.1.10)$$

This is a fairly “neutral” assumption, since the temperature profile of  ${}^{63}V_{ab}(T)$  is seen to be very flat for both YBCO7 and YBCO6.63 in Fig. 5.3, but particularly in the former case. In any case, the fit to the data for  $1/{}^{63}T_{1c}T$ , shown in Fig. 5.5(a) and (b), is seen to be excellent, and furthermore, extends up beyond 700 K. Note that the 100 K–350 K data set from Raffa et al., [20] (crosses) has been augmented with high-temperature data from Curro et al., [21] (triangles pointing right) and from Tomeno et al., [22] (triangles pointing down).

Although the profile of  $\tau_{eff}(T)$  may be slightly different from what one would find with a full-blown analysis such as that for YBCO7, it behaves in a very interesting fashion as shown in Fig. 5.4(b). Here there is only one

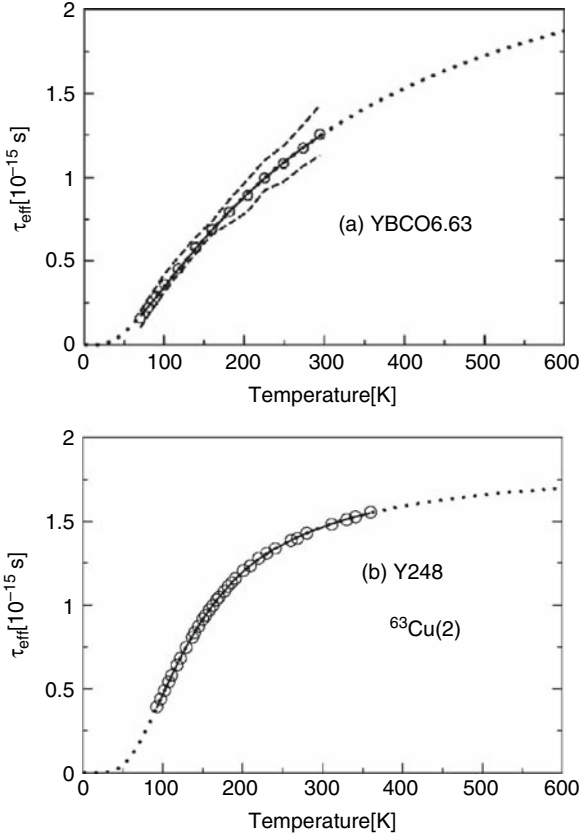


**Fig. 5.4.** (a) The data for  $\tau_{\text{eff}}(T)$  derived from the fit to several relaxation curves from YBCO6.63, as described in Sect. 5.1.3. The circles plot the average values of  $\tau_{\text{eff}}$ , and the dashed lines show the most extreme values. The dotted line is a fit of (5.1.7) and (5.1.9) to the average values, extrapolated to 0 K and 600 K. (b) Values for  $\tau_{\text{eff}}(T)$  derived from the fit to the relaxation curve for  $^{63}\text{Cu}(2)$  in Y248, shown in Fig. 5.5, as described in Sect. 5.1.4. The dotted line is a fit of (5.1.7) and (5.1.9) to the data (circles), extrapolated to 0 K and 600 K. Parameters from the fits shown are presented in Table 5.2 and discussed in the text. Reprinted figures from A. Uldry and P.F. Meier, Phys. Rev. B **72**, 094508 (2005). Copyright 2005 American Physical Society

data set from the fit (circles), which has very little scatter. The dotted line is a fitting of the ansatz (5.1.7) with the gap modification (5.1.9) used for YBCO6.63. The parameters from this fit are given in Table 5.2, where they may be compared with those for YCBO7 and YBCO6.63.

The parameters in Table 5.2 show an interesting progression for the three YBCO-related systems. Although the forms of  $\tau_{\text{eff}}(T)$  in (5.1.7) and (5.1.9) are really just educated guesses, they match the temperature dependence from

**Table 5.2.** Parameters from fits to the ansatz (5.1.7) for YBCO7 and with the gap modification (5.1.9) for YBCO6.63 and Y248 are listed, showing  $a$ ,  $\tau_2$ , and the gap, crossover, and Fermi temperatures derived from their respective (average) data curves for  $\tau_{\text{eff}}(T)$ . The crossover temperature is where  $\tau_1 = \tau_2$ , and the estimated Fermi temperature is obtained from  $T_F \sim (\hbar/k_B a)^{1/2}$ . These results are discussed in the text

| System   | $a$ (s/K)            | $\tau_2$ (s)          | $T_g$ (K) | $T_{cr}$ (K) | $T_F$ (K) |
|----------|----------------------|-----------------------|-----------|--------------|-----------|
| YBCO7    | $7 \times 10^{-18}$  | $3.0 \times 10^{-15}$ | 0         | 420          | 1,050     |
| YBCO6.63 | $10 \times 10^{-18}$ | $2.9 \times 10^{-15}$ | 97        | 375          | 880       |
| Y248     | $44 \times 10^{-18}$ | $1.9 \times 10^{-15}$ | 195       | 154          | 420       |

the fits better than one might have expected, giving very convincing extrapolations to higher and lower temperatures. After modest changes between YBCO7 and YBCO6.63, with the appearance of a  $\sim 100$  K gap in the latter case, the jump to Y248 shows a doubling of the density of states ( $\propto \sqrt{a}$ ) and a corresponding reduction by half of the estimated degeneracy temperature, as well as a doubling of the gap energy, which now exceeds the cross-over temperature.

A somewhat different view of the dynamic magnetism of Y248 via dynamical scaling theory is presented in Sect. 6.4.

### *The Wider Role of the Uldry-Meier Model Analysis*

The UM analysis has offered a highly revealing and greatly unifying look into the microscopic phenomena associated with the cuprate  $T_1$  processes. From this perspective, the difference between different sites and nuclear species essentially ceases to be an issue. This analysis is in no sense a theory, though it incorporates a widely accepted and time-tested formulation of the  $T_1$  process, and it puts the Mila-Rice HF Hamiltonian to a severe test, which it mostly passes in good order. Note that this Hamiltonian is essentially unique to cuprates among metallic environments. It is worth emphasizing that the UM picture is also implicit in the general  $\chi''(\mathbf{q}, \omega)$  formulation of the  $T_1$  process, as demonstrated in Sect. 3.5.

Perhaps the most significant advantage of the UM analysis is that it partitions the  $T_1$  problem into three independent phenomenological pieces. These are (i) HF constants, which are essentially inert, (ii) AFM correlation factors, which are much larger and universally more important than hitherto realized, and (iii) a comprehensive fluctuation rate, which embodies all of the low-frequency spin fluctuation physics of the cuprates, including, but not limited to, Fermi liquid, spin pseudogap, and exchange-coupled local moments. The ability to separate elements (ii) and (iii) in either an experimental or theoretical evaluation is a considerable simplification and an enormous advantage over previous practice. We emphasize that this analysis offers a useful way to evaluate model theories of  $\chi''(\mathbf{q}, \omega)$ . One can simply evaluate (ii) and (iii)

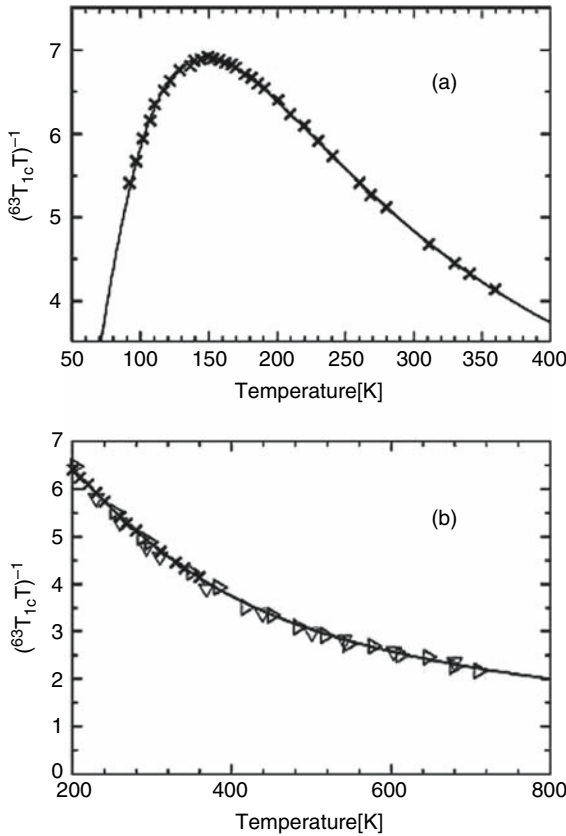


**Fig. 5.5.** (a)  $^{63}\text{Cu}(2)$  NQR data from [20] for Y248 (*crosses*) are plotted as  $1/T_1T$  vs.  $T$ . The solid line shows the Uldry-Meier fit to these data described in Sect. 5.1.4. (b) The fit curve shown in part (a) is extended to above 700 K. Also shown there are high-temperature data by Curro et al., [21] (*triangles pointing right*) and by Tomeno et al., [22] (*triangles pointing down*). The data and the fit are seen to be extremely precise. Reprinted figures from A. Uldry and P.F. Meier, Phys. Rev. B **72**, 094508 (2005). Copyright 2005 American Physical Society

as defined above and judge these components separately on their own merits. This procedure offers a new perspective on theory building for the cuprates and quite possibly for other materials as well.

## 5.2 The Millis, Monien, and Pines Model for $T_1$ in Cuprates

This straightforward phenomenological model [4, 5] served the important role of discussing and testing certain key ideas in the early days when both NMR

shift and relaxation data were still unfolding. This model emerged at a time when there was still a great deal of uncertainty about what the ultimate theoretical basis for cuprate  $T_1$  processes was going to be. Of the several lines of theoretical approach to cuprate spin dynamics which we discuss in this chapter, the conceptually simple MMP model is a good place to begin.

One of the main objectives of MMP was to show that the relaxation of  $^{63}\text{Cu}(2)$ ,  $^{17}\text{O}(2,3)$ , and  $^{89}\text{Y}$  can all be accounted for with a single dynamical variable associated with each  $\text{Cu}^{2+}$  site. In this matter they largely succeeded, although as noted in Sects. 4.3 and 5.1 there are other apparent contributions to the  $^{89}\text{Y}$  relaxation process. However, there is no evidence for another set of dynamical variables besides the  $\text{Cu}^{2+}$  spin moments.

In addition to the foregoing, these two papers [4, 5] give an in-depth discussion of the physics issues surrounding the NMR  $T_1$  problem in cuprates. Although the actual model they expound is a phenomenological treatment of the Mila-Rice Hamiltonian [1], they present a derivation [5] showing that such treatment is equivalent to a tight-binding, band-theory model of an interacting Fermi liquid.

The MMP model is based on a mean-field treatment of AFM exchange interaction effects in a system of itinerant quasiparticles, i.e. a metal, which would be a simple Fermi liquid without the exchange interactions. We begin by reviewing their derivation of the mean-field dynamic susceptibility, in the course of which the relevant parameters are introduced and discussed. The following is just a brief summary. We refer the interested reader to the original papers for greater detail [4, 5] dynamical susceptibility, RPA model.

The mean-field complex susceptibility  $\chi(\mathbf{q}, \omega) = \chi'(\mathbf{q}, \omega) + i\chi''(\mathbf{q}, \omega)$  of an interaction spin system is given by

$$\chi(\mathbf{q}, \omega) = \frac{\bar{\chi}(\mathbf{q}, \omega)}{1 - J_{\mathbf{q}}\bar{\chi}(\mathbf{q}, \omega)}, \quad (5.2.1)$$

where  $\bar{\chi}(\mathbf{q})$  is the noninteracting susceptibility, and  $J_{\mathbf{q}}$  is the interaction potential. Since NMR frequencies are generally much smaller than the electronic frequencies in such a system, we are concerned here with the region near  $\omega \rightarrow 0$ . In this limit it is assumed that

$$\bar{\chi}''(\mathbf{q}, \omega)|_{\omega \rightarrow 0} \rightarrow \pi \frac{\omega}{\Gamma_{\mathbf{q}}} \bar{\chi}'(\mathbf{q}, \omega = 0) \equiv \pi \frac{\omega}{\Gamma_{\mathbf{q}}} \bar{\chi}_{\mathbf{q}}, \quad (5.2.2)$$

where  $\Gamma_{\mathbf{q}}$  is a characteristic energy for spin fluctuations at wave vector  $\mathbf{q}$ . Correspondingly, in the same limit (5.2.1) gives

$$\chi''(\mathbf{q}, \omega) \longrightarrow \pi \frac{\omega}{\Gamma_{\mathbf{q}}} \bar{\chi} \frac{1}{(1 - G_{\mathbf{q}})^2 + (\pi\omega/\Gamma_{\mathbf{q}})^2 G_{\mathbf{q}}^2}, \quad (5.2.3)$$

where  $J_{\mathbf{q}}\bar{\chi}_{\mathbf{q}} \equiv G_{\mathbf{q}}$ . As we are treating AFM fluctuations which appear to be diverging as the system is approaching a Neél point,  $G_{\mathbf{q}}$  is assumed to be peaked at the AFM point  $\mathbf{Q} = (\pi/a, \pi/a)$ , at which point it has a value of

slightly less than 1. For (5.2.3) we expand  $G_{\mathbf{q}}$  about the AFM point:  $G_{\mathbf{q}} \approx G_{\mathbf{Q}} - \mathbf{q}^2 \beta_0^2$ , where  $\mathbf{q}$  is measured from  $\mathbf{Q}$ . The correlation length is defined by  $G_{\mathbf{Q}} = 1 - \xi_0^2/\xi^2$ . Setting  $G_{\mathbf{q}} = 1$  in the second term of the denominator of (5.2.3), we obtain

$$\frac{\chi''(\mathbf{q}, \omega)}{\omega} = \frac{\pi \chi_0}{\Gamma} \frac{(\xi/\xi_0)^4}{(1 + q^2 \xi^2)^2 + (\pi \omega / \bar{\Gamma})^2 (\xi/\xi_0)^4} \simeq \frac{\pi \bar{\chi}}{\bar{\Gamma}} \frac{(\xi/\xi_0)^4}{(1 + q^2 \xi^2)^2}. \quad (5.2.4)$$

Because of the peaked nature of this function, the  $\mathbf{q}$ -dependence of the parameters  $\bar{\chi}_{\mathbf{q}}$  and  $\bar{\Gamma}_{\mathbf{q}}$  has been dropped. They argue further that when  $\mathbf{q}$  is far away from  $\mathbf{Q}$ ,  $\chi''(\mathbf{q}, \omega)$  should be comparable with the uncorrelated value, so a  $\mathbf{q}$ -independent term of that magnitude is added in, giving

$$\left. \frac{\chi''(\mathbf{q}, \omega)}{\omega} \right|_{\omega \rightarrow 0} = \frac{\pi \bar{\chi}}{\bar{\Gamma}} \left[ 1 + \beta \frac{(\xi/a)^4}{(1 + q^2 \xi^2)^2} \right], \quad (5.2.5)$$

where  $\beta = (a/\xi_0)^4 (\bar{\chi}/\chi_0) (\Gamma/\bar{\Gamma})$ ,  $\chi_0$  is the uniform susceptibility, and  $\Gamma$  is the spin fluctuation frequency of the noninteracting system. Equation (5.2.5) may then be used to model quasiparticle dynamics for cuprate systems not too far from an AFM instability, i.e. when  $\xi/a \gg 1$ . From (5.2.4) we also see that the effective spin fluctuation frequency is

$$\omega_{SF} \sim \frac{\bar{\Gamma} \xi_0^2}{\xi^2}, \quad (5.2.6)$$

which can be greatly diminished if  $\xi \gg \xi_0$ .

The  $\mathbf{q}$ -dependent HF coupling Hamiltonian terms are denoted  ${}^k F_{\alpha}(\mathbf{q})$  here (3.5.6) for nuclear spin species  $k$  and axis  $\alpha$ . Thus, the relaxation rate  ${}^k W_{\alpha} \equiv 1/{}^k T_{1\alpha}$  is given by [5]

$${}^k W_{\alpha} = \frac{k_B T}{4\mu_B^2} \sum_{\mathbf{q}} \left[ {}^k F_{\beta}(\mathbf{q})^2 + {}^k F_{\gamma}(\mathbf{q})^2 \right] \left. \frac{\chi''(\mathbf{q}, \omega)}{\omega} \right|_{\omega \rightarrow 0}, \quad (5.2.7)$$

where  $(\alpha, \beta, \gamma)$  is any permutation of the (a, b, c) axes. In (5.2.7) the  ${}^k F_{\alpha}(\mathbf{q})$  have the dimension of s (cf. (3.5.10)), where g-factor anisotropy is not included. For YBCO the  ${}^k F_{\alpha}(\mathbf{q})$  are

$${}^{63} F_{\alpha}(\mathbf{q}) = {}^{63} A_{\alpha} - 2B(\cos q_x a + \cos q_y a), \quad (5.2.8a)$$

$${}^{17} F_{\alpha}(\mathbf{q}) = 2 C_{\alpha} \cos^2(q_{x,y} a/2), \quad (5.2.8b)$$

$${}^{89} F_{\alpha}(\mathbf{q}) = 8 D_{\alpha} \cos(q_x a/2) \cos(q_y a/2) \cos(q_z a/2) \quad (5.2.8c)$$

(see (3.5.10) - (3.5.14)).

The fitting procedure, which is described briefly below, thus consists of estimating the HF constants (A, B, C, D's) from NMR shift and susceptibility data, and then adjusting the parameters  $\Gamma$ ,  $\beta_0$ , and  $\xi$  from (5.2.5) to match the calculated rates  ${}^k W_{\alpha}(T)$  as well as possible with experimental data.

### *The MMP Fitting Process for YBCO7*

Here we summarize the issues regarding this fitting procedure as well as a brief description of the procedure itself. We first note that the squared Lorentzian form for  $\chi''(\mathbf{q}, \omega)$  in (5.2.5) is valid when  $\xi/a \gg 1$ , whereas the deduced YBCO7 values of  $\xi/a$  are of order unity. For this reason, MM also discussed the case of a Gaussian form for the peak at  $\mathbf{Q}$  [5]. The latter is more nearly consistent with peaks in  $\chi''(\mathbf{q}, \omega)$  which have been reported from neutron scattering studies [23]. The latter results also showed some sign of incommensurability, which is also a major effect in LSCO. The question is whether the incommensurability observed by neutron scattering at energies of more than 1 meV is still present at NMR frequencies, which are roughly four orders of magnitude smaller. In Chap. 6 it will be shown that incommensurability in  $\chi''(\mathbf{q}, \omega)$  is incompatible with NMR data on LSCO. We assume this is also true here and adopt with MM [5] a picture with commensurate AFM fluctuations.

The HF parameters used by MM are compared with those from the UM fit as well as those from NMR shift values in Chap. 3 (see Table 5.1) in Table 5.3. In MM the HF values are given in units of  $\mu_B^2/\chi_0$ . Here we convert them to units of  $10^{-6} \text{ eV}$ . Since the susceptibility is assumed to be isotropic, we have used the powder average susceptibility *per Cu(2) ion* from Table 3.4 for this purpose. It was also assumed that  $A_c + 4B = 0$ , essentially consistent with earlier practice. The other MM values show some small differences with the other values listed. The ratio  $C_a$  to  $C_c$  is  $\sim 1.5$ , in rough agreement with the others. However, the ratio  $C_a/D \simeq 69$  is rather smaller than the “Shift Coef.” value  $\simeq 113$ , so that the “problem” with the  $T_1$  of  $^{89}\text{Y}$  (see Sect. 4.1.2) will not arise here. We firmly believe this problem to exist.

In the MM fit there was no value available for  $A_{ab}$ , so this was left as a parameter to be “fitted”. From the Cu(2)  $T_1$  anisotropy  $^{63}W_{ab}/^{63}W_c$  it was decided that  $0.1 \leq A_{ab}/4B \leq 0.2$ , which is not unreasonable. This estimation is compared with other values in Table 5.3. The susceptibility parameters  $\beta$  and  $\xi$  from (5.2.5) – and their temperature dependences – were to be extracted

**Table 5.3.** The HF parameters for YBCO7 and YBCO6.63 used by MM [5] are compared with values from the UM fit and those derived from NMR shift coefficients in Chap. 3 (both given in Table 5.1). The coefficients in MM were given in units of  $\mu_B^2/\chi_0$ , which have been converted to eV using the powder average susceptibility based on values given in Table 2.4, where  $\chi_0$  is interpreted to be the value for a single Cu(2) site. The values for  $C_a$  and  $C_c$  have been reversed, since the larger value corresponds to the Cu-O-Cu ( $a$ ) axis and the smaller one to the  $c$  axis. Parameters are given in units of  $10^{-6} \text{ eV}$

| Source      | $A_{ab} + 4B$ | $A_{ab}/4B$ | $C_a$ | $C_c$ | $D$     |
|-------------|---------------|-------------|-------|-------|---------|
| MM [5]      | 1.45          | 0.1-0.2     | 0.33  | 0.22  | 0.0048  |
| UM Fit      | 1.92          | 0.096       | 0.259 | 0.196 | 0.00303 |
| Shift Coef. | 1.69          | 0.03        | 0.355 | 0.209 | 0.00314 |

from the data fits. This was not a simple matter, since these parameters have qualitatively similar effects on the results. There were two main questions to be decided: (i) Can the relaxation of all three nuclei be quantitatively accounted for with (5.2.5) and (5.2.8); and (ii) does a picture of AFM correlations emerge here, where  $\xi(T)$  increases when  $T$  descends toward  $T_c$ ?

The first answer is definitely “yes”, but the second one is a bit more murky. It depended on the relative behavior of  $^{17}W_\alpha(T)$  and  $^{89}W_\alpha(T)$ , for which the available data for the input parameters were not particularly accurate. Calculated ratios of these relaxation rates from MM are shown in Fig. 5.6 for the cases of Gaussian and Lorentzian models for  $\chi''(\mathbf{q}, \omega)$  and several sets of parameters. The calculations are based on the assumption that  $^{63}W_c/^{17}W_c = 19$  at 100 K and  $^{63}W_c/^{17}W_c = 10$  at 300 K, these values being taken from experiment. Shown is the variation of  $^{17}W_c(T)/^{89}W_c(T)$  between 100 K and 300 K for several sets of parameters, which are shown in Table 5.4. There are two assumed cases here: (i)  $\beta$  is constant and  $\xi$  varies with temperature, and (ii)  $\xi$  is constant and  $\beta$  varies with temperature. The experimental ratio is around 1,300 and is very nearly flat. These circumstances favor the Gaussian form for  $\chi''$  and the assumption of a constant  $\beta$  with temperature-varying  $\xi$ , and thus the solid line in Fig. 5.6(b), case (B).

Thus, it was concluded that the constant  $\beta$  picture was more the satisfactory, because if  $\beta$  varies, while  $\xi$  is constant, then  $\Gamma$  must have a compensating temperature dependence to keep the pre-factor in (5.2.5) approximately constant. This may be difficult to account for. MM also concluded that  $\xi/a \simeq 1.0$ –1.5 for the Gaussian case and 1.5–2.0 for the Lorentzian case, while  $\beta \sim 15$  or greater.

It is interesting to view the results of the MMP analysis in the context of the results of the UM analysis of Sect. 5.1. The parameter values obtained in these cases are similar with some important differences. The MMP scheme assumed HF parameters derived from NMR shift measurements which are at

**Table 5.4.** Parameter values for the calculated curves in Fig. 5.6 are listed for the three cases plotted for a Lorentzian susceptibility peak (a) and for a Gaussian peak (b). Two curves are plotted for each case, both with the same parameters at  $T = 100$  K and at 300 K with a constant value of  $\beta$  with  $\xi$  varied (first values listed) and with both  $\xi$  and  $\beta$  varied (values in parentheses). The constant  $\beta$  curves are solid lines and those for varying  $\beta$  are dashed lines

| Case | T(K) | $\xi$ (Lor.) | $\beta$ (Lor.) | $\xi$ (Gauss.) | $\beta$ (Gauss.) |
|------|------|--------------|----------------|----------------|------------------|
| A    | 100  | 1.9          | 30             | 1.4            | 30               |
| A    | 300  | 1.3(1.9)     | 30(16)         | 1.1(1.4)       | 30(11)           |
| B    | 100  | 2.4          | 10             | 2.0            | 10               |
| B    | 300  | 1.7(2.4)     | 10(3.4)        | 1.4(2.0)       | 10(4)            |
| C    | 100  | 3.7          | 3.0            | 3.3            | 3.0              |
| C    | 300  | 2.5(3.7)     | 3.0(1.1)       | 2.2(3.3)       | 3.0(1.2)         |

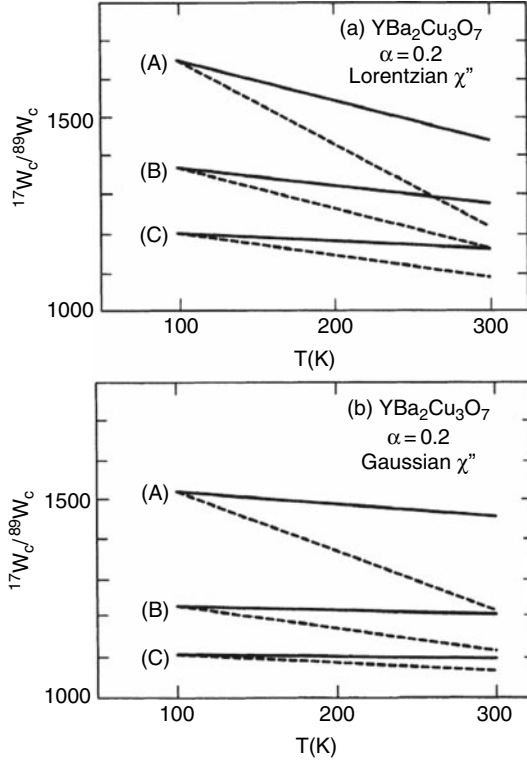


**Fig. 5.6.** Plots of the ratio  $^{17}W_c(T)/^{89}W_c(T)$  vs.  $T$  for  $100\text{ K} \leq T \leq 300\text{ K}$  calculated with the model susceptibility shown in (5.2.5) (Lorentzian case) in panel (a) and a Gaussian version in panel (b). The Gaussian is written as  $\beta \exp(-q^2\xi^2)$  and is centered at  $\mathbf{Q}$ . The calculations are based on the ratios  $^{63}W_c/^{17}W_c = 19$  at 100 K and 10 at 300 K. Since the variation of  $^{17}W_c(T)/^{89}W_c(T)$  is roughly linear, straight lines are drawn between values calculated for the two extremal temperatures. Calculations are carried out for constant  $\beta$  and  $T$ -varying  $\xi$  (*solid lines*) and for constant  $\xi$  with  $\beta$  varying (*dashed lines*). The parameter sets used are listed in Table 5.4. The same parameters are used at 100 K, but then different ones for 300 K. These calculated results are simply connected with a straight line. Reprinted figures from A. J. Millis and H. Monien, Phys. Rev. B **45**, 3059 (2005). Copyright 1992 American Physical Society

least a rough facsimile of those obtained in Chap. 3 and of those obtained from the UM fit (Table 5.3). The coherence lengths appear to be similar, though it is not clear whether  $\xi$  from MMP can be directly compared with the  $\lambda_\alpha$ 's in Fig. 5.2(a). The trend with temperature is, of course, the same.

One trouble spot in this comparison is the variation of the integrated area  $\sum_{\mathbf{q}} \chi''(\mathbf{q}, \omega)/\omega$  with temperature. For the UM picture, this simply goes as  $\tau_{\text{eff}}/T$ , while in the MMP case (i.e. from (5.2.5)) this area is very nearly equal to

$$\sum_{\mathbf{q}} \chi''(\mathbf{q}, \omega) / \omega \simeq \frac{\pi \bar{\chi}}{T} [1 + \beta \xi^2]. \quad (5.2.9)$$

If the prefactor is independent of  $T$  as one might suppose for YBCO7, then the known behavior of  $\tau_{\text{eff}}(T)$  from the UM fits tells us that  $\beta \xi^2$  from the MMP model should be roughly constant. Thus, if  $\xi$  varies appreciably with  $T$ ,  $\beta$  should vary inversely and twice as fast. This does not square well with the MM result.

On the positive side of things, one could say that the results of the UM analysis would be an excellent starting point for someone setting out to model the mean-field dynamic susceptibility as MMP did. As regards the possibility of accounting for cuprate  $T_1$  behavior with an RPA type of model where the  $\mathbf{q}$ -dependence of  $\chi''(\mathbf{q}, \omega)$  (and thus  $\xi$ ) has no temperature dependence, the UM analysis also gives a definite negation of any such possibility.

### *Millis and Monien: Discussion of YBCO6.63 and of Neutron Scattering Characterization of $\chi''(\mathbf{q}, \omega)$*

MM analyze YBCO6.63 in a fashion similar to YBCO7. They note that rather larger values of  $^{63}W_c / ^{17}W_c$  indicate stronger AFM correlations in YBCO6.63, in accord with the UM result. As a result, they note that the constant- $\xi$  option implies a somewhat larger increase in the ratio  $^{17}W_c / ^{89}W_c$  at lower temperatures, inconsistent with preliminary data available at the time. However, the subsequent  $T_1$  results of Takigawa et al., [15] showed an increase in the latter ratio of  $\sim 20\%$  below 300 K, which therefore cannot quite rule out the constant- $\xi$  hypothesis. Again, the UM analysis of YBCO6.63, showing longer and more temperature-dependent correlation lengths in YBCO6.63, would preclude a fixed- $\xi$  scenario.

One slightly troubling point about the MM discussion of YBCO6.63 is the assumption without justification that  $\chi_0$  in (5.2.5) be simply replaced by the gapped  $\chi(T)$  shown in Fig. 4.4 (or its equivalent). Some kind of assumption along these lines is evidently necessary for this model, but then leads to difficulties in accounting for  $^{89}W_\alpha(T)$  and  $^{17}W_\alpha(T)$ , as was noted in Sect. 4.1.2. This played, unfortunately, into the weakness of employing the MMP model to deduce the temperature dependences of both  $\xi$  and  $\beta$  from NMR data alone.

MM offer a deep and useful discussion [5] of the behavior of  $\chi''(\mathbf{q}, \omega)$  at higher frequencies, with an eye to gleaning further insight about its characteristics from inelastic neutron scattering (INS) data. Again, specifically, would it be possible to determine the behavior of  $\xi(T)$  from the width of the peak at  $\mathbf{Q}$ ? They note, with a detailed model example, that there is a tendency at typical INS frequencies for the measured peak width to appear independent of temperature while  $\xi$  is undergoing a significant variation with  $T_1$  and that measurements must be conducted at very low energies to avoid this.

There appears to be relatively little useful data from INS on the  $T$ -dependence of AFM peak widths in cuprates or on pseudogap effects on  $\chi''(\mathbf{q}, \omega)$ , the main exception to this being LSCO. If we take the INS results

of Tranquada et al. [23] as an example, the desired effects are often masked by incommensurability. However, unknown at the time of MMP and MM, penetrating insights about pseudogap behavior in cuprates would come not from INS, but from ARPES (see a brief review of this in Sect. 4.2). This point will be considered further in Chap. 6, where extensive INS studies of LSCO will be discussed.

### 5.3 $T_1$ Model for YBCO Using INS Data for $\chi''(q, \omega)$

In the first two subsections of this chapter we saw how both UM and MMP interpreted cuprate relaxation data in terms of AFM fluctuations with a temperature-dependent correlation length. In the present subsection we review a fit procedure performed by the Berthier group, wherein  $T_1$  data from a YBCO6.9 sample are interpreted in terms of an AFM fluctuation peak characterized by INS measurements [7]. INS data are quoted which show the AFM peak to have a constant width, i.e. *the fluctuations are interpreted to have a temperature-independent correlation length.*<sup>2</sup> Here we review the data and analysis for this interesting case, which also includes extracting dynamic susceptibility parameters from data for  $T_{2g}$ , the Gaussian spin-echo decay from indirect spin-spin couplings (see Chap. 6). We compare this case with the UM fits in Sect. 5.1 in some detail. In the end, it is found that they are strikingly similar, and that the contrast between them reflects a difference in samples rather than one of methods.

When large single crystals of YBCO7 became available, extensive neutron scattering measurements were reported, e.g. by Regnault et al., [24], Rossat-Mignod et al., [25], and by Tranquada, Sternleib et al., [23, 26]. NMR measurements on  $^{63}\text{Cu}(2)$  and  $^{89}\text{Y}$  in single crystals so characterized have been reported by Auler et al., [7], where they noted that the AFM peaks from INS data on their sample and related samples are well-fitted by a Gaussian, with a *peak width which is essentially independent of temperature*. The sample of YBCO6.9 in question gave some indication of disorder in spite of being nearly fully oxygenated. This was attributed to the presence of  $\text{Sr}^{2+}$  as a dilute substitutional impurity for  $\text{Ba}^{2+}$ , leading to fairly broad NMR lines with field  $\perp$   $c$  axis [27]. However, the NMR measurements were conducted normally. The other apparent consequence of this was that the sample exhibited a somewhat pseudogapped character compared with other YBCO samples with  $T_c = 90 \pm 1$  K.

The pseudogap effect is noticeable in relaxation curves for  $^{63}\text{Cu}(2)$  shown in Fig. 5.7, where the data are seen to roll off below  $T \sim 125$  K for both field orientations. Furthermore, there is no visible break in the relaxation curve at  $T_c$ , which is a characteristic of pseudogapped material. On the other hand, the

---

<sup>2</sup> The MMP picture did not rule this possibility out, but in the absence of reliable INS data favored the scenario with temperature-variable correlation lengths [5].

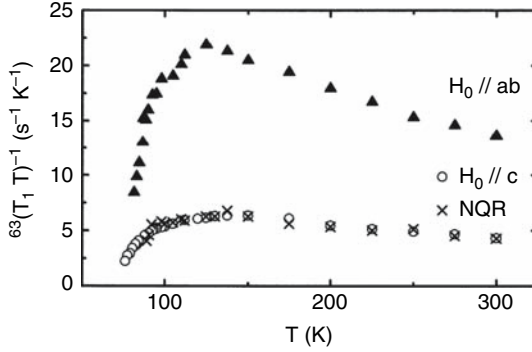


**Fig. 5.7.** Relaxation rate  $1/T_1T$  for  $^{63}\text{Cu}(2)$  in YBCO6.9 [7], showing typical anisotropy for YBCO7, but pseudogap-like rolling off of the data below 120-130 K. Note that there is no break or other feature in the data at  $T_c \sim 90$  K. Reprinted figure from T. Auler, M. Horvatic et al, *Physica C* **313**, 255 (1999). Copyright 1999 Physica C

ratio  $T_{1c}/T_{1ab} \simeq 3.7$  at  $T \sim 100$  K and declines slightly at higher temperatures, which is typical behavior for YBCO7. This YBCO sample is therefore rather unique in having pseudogap features with  $T_c \sim 90$  K.

Both NMR shift and relaxation data for the  $^{89}\text{Y}$  nuclei are shown in Fig. 5.8. The NMR shift is seen to roll off at lower temperatures, much like one of the slightly deoxygenated samples in Fig. 4.2. Correspondingly,  $1/T_1T$  in Fig. 5.8(b) is also seen to decline at lower temperatures, though not quite so much as for YBCO6.6 (see, e.g. Fig. 4.1(b)). Again, like the  $^{63}\text{Cu}(2)$ , the general character is that of a pseudogapped system.

### 5.3.1 The Gaussian Model Susceptibility

The authors introduce their Gaussian susceptibility model as follows [7]. Beginning with the standard form (cf. (4.2.2))

$$\left. \frac{\chi''(\mathbf{q}, \omega)}{\omega} \right]_{\omega \rightarrow 0} = \frac{\chi'(\mathbf{q}, 0)}{\Gamma_{\mathbf{q}}}, \quad (5.3.1)$$

it is supposed that on account of AFM exchange forces  $\chi'(\mathbf{q}, 0)$  is peaked at  $\mathbf{q} \sim \mathbf{Q}$ , and the spin fluctuation frequency  $\Gamma_{\mathbf{q}}$  has a minimum at the same point. Further, it is assumed that  $\chi'(\mathbf{q}) = \chi_{AF}(\mathbf{Q}) f(\mathbf{q} - \mathbf{Q})$  and  $\Gamma_{\mathbf{q}}^{-1} = \Gamma_{AF}^{-1} f(\mathbf{q} - \mathbf{Q})$  have the same functional form in the vicinity of  $\mathbf{Q}$ , which is taken to be a Gaussian

$$f(\Delta\mathbf{q}) = \exp(-|\Delta\mathbf{q}|^2 \xi^2/4). \quad (5.3.2)$$

The value  $\xi = 1.3a$  is taken from INS measurements on the same sample material [7]. Then, if we put the origin in  $\mathbf{q}$ -space at  $\mathbf{Q}$ , we may write  $f(\Delta\mathbf{q})$

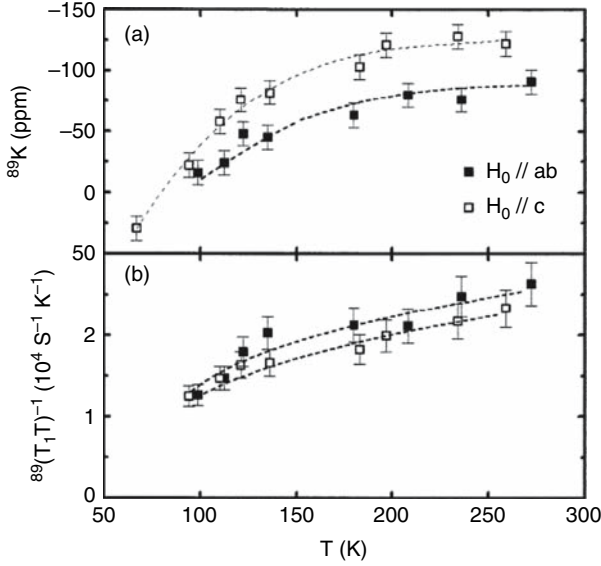


**Fig. 5.8.** (a) NMR shift data for  $^{89}\text{Y}$  in YBCO6.9 from [7] for field oriented both  $\parallel$  and  $\perp$   $c$  axis.  $^{89}K_\alpha(T)$  shows pseudogap-like decline below  $T \sim 200$  K. (b) Data for the  $^{89}\text{Y}$  relaxation rate  $1/T_1 T$  for the same sample and conditions as in part (a) Reprinted figure from T. Auler, M. Horvatic et al, *Physica C* **313**, 255 (1999). Copyright 1999 Physica C

$= \exp[-0.4225 (qa)^2]$ . As in the MMP model, a noninteracting,  $\mathbf{q}$ -independent term  $\chi_0/\Gamma_0$  is added to give the relations

$$\left. \frac{\chi''(\mathbf{q}, \omega)}{\omega} \right]_{\omega \rightarrow 0} = \frac{\chi_0}{\Gamma_0} + \frac{\chi'_{AF}(\mathbf{Q})}{\Gamma_{AF}(\mathbf{Q})} \exp[-0.845 (qa)^2] \quad (5.3.3a)$$

$$\chi'(\mathbf{q}) = \chi_0 + \chi'_{AF}(\mathbf{Q}) \exp[-0.4225 (qa)^2]. \quad (5.3.3b)$$

The parameters in this model ((5.3.2) and (5.3.3)) were then extracted from experimental data. We give here just a brief summary of the procedure.  $\chi_0(T)$  was defined to be the uniform susceptibility, the temperature-dependence of which is derived from NMR shift data in Fig. 5.8(a), where the orbital shift value  $^{89}K_{c,orb} = 160$  ppm is taken from [15]. The scale factor for  $\chi_0(T)$  was obtained by comparing shift coefficients for  $^{89}\text{Y}$  and  $^{17}\text{O}$  with values from the literature [7]. The resulting curve of  $\chi_0(T)$  vs.  $T$  is shown in Fig. 5.9(a). In that same figure is shown the curve for  $\chi'_{AF}(T)$ . This was extracted from data for  $^{63}\text{T}_{2g}(T)$ , which is shown in Fig. 5.9(b), using the relations

$$\frac{1}{^{63}T_{2g}^2} = \frac{c_{63}}{8} \left[ \sum_{\mathbf{q}} (a_{ind}^z(\mathbf{q}))^2 - \left[ \sum_{\mathbf{q}} a_{ind}^z(\mathbf{q}) \right]^2 \right] \quad (5.3.4)$$

with

$$a_{ind}^z(\mathbf{q}) = \frac{\gamma_{63}\hbar\chi'(\mathbf{q})}{g_c^2\mu_B^2}[A_c + 4B \cos q_x a]^2. \quad (5.3.5)$$

These formulas are derived and discussed in Chap. 6. Here, we simply note that the  $T_{2g}$  data of Fig. 5.9(b) were analyzed with the foregoing equations to obtain the plot of  $\chi'_{AF}(T)$  shown in Fig. 5.9(a).

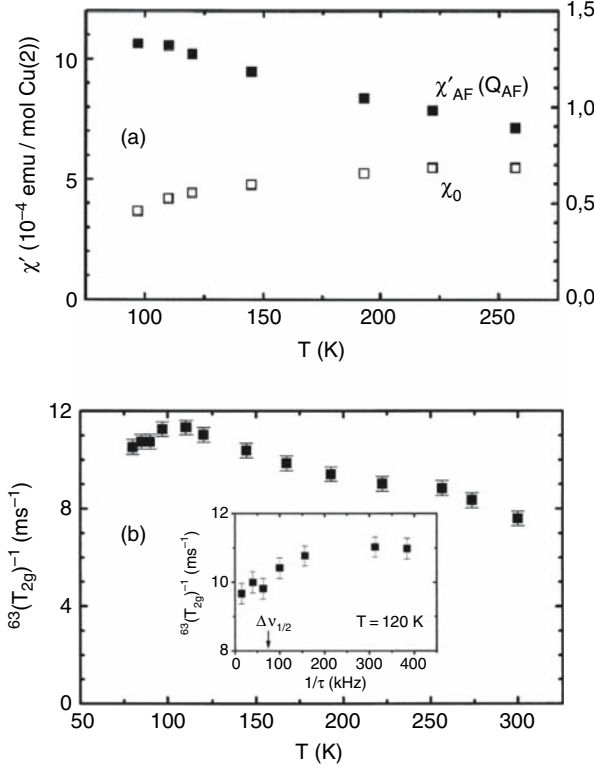


**Fig. 5.9.** (a) The susceptibilities  $\chi_0$  and  $\chi'_{AF}$  are plotted as a function of temperature.  $\chi_0$  is the uniform susceptibility, with temperature dependence and amplitude scale derived principally from  $^{89}\text{Y}$  NMR shift measurements as discussed in the text.  $\chi'_{AF}$  is the amplitude of the AFM fluctuation peak at  $Q$ . Its value as a function of temperature was derived from measurements of  $T_{2g}$  for the  $^{63}\text{Cu}(2)$  NMR line. Equations (5.3.4) and (5.3.5) were used to interpret  $T_{2g}$  data shown in part (b) of this figure. See text and Chap. 6 for more details [7]. (b) Data for  $T_{2g}$  on  $^{63}\text{Cu}(2)$  taken in the present study [7]. These data were interpreted to yield the values of  $\chi'_{AF}$  shown in part (a) of this figure. See text and Chap. 6 for more details of interpretation. The inset shows how data vary with the bandwidth of the refocussing  $\pi$ -pulse of the echo sequence, where a large bandwidth is essential to obtain accurate data. Reprinted figures from T. Auler, M. Horvatic et al, *Physica C* **313**, 255 (1999). Copyright 1999 Physica C

The final step, which is to evaluate the spin fluctuation parameters  $\Gamma_0$  and  $\Gamma_{AF}$  as functions of temperature, requires a bit more explanation. Auler et al., [7] note that the dipolar interaction makes an appreciable contribution to  $1/^{89}\text{T}_1$ , which is not taken account of by the “D” terms of the HF tensor (3.3.2). This point has been noted by Takigawa et al., [15] and was discussed briefly in Sect. 4.1.2. Auler et al., provide a separate calculation to estimate the extra dipolar relaxation terms, which behave a bit like the  $^{63}\text{Cu}(2)$  terms in that they do not cancel at  $\mathbf{q} = \mathbf{Q}$ . In evaluating  $\Gamma_0$  and  $\Gamma_{AF}$  as functions of temperature, these authors present several “options” regarding the dipolar terms. We first describe their procedure for obtaining the  $\Gamma$ ’s and then describe the options.

The values of  $\Gamma_0$  and  $\Gamma_{AF}$  are obtained by fitting the  $^{63}\text{Cu}(2)$  and  $^{89}\text{Y}$   $T_1$  data with the model susceptibility (5.3.3) with (5.3.2), using (3.5.11)-(3.5.14), i.e. the standard Mila-Rice HF Hamiltonian. As an example, these authors note that if the AFM susceptibility peak were narrow enough it would not make a significant contribution to  $1/^{89}\text{T}_1T$ , which would then be given by [7]

$$\frac{1}{^{89}\text{T}_1T} = \frac{2\hbar\gamma_{89}^2 k_B D_{ab}}{g_{ab}\mu_B \Gamma_0(T)} {}^{89}K_{ab}(T), \quad (5.3.6)$$

so that  $\Gamma_0(T)$  could be extracted directly from the data for  $^{89}K_{ab}(T)$  and  $^{89}\text{T}_1(T)$ . In practice, (5.3.6) is not a good approximation, but serves to illustrate the method. In general, one has to use the data mentioned plus  $^{63}\text{T}_1(T)$  to evaluate both  $\Gamma_0$  and  $\Gamma_{AF}$  simultaneously. For this purpose they have used values of the  $^{63}\text{Cu}(2)$  and  $^{89}\text{Y}$  HF tensors, in units of  $10^{-6} \text{ eV}$ , as follows:  $A_c = -1.56$  (-1.64),  $A_{ab} = 0.35$  (0.16);  $B = 0.39$  (0.41);  $D_{ab} = -0.0035$  (-0.0028); and  $D_c = -0.0043$  (-0.0035), where the values in parentheses are the fitted values from the UM analysis in Table 4.1 for comparison. Apart from  $A_{ab}$ , which is small and difficult to evaluate, these are all quite reasonable.

The values derived for  $\Gamma_0$  and  $\Gamma_{AF}$  are plotted in Fig. 5.10(a) and (b), respectively. The down triangles are obtained ignoring the dipolar terms altogether, while the open circles correspond to taking the dipolar terms fully into account. For the up triangles the value of  $A_{ab}$  was also increased by 25%. Our main concern here will be the open circles, which correspond to apportioning a sizeable fraction of the  $^{89}\text{Y}$  relaxation to dipolar terms.

Since the susceptibility model has an AFM peak with a temperature-independent width, the temperature dependence of the  $T_1$  data has to be accounted for by assigning the temperature variation (of  $1/T_1T$ ) to the susceptibilities  $\chi_0$  and  $\chi'_{AF}$  and to the spin-fluctuation parameters  $\Gamma_0$  and  $\Gamma_{AF}$ . The value of  $\Gamma_0$  is seen to approximately double from 250 K down to 100 K and  $\Gamma_{AF}$  to change by less than that. It is, of course, very difficult to know whether this is a reasonable scenario from the standpoint of microscopic physics, but it describes the data well enough. What is interesting is to compare this outcome with the results of the UM analysis, for which a temperature-dependent correlation length  $\xi(T)$  was employed (Sect. 5.1).

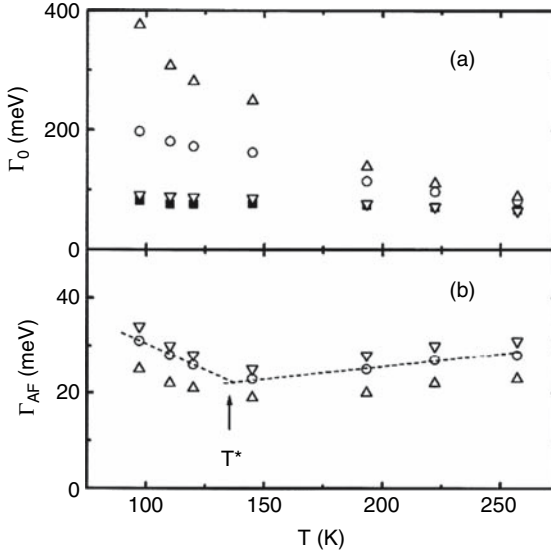


**Fig. 5.10.** (a) Values of the spin-fluctuation frequency  $\Gamma_0$  deduced from fitting the relaxation data for both  $^{63}\text{Cu}(2)$  and  $^{89}\text{Y}$  to the form for  $\chi''(\mathbf{q}, \omega)$  (5.3.3) discussed in the text. Results from the oversimplified approximation in (5.3.6) are shown as solid squares. Open circles show values obtained when the dipolar terms for the  $^{89}\text{Y}$  relaxation are taken into account, and down triangles show values obtained when they are not. The up triangles result when the dipolar terms are kept, and the value of  $A_{ab}$  is increased by 25% over that given in the text. See text for discussion. (b) Values of  $\Gamma_{AF}$  (see (5.3.3)) obtained in same way as in (a), with symbols indicating the same cases listed there. Reprinted figures from T. Auler, M. Horvatic et al, *Physica C* **313**, 255 (1999). Copyright 1999 Physica C

### 5.3.2 Comparison with the UM Analysis Results for YBCO7

To effect a comparison with the UM analysis, we use (3.5.17) and (3.5.18) to calculate  $\tau_{eff}$  and the  $\mathcal{K}_{ij}$ 's, since  $\chi''(\mathbf{q}, \omega)$  is fully specified by (5.3.3) and (5.3.2) with the parameter values in Fig. 5.9(a) and Fig. 5.10(a) and (b) (circles). For these evaluations we use the other parameter values from [7], which were stated above. We first note the contrast in parameterization of the  $\mathcal{K}_{ij}$ 's between UM and the present work. We adopt a general form

$$\mathcal{K}_{ij} = \mathcal{K}_0 g(r_{ij}/\lambda), \quad (5.3.7)$$

where  $\mathcal{K}_0$  and  $\lambda$  are both possible functions of temperature. In the UM analysis,  $\mathcal{K}_0$  was taken to be unity and  $g(r_{ij}) = \exp(-2r_{ij}/a\lambda)$ , with all temperature dependence in the correlation length  $\lambda$ . For the Gaussian  $\chi''(\mathbf{q}, \omega)$  model of Auler et al., [7], however, the width parameter  $\xi$  is fixed. The temperature variation has to reside in  $\mathcal{K}_0(T)$ . Thus, it is possible to have temperature

varying correlations even when there is a fixed correlation length. Calculations of the  $\mathcal{K}_{ij}$ 's (see below) reveal that  $\mathcal{K}_{01}(T)$  reaches a value of  $-0.47$  at 100 K and is about half that value at 250 K. These are typical numbers from the UM analysis.

For comparison purposes the quantities  $\tau_{eff}(T)$  and the  $^{63}\text{V}_\alpha$ 's have been evaluated using the model susceptibility parameters given by the analysis of Auler et al., described above. First, we evaluate  $\tau_{eff}(T)$  using (3.5.17) and (5.3.3), finding

$$\tau_{eff}(T) = \frac{\hbar k_B T}{4\mu_B^2 N_A} \left[ \frac{\chi_0}{\Gamma_0} + 0.0936 \frac{\chi'_{AF}}{\Gamma_{AF}} \right], \quad (5.3.8)$$

where the prefactor has been adjusted for susceptibilities in (emu/mole). Using the parameters from Fig. 5.9(a) and 5.10(a) and (b) (circles), we find the values plotted in Fig. 5.11(a) vs.  $T$  (open squares). For comparison, The curves of  $\tau_{eff}(T)$  for YBCO7 (open circles) and YBCO6.63 (closed circles) from the UM analyses (Fig. 5.2(b) and 5.4(a), respectively) are plotted. Recalling that the YBCO6.63 curve was “gapped”, we see that there is a remarkably close correspondence in absolute magnitudes for  $\tau_{eff}$  and that the values from the present study are definitely “gapped” as well. As we noted earlier, the NMR shift and relaxation curves showed definite signs of a spin pseudogap.

Corresponding to the foregoing expression for  $\tau_{eff}$ , we find for the  $\mathcal{K}_{ij}$ 's,

$$\mathcal{K}_{ij} = \frac{0.0936 \chi'_{AF} \Gamma_0}{\chi_0 \Gamma_{AF} + 0.0936 \chi'_{AF} \Gamma_0} [-0.745; 0.555; 0.309], \quad (5.3.9)$$

where the numbers in the brackets represent  $\mathcal{K}_{01}$ ,  $\mathcal{K}_{12}$ , and  $\mathcal{K}_{13}$ , respectively. To plot  $^{63}\text{V}_c$  and  $^{63}\text{V}_{ab}$ , this expression was used with interpolated data from Fig. 5.9(a) and 5.10(a) and (b) to calculate the  $^{63}\text{V}_\alpha$ 's shown in Fig. 5.11(b) (filled squares for  $^{63}\text{V}_c$  and filled diamonds for  $^{63}\text{V}_{ab}$ ). For comparison the same quantities for YBCO7 from the UM analysis (Fig. 5.3(a)) are plotted as solid lines. Again, considering that these materials are quite different in detail, the correspondence is remarkably close. Notice that the three  $\mathcal{K}_{ij}$ 's are in a constant ratio of  $-0.745:0.555:0.309$  at all temperatures, but their coefficient changes by about a factor two over  $100 \text{ K} \leq T \leq 250 \text{ K}$ .

It seems, then, that there may be a variety of parameterizations which will give the same form for  $\tau_{eff}(T)$  and  $^k\text{V}_\alpha(T)$ , which is all that is needed to fit the relaxation data. It follows that it will be very difficult to work backward from such data to try to determine the details of some particular parameterization, as was the case with MMP. In first-principles model theories such as those in the next two subsections, however, we suggest that it would be very useful and informative to calculate both  $\tau_{eff}$  and the  $\mathcal{K}_{ij}$ 's as diagnostics.

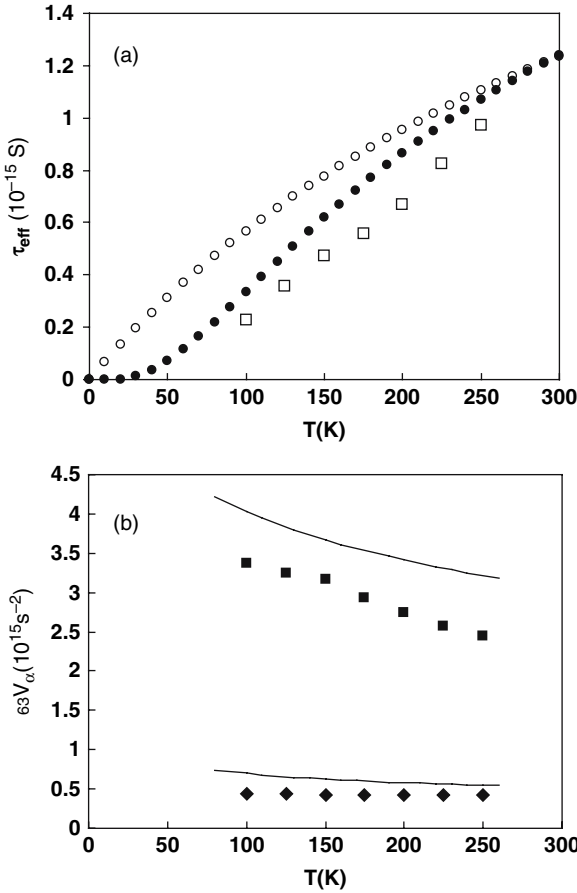


**Fig. 5.11.** (a) Data for  $\tau_{eff}(T)$  have been calculated using (5.3.8) with interpolated data from Fig. 5.9(a) and 5.10(a) and (b) (*open squares*). These are compared with plots of  $\tau_{eff}(T)$  for YBCO7 (*open circles*) and for YBCO6.63 (*dots*), which have been calculated using (4.1.17) and (4.1.19) with parameter values from Table 4.2. Comparison shows a marked similarity with a clearly gapped character for the present YBCO6.9 sample. The main difference between the present case and the UM YBCO7 fit is the marked pseudogap character of the results. (b) Plots of  $^{63}V_c$  (*filled squares*) and  $^{63}V_{ab}$  (*filled diamonds*) for the same series of temperatures shown for  $\tau_{eff}$  in part (a). These quantities have been calculated with the HF parameter values from [7] given in the text using (5.3.9). Shown for comparison are the same quantities from the YBCO7 fit by UM (Fig. 5.3(a)) (*solid lines*), where the discrepancy in both cases is a scale factor of order unity

## 5.4 A Small-U Hubbard Model of Cuprate Spin Dynamics

Extensive model calculations of NMR shift and relaxation behavior have been performed by Bulut et al. [8], using the 2D Hubbard model to represent a cuprate-like system with enhanced magnetic fluctuations near the AFM wavevector  $\mathbf{Q}$ . These calculations with the Hubbard model bear some similarity to the mean-field phenomenological model of MMP, the difference being that one is actually doing a first-principles calculation of quasiparticle dynamics using a simplified Hamiltonian and approximate methods. The up side of this is that the results of such calculations have been adapted to realistic cuprate (i.e. Mila-Rice-Shastry) HF couplings and form factors to obtain shift and relaxation behavior which is not unlike typical experimental data. If there is a down side, it is that the 2D Hubbard model, as solved in this way, presents some rather quirky behavior with certain parameters which have no clear relation to microscopic physics. There is also some “implausible fine tuning” of parameters to obtain desired behavior. The authors argue that this is simply a necessary aspect of using such a Hubbard model.

In this section we present a brief summary of Hubbard model behavior and some calculated results for the NMR shift and relaxation of  $^{63}\text{Cu}(2)$  and  $^{17}\text{O}(2,3)$  sites of YBCO7. Behavior at  $T < T_c$  has also been treated in detail with these methods. The latter results will be presented in Sects. 5.7 and 6.2, along with other model results for the superconducting state.

### 5.4.1 Basic Formulation of the Dynamic Susceptibility

The following is a summary and discussion of results for the square-lattice Hubbard model of a doped system with metallic behavior. For derivations the reader is referred to the original papers [8] and references therein. The basic Hamiltonian is

$$\mathcal{H} = -t \sum_{\langle ij \rangle \alpha} [c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}] + U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad (5.4.1)$$

consisting of nearest-neighbor hopping terms and on-site coulomb repulsion, where  $U$  is actually a renormalized interaction parameter. The basic ( $U = 0$ ) band profile has width  $W = 8t$  with a logarithmic singularity at the center. The band filling is  $0 \leq n \leq 2$  particles per site. Near half filling there are commensurate and incommensurate spin-density wave phases, which must be avoided. For the assumed ratio  $U/W = 0.25$ , the critical value is  $n_c = 0.865$ , above which there is an “unphysical phase transition” for the Hubbard model where  $U\chi(\mathbf{q}^*, 0) = 1$ . The amount by which  $n$  falls below  $n_c$  determines the temperature  $T^*$  at which the amplitude of AFM fluctuations saturates on lowering the temperature. Thus,  $n$  is only qualitatively related to the doping level parameter of the cuprate being modeled.

The basic solutions to the Hubbard model (5.4.1) are as follows: The band energy is  $\mathcal{E}(\mathbf{k}) = -2t(\cos k_x a + \cos k_y a)$  and the single-particle density of states is

$$N(\mathcal{E}) = \frac{1}{2\pi^2} K[(1 - (\mathcal{E}/4)^2)^{1/2}], \quad (5.4.2)$$

where  $K[]$  is the complete elliptic integral. The  $U = 0$  (noninteracting) susceptibility is then given by

$$\chi_0(\mathbf{q}, \omega) = \frac{1}{N} \sum_{\mathbf{p}} \frac{f(\mathcal{E}_{\mathbf{p}+\mathbf{q}}) - f(\mathcal{E}_{\mathbf{p}})}{\omega - (\mathcal{E}_{\mathbf{p}+\mathbf{q}} - \mathcal{E}_{\mathbf{p}}) + i0^+}, \quad (5.4.3)$$

where  $f(\mathcal{E}_{\mathbf{p}}) = 1/[\exp(\beta(\mathcal{E}_{\mathbf{p}} - \mu)) + 1]$  is the Fermi occupation function and  $\mu$  is the chemical potential.

For the interacting system the authors use the RPA to approximate  $\chi(\mathbf{q}, \omega)$ , giving

$$\chi(\mathbf{q}, \omega) = \frac{\chi_0(\mathbf{q}, \omega)}{1 - U\chi_0(\mathbf{q}, \omega)}, \quad (5.4.4)$$

closely analogous to (4.2.1). However, while (4.2.1) gave a peak near  $\mathbf{Q}$  which dominated the behavior of interest or could be modeled with something else, here it was pointed out that the RPA approximation (5.4.4) does not accurately render the detailed dependences of  $K(T)$  and  $1/T_1$  on  $U$  and on the band filling  $n$  [8]. The best one can hope for is to choose  $U$  and  $n$  appropriately to extract the essential features of large- $\mathbf{q}$  spin fluctuations.

If we choose a band filling  $n$  near to but less than  $n_c$ , then AFM fluctuations will grow with declining temperature down to some point  $T^*$  where their amplitude saturates.  $T^*$  is controlled by the value of  $n$ . By choosing  $U/W = 0.25$  and  $n = n_c$ , the authors presented results for a case with large AFM enhancement effects and a peak in  $\chi''(\mathbf{q}, \omega)$  near (but not precisely at)  $\mathbf{Q}$ . The calculated NMR properties then give for the shift at low temperatures

$$K = \frac{2\gamma_e}{\gamma_n} A(0) \frac{N(\mu)}{1 - U N(\mu)}, \quad (5.4.5)$$

for a HF interaction parameter  $A(\mathbf{q})$ , and for the relaxation rate

$$\frac{1}{T_1} = \frac{k_B T}{N} \sum_{\mathbf{q}} A(\mathbf{q})^2 \frac{\chi''(\mathbf{q}, \omega_0)}{\omega_0}, \quad (5.4.6)$$

where  $A(\mathbf{q})$  has the dimensions of frequency and  $\chi''(\mathbf{q}, \omega)$  of inverse energy (see (3.5.8)), and where the actual form of  $A(\mathbf{q})$  varies from site to site as usual. With the RPA susceptibility (5.4.4), (5.4.6) can be rewritten

$$\frac{1}{T_1} = \frac{k_B T}{\hbar N} \left\langle \frac{|A(\mathbf{p} - \mathbf{p}')|^2}{[1 - U\chi_0(\mathbf{p} - \mathbf{p}')]^2} \right\rangle, \quad (5.4.7)$$

where the brackets indicate that  $\mathbf{p}$  and  $\mathbf{p}'$  are to be summed over the Fermi surface.

The foregoing formalism has been used to calculate approximations to the NMR shift and relaxation behavior for  $^{63}\text{Cu}(2)$ ,  $^{17}\text{O}(2,3)$ , and  $^{89}\text{Y}$  in YBCO7. For this purpose calculations on the simple square-lattice Hubbard model have been generalized to include the effects of Cu-O hybridization in a Hubbard model of  $\text{CuO}_2$  [8]. With a 3-center unit cell, the  $\text{CuO}_2$  lattice is modeled using “partial susceptibilities”, with coulomb repulsion only on the Cu site [8].  $T_1$  calculations were presented with and without this modification and, remarkably, the differences in  $T_1$  behavior were found to be fairly subtle. Here we present some of the results for each model.

The NMR shifts at all sites undergo some Stoner enhancement according to (5.4.5), with very little temperature dependence. In Figs. 5.12 and 5.13, some of the  $T_1$  results are displayed, to be compared with experimental data for YBCO7. The bandwidth  $W$  is set at 1.2 eV, with  $U/W = 0.70$ , and  $n = 0.865$ , very near to the critical value. The field is placed along the  $c$  axis. An on-site HF coupling form has been used for both the Cu(2) and O(2,3) for the first two results shown. In Fig. 5.12(a), the relaxation curves for Cu(2) and O(2,3) are compared, where each is plotted as a fraction of its value at  $T/W = 0.025$ , which is approximately room temperature. The Cu(2) relaxation rate is seen to level off completely by room temperature, with rather more downward curvature than exhibited by the data (see Fig. 3.7), while the O(2,3) data also exhibit a slight downward curvature which is not unlike the experimental data (Fig. 4.9(a)). It seems that this extreme rollover of the Cu(2) relaxation is necessary in order to achieve the desired level of enhancement. The enhancement is shown for both Cu(2) and O(2,3) in Fig. 5.12(b), where the Korringa products  $(T_1TK^2)^{-1}$  are plotted vs.  $T$  as fractions of the noninteracting values  $(T_1TK^2)_0^{-1} = [(4\pi\hbar/k_B)(\gamma_n/\gamma_e)^2]$ . This gives an enhancement of  $\simeq 4$  for the Cu(2) and slightly greater than 1 for the O(2,3). The authors quote experimental values of 5.5 for Cu(2) and 1.4 for O(2,3) [12], in reasonable accord with their calculations. The Cu(2) enhancement, however, has declined to near the noninteracting value by just above room temperature, which is rather unlike the experimental results.

Finally, we show in Fig. 5.13 a comparison of Hubbard model calculations with experimental data for  $^{63}\text{Cu}(2)$  and  $^{17}\text{O}(2,3)$  in YBCO7. For these calculations, the simple Hubbard model results were used [8] with realistic Mila-Rice-Shastry HF coupling form factors (i.e.  $|A_{ab}/A_c| = 0.21$  and  $|B/A_c| = 0.22$ ), where we note that  $A_{ab}$  is a bit larger here than usual estimates. In this case the Hubbard model parameters were also slightly different from the foregoing, with  $U/W = 0.25$  and  $n = 0.86$  slightly below the critical value. Taken with the others, these calculations show that a fair range of  $T_1$  behaviors can be obtained with this model.

### 5.4.2 Remarks on the Hubbard Model Calculations

One must, of course, evaluate the merits of this model in terms of the time frame of its development, in which case it was obviously highly successful. This

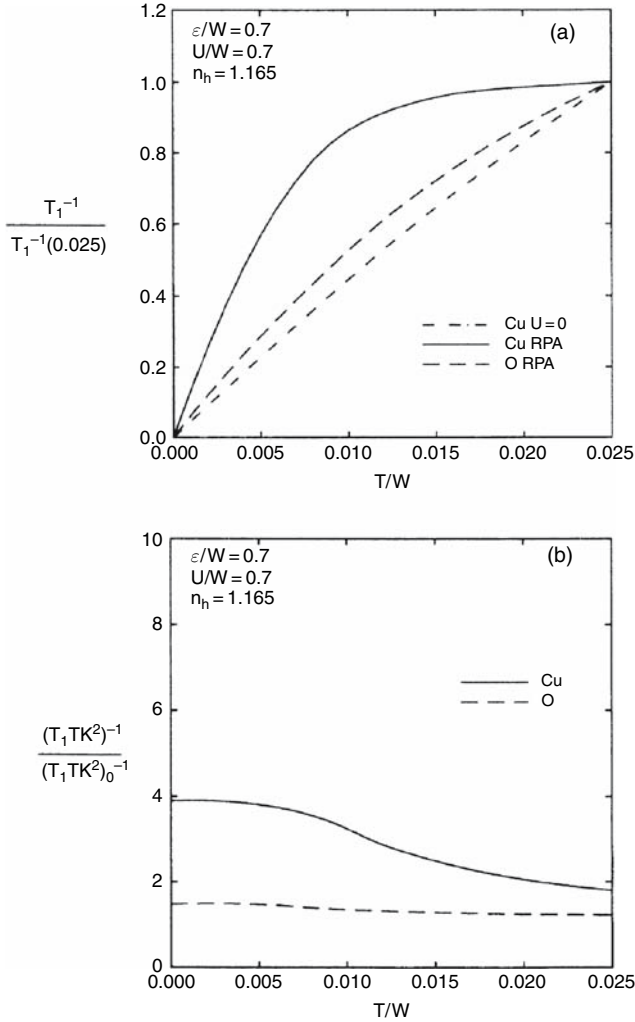


**Fig. 5.12.** (a) Relaxation rates  $1/T_1$  calculated for the Cu(2) and O(2,3) sites in YBCO7 and scaled to their values at  $T/W = 0.025$  (approx. 300 K) are plotted vs.  $T/W$ . Calculations are made with the  $\text{CuO}_2$  model described in the text and references, using on-site HF couplings. The  $U = 0$  (dashed) curves are also shown for reference. Conditions shown are  $\mathcal{E} = 0$ ,  $U/W = 0.7$ , and  $n_h = 2 - n = 1.165$ , where  $\mathcal{E}$  is the energy of the O(2p $\sigma$ ) orbitals where  $\mathcal{E}_d = 0$ , and  $n_h$  is somewhat above the critical value  $n_h = 1.135$ . (b) The Korrunga ratios for both Cu(2) and O(2,3) are plotted as a function of  $T/W$  in units of their noninteracting fermion values  $(4\pi\hbar/k_B)(\gamma_n/\gamma_e)^2$ . The low-T enhancement  $\sim 4$  for the Cu(2) has decayed most of the way to its noninteracting, high-T limit by 300 K. Reprinted figure from N. Bulut, D. W. Hone, D. J. Scalapino, and N. E. Bickers, Phys. Rev. B **41**, 1797 (1990). Copyright 1990 American Physical Society

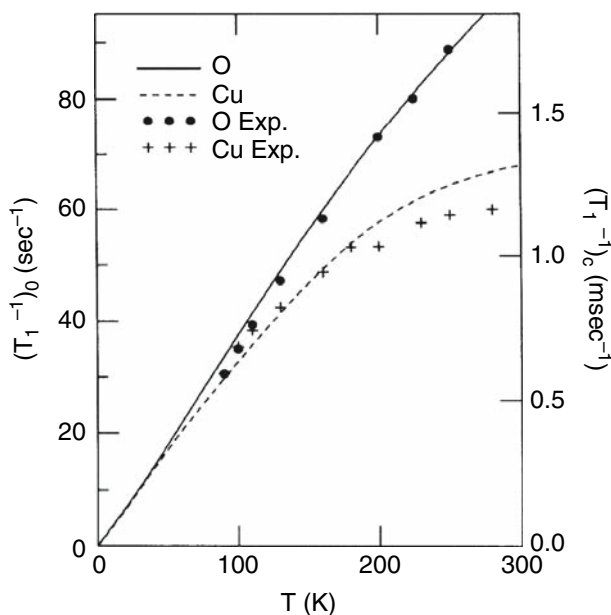


**Fig. 5.13.** Small-U Hubbard model calculations, similar to those for Fig. 5.12, have been applied to fitting  $T_1$  data, where the Mila-Rice HF tensor given in the text has been used. Calculated  $T_1$  curves have been fitted to  $^{63}\text{Cu}(2)$  (+) and  $^{17}\text{O}(2,3)$  (●) data curves from [12] and [28], respectively. The conditions are slightly different from Fig. 5.12, with  $U/W = 0.25$  and  $n = 0.86$ . Reprinted figure from N. Bulut, D. W. Hone, D. J. Scalapino, and N. E. Bickers, *Phys. Rev. Lett.* **64**, 2723 (1990). Copyright 1990 American Physical Society

is a first-principles model for the spin dynamics of superconducting cuprates which gives a remarkable facsimile of experimental behavior with a single dynamical variable. The model was also an important test for the use of suitable form factors to shield the O(2,3) sites from enhanced AFM fluctuations while the Cu(2) sites are very directly affected by them. That said, the authors note that this model probably cannot be made to give a truly quantitative account of the NMR data in the normal state. The physics of the high-temperature region is quite different from an actual cuprate, which typically approaches the degeneracy temperature not far above room temperature. The Hubbard model spin dynamics will clearly be Korringa-like up to any experimentally attainable temperature, while it seems that the cuprates are making a transition to insulator-like dynamics at high temperatures. The latter result is illustrated by the behavior of  $\tau_{\text{eff}}(T)$  for several systems in Sect. 5.1.

In spite of the apparent drawbacks, however, the authors went on to treat relaxation in the superconducting state with the Hubbard model, yielding very interesting results. The latter results are discussed in Sects. 5.7 and 6.2.

## 5.5 The Large-U Hubbard Model of Si, Levin et al

An RPA model of cuprate quasiparticle dynamics, which is of the same class of models as the MMP mean-field model [4, 5] and the small-U Hubbard model of Bulut et al., [8], has been developed and discussed extensively by Si, Levin, and co-workers [9, 29, 30, 31]. This is a 3-band Hubbard model with  $U$  essentially infinite, wherein the nearest-neighbor AFM exchange from combined  $O^{2-}$ -mediated superexchange plus RKKY sources is incorporated using the RPA approximation. Thus, it is similar to the foregoing models, except that the authors report that they have microscopically derived the Lindhard (noninteracting) susceptibility. As we shall see, this is not only a first-principles calculation, but one with entirely realistic physical parameters. Here we will comment very briefly on their results, and discuss a comparison with INS data and with  $T_1$  curves for  $^{63}\text{Cu}$  and  $^{17}\text{O}$  nuclei in the  $\text{CuO}_2$  planes. We suggest below that further calculations with this theory would be very interesting.

The interesting difference between this model and those mentioned in previous subsections is that on a decrease in doping level, the system nears a *localization transition* rather than a magnetic (AFM) one. Moreover, owing to strong coulomb correlation effects, the renormalized antibonding band narrows as the insulating limit is approached. Thus, the principal bandwidth parameter  $t_{pd} \rightarrow t_{pd}(1 - n_d)^{1/2}$ , where Mott localization occurs as the electron concentration  $n_d \rightarrow 1$ . The latter effect, then, lowers the *coherence temperature* at which Fermi liquid behavior gives way to temperature-independent relaxation. In cases under consideration, this has been estimated to occur at a few hundred Kelvin [9, 29, 30]. Evidence for such effects is clearly present in the Uldry-Meier analysis of cuprate  $T_1$  data in Sect. 5.1. For example, in Table 4.2 the effective degeneracy temperature for  $\text{YBa}_2\text{Cu}_4\text{O}_8$  (Y248) is seen to be as low as 420 K. It would be very interesting if the large-U, tight-binding, Hubbard model calculation could account for this effect.

Extensive calculations of dynamical susceptibilities have been made with the method described [31]. These results may then be compared with INS data and with  $T_1$  data for both the  $^{63}\text{Cu}$  and  $^{17}\text{O}$  nuclei in the  $\text{CuO}_2$  plane. Plots of the structure factor  $S(\mathbf{q}, \omega)$  (i.e.  $\chi''(\mathbf{q}, \omega)$ ) for two different scans in  $\mathbf{q}$  – *space* (see figure caption) are shown in Fig. 5.14(a) for YBCO7 and (b) for YBCO6.7.<sup>3</sup> These results were calculated with the expression

$$\chi_{rr'}(\mathbf{q}, \omega) = \chi_{rr'}^0(\mathbf{q}, \omega) + \frac{\chi_{rd}^0(\mathbf{q}, \omega)[-J_H(\mathbf{q})\chi_{dr'}^0(\mathbf{q}, \omega)]}{1 + J_H(\mathbf{q})\chi_{dd}^0(\mathbf{q}, \omega)}, \quad (5.5.1)$$

where the  $\chi_{rr'}$ 's are “partial susceptibilities” [32], with  $r = p$  or  $d$ ,  $\chi_{rr'}^0(\mathbf{q}, \omega)$  is the microscopically-derived Lindhard function [32], and  $J_H(\mathbf{q})$  is the composite Cu-Cu exchange coupling, which is modeled here with

<sup>3</sup> Similar results were also presented for LSCO. These are invoked in a discussion of that system in Chap. 6.

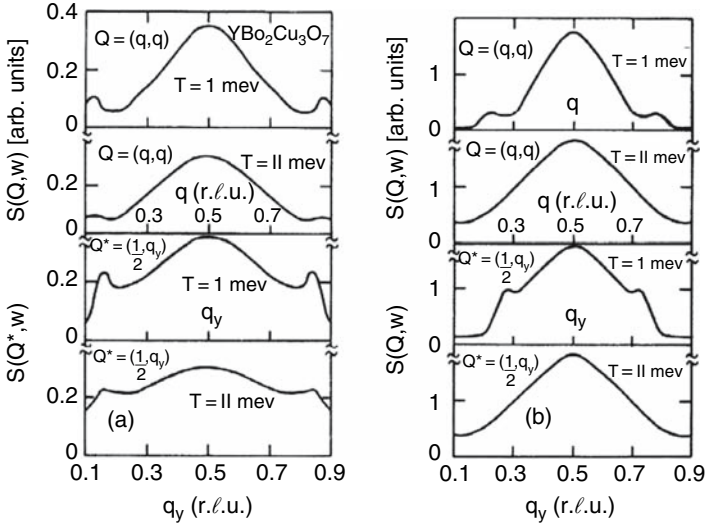


**Fig. 5.14.** (a) Cross sections of  $S(\mathbf{q}, \omega)$  for YBCO7 are shown for  $\omega = 15$  meV, first along the diagonal at  $T = 1$  meV and 11 meV, and then along the  $q_y$  axis for  $\mathbf{q} = (\frac{1}{2}, q_y)$  for the same two temperatures. (b) Cross sections of  $S(\mathbf{q}, \omega)$  for YBCO6.7 are shown for the identical set of conditions as in part (a). See the original papers for details of these calculations. Reprinted figures from Q. Si, Y. Zha, K. Levin, and J. P. Lu, Phys. Rev. B **47**, 9055 (1993). Copyright 1993 American Physical Society

$$J_H(\mathbf{q}) = J_0[\cos q_x a + \cos q_y a]. \quad (5.5.2)$$

There is a critical value  $J_0 = J_c$ , above which  $\chi_{rr'}(\mathbf{q}, \omega)$  is unstable. For YBCO7,  $J_0$  was taken to be  $0.5J_c$  and for YBCO6.7  $J_0 = 0.7J_c$ , while the doping for these two was  $x = 0.18$  and  $0.36$ , respectively. For other details we refer the reader to [31] and [32].

Referring to the theoretical scan results in Fig. 5.14, plots of  $\chi''(\mathbf{q}, \omega)$  are shown for  $T \sim 12$  K and  $T \sim 120$  K. The AFM peak is commensurate and noticeably narrower for YBCO6.7, as expected. Although the authors emphasize the constancy of these results with temperature [31], the peaks in all cases seem somewhat lower and wider at 120 K, this effect being incrementally greater for YBCO6.7. One can only imagine that at 300 K the peaks would be even wider, giving a palpable temperature dependence to the correlation lengths. Comparing these results with the INS data for reduced oxygen YBCO given by Tranquada et al., in Fig. 4.8 [23], there is some difference in peak shape, with the INS scan distinctly narrower. On the other hand, the INS crystal had a nominally lower doping level at  $x = 0.6$  with  $T_c \simeq 50$  K. The frequency of the measurement was  $\omega \sim 15$  meV, while that of the calculation is 10 meV. All in all, one would say that the correspondence is satisfactory.

The authors also use their results for  $\chi''(\mathbf{q}, \omega)$  to simulate relaxation rate curves for  $^{63}\text{Cu}$  and  $^{17}\text{O}$  as a function of temperature, using the same HF

tensors as those employed by Bulut et al., in [8]. The results are shown for both compositions in Fig. 5.15 as temperature plots up to 360 K [31]. We make the following remarks about the nature and significance of these results.

- Comparing these plots with experimental data (see Fig. 4.9), certain trends are seen to be qualitatively correct. The deviation from Korringa behavior is greater for the  $^{63}\text{Cu}$  than for the  $^{17}\text{O}$ , and greater for the YBCO6.7 than for the YBCO7.
- The amplitude trends are dramatically different from the experimental data, where for  $^{63}\text{Cu}$ , the experimental curves are intertwined so that YBCO6.7 rises above YBCO7 at  $T \sim 150\text{ K}$ , but falls below YBCO7 at room temperature. For  $^{17}\text{O}$  the curves are reversed, where experimentally (Fig. 4.9(a)),  $1/T_1 T$  for YBCO7 is relatively flat and lying above the curve for YBCO6.7, which descends to a small fraction of its room temperature value at  $T = T_c \sim 60\text{--}65\text{ K}$ .
- The latter circumstances arise, in part, because YBCO6.7 exhibits a spin pseudogap effect in which the susceptibility, as well as  $1/T_1 T$  for the  $^{17}\text{O}$ , decline at low temperatures  $\propto \exp(-\Delta/k_B T)$ , where  $\Delta/k_B = 104\text{ K}$  (see Sect. 4.1.2). The Hubbard model discussed here [31, 32] does not have this feature, so that comparison with YBCO6.7 data, especially at low temperatures, is not meaningful. A model of low-frequency spin fluctuations for the case of a pseudogap has been given by Varma [33].
- The authors have some concern that the  $^{17}\text{O}$  results are not as Korringa-like as the experimental data for YBCO7 and/or are not compatible with their calculation for  $^{63}\text{Cu}$ . The straightforward answer to this is found in the Uldry-Meier analysis of  $T_1$  data, presented in Sect. 5.1. This type

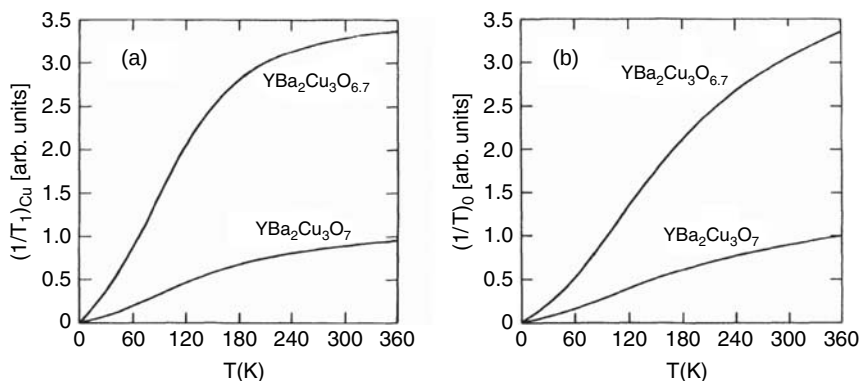


**Fig. 5.15.** (a) Relaxation rates  $1/T_1$  for  $^{63}\text{Cu}$ , calculated for both YBCO7 and YBCO6.7 using the results for  $\chi''(\mathbf{q}, \omega)$  shown in Fig. 5.14 and the HF tensor given by Bulut et al., [8], are plotted as a function of temperature [31]. (b) Similar calculated results are plotted vs.  $T$  for the case of planar  $^{17}\text{O}$ , using the same methods. Reprinted figures from Q. Si, Y. Zha, K. Levin, and J. P. Lu, Phys. Rev. B **47**, 9055 (1993). Copyright 1993 American Physical Society

of analysis was not, of course, available in the early 1990's when the Hubbard-model calculations were being developed.

The main significance of the UM analysis is that it separates the dynamical spin-spin correlations ( $\mathcal{K}_{ij}$  from (2.5.17)–(2.5.18)) from the quasiparticle dynamical function (2.5.17)  $\mathcal{X}_{at}(T) = \sum_{\mathbf{q}} [\chi''(\mathbf{q}, \omega)/\omega]_{\omega \rightarrow 0}$ . (The UM analysis uses the related parameter  $\tau_{eff}(T) = (k_B T/\hbar) \mathcal{X}_{at}(T)$ .) Given a theory for  $\chi''(\mathbf{q}, \omega)$ , then  $\mathcal{K}_{ij}$  and  $\tau_{eff}$  are straightforward quantities to evaluate. In the latter formulation, the  $^{63}\text{Cu}$  and  $^{17}\text{O}$  curves contain the same dynamical information, but very different correlation effects. The latter may be seen in Fig. 5.3(a) and (b). The experimental dynamical function for YBCO7 is shown in Fig. 5.2(b).

- Si et al., attributed the strong curvature of the  $^{63}\text{Cu}$   $1/T_1$  curve to a *coherence temperature* [29]. This may be something of a misapprehension, since the curve is strongly affected by T-dependent spin-spin correlations. The true picture of dynamical behavior with temperature would be given by  $\tau_{eff}$  vs.  $T$ . It would be most interesting to see whether this theory would provide an explanation for the flattening off of dynamical fluctuations at high temperatures, *since at the present time there is no theory for this available*. The large-U RPA model seems especially suited to this, because the band-narrowing effect with hole dilution [9] is similar to what is observed in practice (see Table 4.2).
- We further suggest that the reason for the strong deviation from Korringa-like behavior for the  $^{17}\text{O}$  in Fig. 5.15(b) is that the corresponding peak in Fig. 5.14 has much wider wings than the INS-measured peak in Fig. 4.8. This situation is a bit like the Lorentzian vs. Gaussian models by MM [5], where the Gaussian model with steeper sides gives far less contribution to the  $^{17}\text{O}(2,3)$  relaxation rate. The downward curvature of the plot of  $1/T_1$  for the  $^{17}\text{O}$  is probably mainly due to the dynamical correlation factor, leaving the impression that  $\tau_{eff}(T)$  may be nearly linear in  $T$ .
- Nonetheless, an actual evaluation of  $\tau_{eff}$  for different carrier levels would answer a very interesting question about the large-U Hubbard model, namely whether it can account for the high-temperature transition in the dynamics seen in the experimental data, such as Fig. 5.2(b) and Fig. 5.4(b).

## 5.6 Relaxation via Orbital Currents proposed by Varma

Up to this point only spin-paramagnetic  $T_1$  processes have been considered for the doped cuprate superconductors. However, in 1989 a somewhat radical idea was proposed for these systems, namely that for a certain class of charge excitations the polarizability has a term which obeys [34]

$$Im\tilde{P}(\mathbf{q}, \omega) \sim \begin{cases} -N(0)(\omega/T) & \text{for } |\omega| < T \\ -N(0) \operatorname{sgn}(\omega) & \text{for } |\omega| > T \end{cases}, \quad (5.6.1)$$

where  $N(0)$  is the one-particle density of states. Applying this marginal Fermi liquid (MFL) *ansatz* to magnetic processes at NMR frequencies  $\omega_0 \ll k_B T / \hbar$ , we have

$$\chi''_{mfl}(\mathbf{q}, \omega) = \frac{\hbar^2 N(0) \omega_0}{k_B T}, \quad (5.6.2)$$

where we have added the factor  $\hbar^2/k_B$  to make clear that this is dimensionally a correlation time.

To apply this *ansatz* to an HF perturbation process, we suppose that there is a quasiparticle interaction term  $\gamma_n H_{mfl} \mathbf{I} \cdot \mathbf{f}(\mathbf{q})$  with a (dimensionless)  $\mathbf{q}$ -dependence factor  $\mathbf{f}(\mathbf{q})$ . Then, by the usual argument ((3.5.8)–(3.5.9)) this generates a temperature-independent  $T_1$  process

$$\frac{1}{T_1} = \frac{4\gamma_n^2 H_{mfl}^2 k_B T}{\hbar} \sum_{\mathbf{q}} f_{\perp}(\mathbf{q})^2 \frac{\chi''_{mfl}(\mathbf{q}, \omega_0)}{\omega_0} = 4\hbar\gamma_n^2 H_{mfl}^2 N(0) \sum_{\mathbf{q}} f_{\perp}(\mathbf{q})^2, \quad (5.6.3)$$

where the second step used (5.6.2), and  $\hbar N(0) \sim \hbar/E_F$  is a correlation time. Such processes in metals would be very strong. It has already been noted that such a dynamic would not apply to spin fluctuation processes in cuprates.

However, it was subsequently proposed by Varma [10] that the MFL scenario could be applied to magnetic fluctuations which result from circulating orbital currents, yielding a  $T_1$  process for the Cu(2) sites. Here we review the arguments leading to an estimate given for  $^{63}\text{Cu}$  [10]. The proposed  $T_1$  mechanism would operate via the orbital HF interaction (see (2.2.1))

$$\mathcal{H}_{orb} = \mathbf{I} \cdot \mathbf{M}_{orb} = i\hbar \mathbf{I} \cdot \mathbf{L}/r^3 = i\hbar \mathbf{I} \cdot \mathbf{r} \times \nabla/r^3, \quad (5.6.4)$$

where the local angular momentum operator  $\mathbf{L}$  is associated with the Cu(2) site.  $\mathcal{H}_{orb}$  could then act to scatter quasiparticles from  $\mathbf{k} + \mathbf{q}/2$  to  $\mathbf{k} - \mathbf{q}/2$ , where the squared matrix element for the relaxation process would be summed over  $\mathbf{k}$  and  $\mathbf{q}$ . However, since the occupied  $3d$  wavefunction in the cuprates is thought to be purely  $d_{x^2-y^2}$ , the orbital HF matrix element

$$\langle \mathbf{k} + \mathbf{q}/2 | \mathbf{M}_{orb} | \mathbf{k} - \mathbf{q}/2 \rangle = \hbar \langle e^{-i\mathbf{q} \cdot \mathbf{r}} \mathcal{U}_{\mathbf{k}+\mathbf{q}/2}^*(\mathbf{r}) \frac{\mathbf{L}}{r^3} \mathcal{U}_{\mathbf{k}-\mathbf{q}/2}(\mathbf{r}) \rangle, \quad (5.6.5)$$

( $\exp[i(\mathbf{k} + \mathbf{q}/2) \cdot \mathbf{r}] \mathcal{U}_{\mathbf{k}+\mathbf{q}/2}(\mathbf{r})$  is a typical Bloch function) will have no intrasite contribution  $\sim \hbar f_{orb} \gamma_n \mu_B \langle r^{-3} \rangle$ , where  $f_{orb}$  is the orbital symmetry factor (see Fig. 2.9) and  $\langle r^{-3} \rangle \sim 6$  a.u. for  $3d$  electrons. Thus, for a  $d_{x^2-y^2}$  ground state  $f_{orb} = 0$ . It is for this reason that the conventional orbital  $T_1$  mechanism, which is often predominant in d-band metals, is absent in the cuprates.

The leading contribution to (5.6.5) will come from cross terms between the Cu(2) site and its oxygen neighbors. To show how this develops, the behavior of  $\langle \mathbf{k} + \mathbf{q}/2 | \mathbf{M}_{orb} | \mathbf{k} - \mathbf{q}/2 \rangle$  was examined [10] for  $\mathbf{k} \sim 0$  and small values of  $\mathbf{q}$ . In this limit,  $\mathcal{U}_{\mathbf{k}+\mathbf{q}/2}(\mathbf{r}) \sim \mathcal{U}_0(\mathbf{r})$  can be written

$$\mathcal{U}_0(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{i,\alpha} \mathcal{A}_{i,\alpha}(0) \phi(\mathbf{r} - \mathbf{R}_{i,\alpha}), \quad (5.6.6)$$

where  $\alpha$  is summed over the three sites in the  $\text{CuO}_2$  unit cell, and  $i$  is summed over cells. The local wavefunctions are  $\phi(\mathbf{r} - \mathbf{R}_{i,\alpha}) \sim d_{x^2-y^2}$  in a  $\text{Cu}(2)$  site and  $\sim p_\sigma = p_{x,y}$  on the oxygen neighbors. The phase factors  $\mathcal{A}_{i,\alpha}(0) = \pm 1$  must be adjusted appropriately (see [10], Fig. 1).

The principal HF fluctuations from orbital currents will be along the  $c$  axis, which we label  $z$ . Since  $L_z \phi_d(\mathbf{r}) \sim d_{xy}$  for  $\phi_{d_{x^2-y^2}}$  at the origin, one must find  $d_{xy}$ -like symmetry on the oxygen neighbors. For small  $\mathbf{q}$  the relevant term (5.6.5) becomes

$$\langle \mathbf{k} + \mathbf{q}/2 \mid M_{orb} \mid \mathbf{k} - \mathbf{q}/2 \rangle \simeq i\hbar \sum_n \mathbf{q} \cdot \langle \mathbf{r} \phi_p(\mathbf{r} - \mathbf{R}_n) \frac{L_z}{r^3} \phi_d(\mathbf{r}) \rangle, \quad (5.6.7)$$

where  $n$  is summed over the neighbors. One can then choose the term from  $\mathbf{r} \phi_p(\mathbf{r} - \mathbf{R}_n)$  which has  $xy$  symmetry to obtain a non-zero matrix element. There will evidently be a non-zero contribution from larger values of  $\mathbf{q}$  as well. On the other hand it is argued that there is no corresponding non-zero Cu-O term if the origin is placed on the oxygen site. This is fairly obvious, because at  $\mathbf{r} \sim \hat{i}x$ ,  $L_z p_x \sim p_y$ , and  $x p_y$  is orthogonal to  $d_{x^2-y^2}$ . So the orbital currents can produce a  $z$ -axis  $T_1$  fluctuation, and possibly through the apical oxygens some smaller in-plane fluctuations at the  $\text{Cu}(2)$  site, but not at the  $\text{O}(2,3)$  sites.

To estimate the strength of the corresponding  $T_1$  process, we can write the orbital dynamical structure factor, in analogy with (3.5.4)–(3.5.7), as

$$\begin{aligned} \frac{1}{T_{1orb}} &= \frac{2k_B T}{\hbar \omega_0} \frac{\gamma_{63}^2 \mu_B^2}{\hbar^2} \sum_{\mathbf{q}} \langle M_{orb}(\mathbf{q}) M_{orb}(-\mathbf{q}) \rangle_{\omega_0} \\ &= \frac{k_B T}{\hbar \omega_0} {}^{63}A_{orb}^2 \sum_{\mathbf{q}} (qa)^2 \chi''_{mfl}(\mathbf{q}, \omega_0), \end{aligned} \quad (5.6.8)$$

where  ${}^{63}A_{orb}$  is  $\gamma_{63} \mu_B / \hbar$  times the intersite matrix element from the right-hand side of (5.6.7). To obtain the final expression for  $T_{1orb}$  the MFL *ansatz* correlation time (5.6.2) is modified by replacing the effective quasiparticle scattering rate  $k_B T / \hbar$  in the denominator by  $k_B T / \hbar + 1/\tau_0$ , where  $1/\tau_0$  is a disorder-generated scattering rate of the order of tens of degrees [10]. With this change, (5.6.8) then gives

$$\frac{1}{T_{1orb}} = \hbar {}^{63}A_{orb}^2 N(0) \frac{k_B T}{k_B T + \hbar/\tau_0}. \quad (5.6.9)$$

In applying this to cuprate relaxation data, we note that for  $T > 100 \text{ K}$  (5.6.9) assumes a nearly constant value  $1/T_{1orb} \simeq \hbar {}^{63}A_{orb}^2 N(0)$ . The HF parameter  ${}^{63}A_{orb}$  is very difficult to estimate from (5.6.7). The main contribution will come from the overlap region between the  $\text{Cu}(2)$  and  $\text{O}(2,3)$  sites, and is probably 1–2 orders of magnitude smaller than the  $3d$  on-site orbital HF field (see Sect. 3.2.3 and Table 3.4)  $H_{orb} = 2\mu_B \langle r^{-3} \rangle_{3d} \sim 125 \text{ kOe} / \mu_B$ . From the UM analysis of Sect. 5.1 (Table 5.2) we estimate  $\hbar N(0) \sim \hbar / k_B T_F \simeq$

$8 \times 10^{-15} \text{ s}$  for YBCO7. In this case, taking an optimal symmetry factor  $f_{orb} = 0.6$ , we find for the maximal, on-site orbital relaxation rate

$$\left. \frac{1}{T_{1orb}} \right]_{opt} = f_{orb} \gamma_{63}^2 H_{orb}^2 \hbar N(0) = 3.8 \times 10^3 \text{ s}^{-1}. \quad (5.6.10)$$

This is  $\sim 3$  times the measured relaxation rate for YBCO7 at  $T = 100 \text{ K}$ . The rate in (5.6.9) is estimated to be a few percent of (5.6.10) at most.

Interestingly, the combination of (5.6.9) and spin-paramagnetic processes which vary as  $1/T_1 \propto T$  have been shown to give a good account of  $^{63}\text{Cu}(2)$  relaxation data for both YBCO7 and optimally-doped LSCO. These results are shown in Fig. 5.16, where they are compared with data from [13] and [35]. For the calculated curves in this figure  $1/\tau_0$  is taken to be 25 K and 100 K for YBCO7 and LSCO, respectively. The quantity  $\hbar^{63} A_{orb}^2 N(0)$  is taken to be  $\sim 3 \times 10^3 \text{ s}^{-1}$ , which is very near the estimated upper limit for an orbital contribution.

A final point has to do with how the orbital relaxation would fit into the scheme of  $T_1$  analysis described in earlier subsections of this chapter. Since the UM analysis in Sect. 5.1, for example, is internally consistent and is consistent with the Mila-Rice, spin Hamiltonian parameters derived from shift measurements in Chaps. 3 and 4, a contribution from  $1/T_{1orb}$  at the 10%

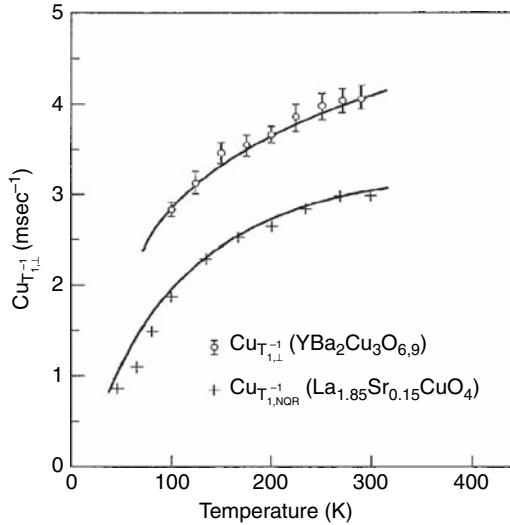


**Fig. 5.16.** Orbital relaxation rates estimated with (5.6.9) are compared with experimental data for YBCO7 [13] and optimally-doped LSCO [35] as shown. For the plotted curves  $^{63}A_{orb}^2 \hbar N(0)$  is taken to be  $3200 \text{ s}^{-1}$  and  $2800 \text{ s}^{-1}$ , and  $1/\tau_0$  is taken to be 25 K and 100 K for YBCO7 and LSCO, respectively. See text for discussion of these calculations. Reprinted figure from C. Varma, Phys. Rev. Lett. **77**, 3431 (1996). Copyright 1996 American Physical Society

level would pose no problem. To accommodate a larger contribution than that would pose something of a challenge to the internal consistency of our current thinking on  $T_1$  in the cuprates.

The presence of orbital current fluctuations in cuprates has now been verified by neutron scattering studies [36], so there is no doubt about their existence. Further, they appear to be closely associated with the pseudogap effect. Whether these fluctuations are observable via NMR (other than the well-known NMR pseudogap effects reviewed in Chap. 4) remains to be established. An important theoretical step toward further elucidation would be a serious effort to evaluate the intersite orbital matrix element in (5.6.7).

## 5.7 Relaxation of Planar $^{63}\text{Cu}$ and $^{17}\text{O}$ at $T < T_c$

In Sect. 3.6 we saw how a straightforward adaptation of the RPA susceptibility model to the BCS formulation of nuclear relaxation by Monien and Pines [3] gave a good account of the NQR  $T_1(T)$  for  $^{63}\text{Cu}(2)$  at  $T < T_c$  (YBCO7). Following that pioneering work there were important developments on the experimental side. As shown in Fig. 3.11(b), there had been a serious discrepancy between high-field NMR  $T_1$  data below  $T_c$  and that obtained with NQR. One suspected that, as was found for the  $\text{V}_3\text{X}$  compounds in Sect. 2.3.5 (see Fig. 2.13), relaxation by spin diffusion to the normal cores becomes appreciable in high fields. Thus, the precise scaling between  $T_1$  curves for  $^{63}\text{Cu}(2)$  and  $^{17}\text{O}(2,3)$  observed by Hammel et al., is strongly dependent on the applied field [12].

In an effort to determine the intrinsic relaxation times for  $^{63}\text{Cu}(2)$ , a careful study of the field dependence of  $T_1$  below  $T_c$  in YBCO7 using oriented powder samples was conducted by Martindale et al., [37]. The results are as follows: For field (i.e. quantization axis) along the  $c$  axis,  $T_1$  was measured in 8.31 T, 4.14 T, and 0 T (NQR). For field  $\perp c$  axis,  $T_1$  was measured in 8.31 and 0.45 T. Measurements were conducted at a series of temperatures  $20\text{ K} \leq T \leq 100\text{ K}$ , with the results plotted semilogarithmically in Fig. 5.17(a). For  $H_0 \parallel c$  axis, the variation of  $T_1$  with field is substantial, where at 20 K and 8 T field increases the relaxation rate by a factor  $\sim 5$ . The field dependence with the field in the  $ab$  plane is measureable, but much smaller.<sup>4</sup>

In the remainder of the discussion, then, NQR data or data taken in very low applied field will be preferred. In Fig. 5.17(b)  $1/^{63}T_{1ab}T$ , scaled to its value at  $T_c$ , is plotted semilogarithmically vs.  $T$ . It is seen to behave very nearly as

$$\frac{1}{^{63}T_{1ab}T} \simeq e^{-b(1-T/T_c)}, \quad (5.7.1)$$

---

<sup>4</sup> The authors refer to the conclusion by Redfield and Genack [38] that relaxation by diffusion to the normal cores in the vortex state is not physically viable. Further analysis of this problem by Furman and Goren seems to have restored the validity of such a  $T_1$  process [39]. Experimental evidence for it is, of course, very strong.

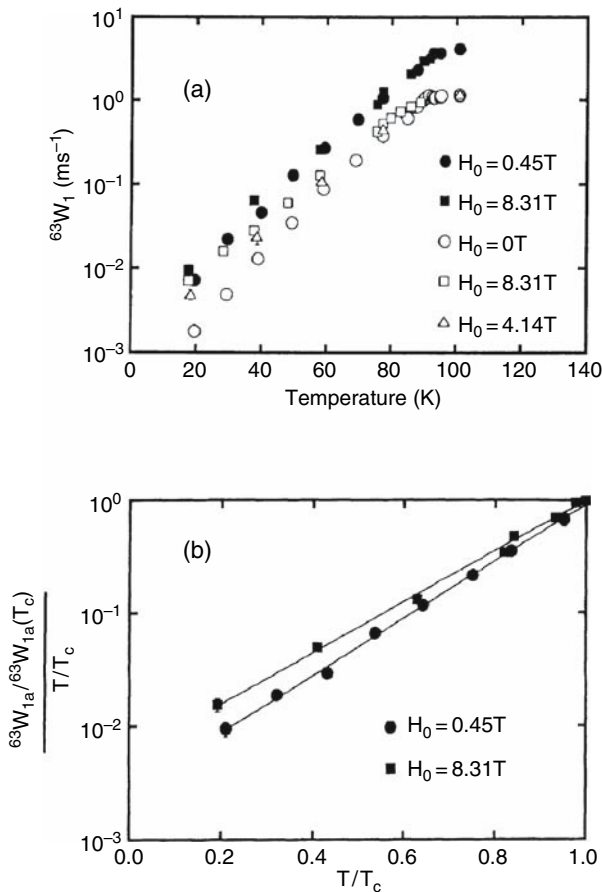


**Fig. 5.17.**  $^{63}\text{Cu}(2)$  relaxation data from the work of Martindale et al., [37]. (a) Semilog plot of  $1/T_1$  for  $^{63}\text{Cu}(2)$  ( $^{63}W_1$ ) vs.  $T$  in the range  $0 \leq T \leq 100$  K for YBCO7. Data are presented for different values of applied field, including NQR data for zero field. The open symbols show data with field (i.e., quantization axis) along the  $c$  axis, while filled symbols are for field  $\perp$  the  $c$  axis. (b) Semilog plot of  $1/T_{1ab}T$  for  $^{63}\text{Cu}(2)$  ( $^{63}W_{1a}/T$ ), normalized to its value at  $T_c$ , as a function of  $T \leq T_c$ . This plot illustrates the exponential behavior, as well as the weak field dependence of  $1/T_{1ab}T$  below  $T_c$ . Reprinted figures from J.A. Martindale, S.E. Barrett, C.A. Klug, K.E. O'Hara, S.M. DeSoto, C.P. Slichter, T.A. Friedmann, and D.M. Ginsburg, Phys. Rev. Lett. **68**, 702 (1992). Copyright 1993 American Physical Society

with  $b \sim 6$ . The  $c$  axis data exhibits similar behavior, except that it begins a bit more slowly and the coefficient  $b$  is slightly larger. Over a decline in relaxation rates of a factor  $\sim 300$ , the ratio  $^{63}T_{1ab}^{-1}/^{63}T_{1c}^{-1}$  behaves as shown in Fig. 5.19(a). To discuss the curves and data presented there, however, we must first review the calculations reported by Bulut and Scalapino [40, 41].

### 5.7.1 $\chi''(\mathbf{q}, \omega)$ for the Small-U Hubbard Model at $T < T_c$

The calculations by Bulut et al., [8] of  $T_1$  behavior in the normal state based on

$$\chi(\mathbf{q}, \omega) = \frac{\chi_0(\mathbf{q}, \omega)}{[1 - U\chi_0(\mathbf{q}, \omega)]}, \quad (5.7.2)$$

where  $U$  is the coulomb repulsion renormalized due to particle-particle correlations, is discussed at some length in Sect. 5.4. This theory was fitted to relaxation data by choosing  $U = 2t$  and band occupation number  $\langle n \rangle = 0.86$ . Their treatment of the superconducting state with these same parameter values [40, 41] is discussed in this subsection.

To model the dynamic susceptibility for  $T < T_c$ , these authors used the RPA form (5.7.2) with the “irreducible BCS susceptibility” given by [41]

$$\begin{aligned} \chi_0(\mathbf{q}, \omega) = & \frac{1}{N} \sum_{\mathbf{p}} \left[ \frac{1}{2} \left[ 1 + \frac{\mathcal{E}_{\mathbf{p}+\mathbf{q}}\mathcal{E}_{\mathbf{p}} + \Delta_{\mathbf{p}+\mathbf{q}}\Delta_{\mathbf{p}}}{E_{\mathbf{p}+\mathbf{q}}E_{\mathbf{p}}} \right] \frac{f(E_{\mathbf{p}+\mathbf{q}}) - f(E_{\mathbf{p}})}{\omega - (E_{\mathbf{p}+\mathbf{q}} - E_{\mathbf{p}}) + i\Gamma} \right. \\ & + \frac{1}{4} \left[ 1 - \frac{\mathcal{E}_{\mathbf{p}+\mathbf{q}}}{E_{\mathbf{p}+\mathbf{q}}} + \frac{\mathcal{E}_{\mathbf{p}}}{E_{\mathbf{p}}} - \frac{\mathcal{E}_{\mathbf{p}+\mathbf{q}}\mathcal{E}_{\mathbf{p}} + \Delta_{\mathbf{p}+\mathbf{q}}\Delta_{\mathbf{p}}}{E_{\mathbf{p}+\mathbf{q}}E_{\mathbf{p}}} \right] \frac{1 - f(E_{\mathbf{p}+\mathbf{q}}) - f(E_{\mathbf{p}})}{\omega + (E_{\mathbf{p}+\mathbf{q}} + E_{\mathbf{p}}) + i\Gamma} \\ & \left. - \frac{1}{4} \left[ 1 + \frac{\mathcal{E}_{\mathbf{p}+\mathbf{q}}}{E_{\mathbf{p}+\mathbf{q}}} - \frac{\mathcal{E}_{\mathbf{p}}}{E_{\mathbf{p}}} - \frac{\mathcal{E}_{\mathbf{p}+\mathbf{q}}\mathcal{E}_{\mathbf{p}} + \Delta_{\mathbf{p}+\mathbf{q}}\Delta_{\mathbf{p}}}{E_{\mathbf{p}+\mathbf{q}}E_{\mathbf{p}}} \right] \frac{1 - f(E_{\mathbf{p}+\mathbf{q}}) - f(E_{\mathbf{p}})}{\omega - (E_{\mathbf{p}+\mathbf{q}} + E_{\mathbf{p}}) + i\Gamma} \right] \end{aligned} \quad (5.7.3)$$

In (5.7.3) the dispersion relation is  $E_{\mathbf{p}} = (\mathcal{E}_{\mathbf{p}}^2 + \Delta_{\mathbf{p}}^2)^{1/2}$  and  $\mathcal{E}_{\mathbf{p}} = -2t(\cos p_x a + \cos p_y a) - \mu$ , where  $\mu$  is the chemical potential and  $\Delta_{\mathbf{p}}$  is the gap function. For  $\Delta_{\mathbf{p}}$  we will consider here the case of a d-wave form

$$\Delta_{\mathbf{p}}(T) = [\Delta_0(T)/2](\cos p_x a - \cos p_y a), \quad (5.7.4)$$

where a BCS temperature dependence is adopted for  $\Delta_0(T)$ . There is a finite broadening parameter  $\Gamma(T)$  to be specified below. Finally, the superconducting transition temperature was taken to be  $T_c = 0.1t$ , where at  $T = T_c$  the  $^{63}\text{Cu}(2)$  relaxation rate has approximately the correct value and degree of AF enhancement to correspond to YBCO7 at 100 K.

In [41] this formalism was used to treat and discuss both s-wave and d-wave gap symmetries with different choices of parameter values. Since this work was completed several years before d-wave symmetry was confirmed for the

cuprates through the observation of phase jumps at the boundaries of Josephson junctions [42, 43], at that time there were still many proponents of s-wave pairing. We shall not dwell on the s-wave case here, but will point out how convincingly the relaxation behavior argues in favor of d-wave pairing in this theory. The early work of Monien and Pines [3] discussed in Sect. 3.6 also weighed heavily on the side of d-wave.

We first look at the behavior of  $T_1$  as treated with this formalism [41]. The usual expression (4.2.7)

$$\frac{1}{T_1} = \frac{k_B T}{4\hbar} \sum_{\mathbf{q}} |A(\mathbf{q})|^2 \left[ \frac{\chi''(\mathbf{q}, \omega_0)}{\omega} \right]_{\omega \rightarrow 0} \quad (5.7.5)$$

is employed with the Mila-Rice-Shastry HF tensors (4.2.8). To see how this model distinguishes s-wave and d-wave behavior, it is useful to consider how the quantity

$$\left[ \frac{\chi''(\mathbf{q}, \omega)}{\omega} \right]_{\omega \rightarrow 0} = \frac{[\chi_0''(\mathbf{q}, \omega)/\omega]_{\omega \rightarrow 0}}{[1 - U\chi_0(\mathbf{q})]^2} \quad (5.7.6)$$

behaves with temperature in different regions of  $\mathbf{q}$ -space. For the s-wave case,  $\chi_0(\mathbf{q}, 0)$  declines for all  $\mathbf{q}$  values below  $T_c$ , so that the enhancement factor  $[1 - \chi(\mathbf{q}, 0)]^{-2}$  will decline for all HF tensors [41]. In contrast, for the d-wave case,  $\chi_0(\mathbf{q}, 0)$  is only suppressed for  $|\mathbf{q}| \leq 1/\xi_{sc}$ , where  $\xi_{sc}$  is the superconducting correlation length. The region around  $\mathbf{Q} = (\pi, \pi)$  is not suppressed because of the nodes in the gap. Thus, AFM fluctuations persist into the SC state for the d-wave case.

The other factor present in (5.7.6) is

$$D_0(\mathbf{q}) = \left[ \frac{\chi_0''(\mathbf{q}, \omega)}{\omega} \right]_{\omega \rightarrow 0}. \quad (5.7.7)$$

Fig. 5.18(a) is a plot of how  $D_0(\mathbf{q})$  varies with temperature for a very small value of  $\mathbf{q}$ , and in part (b) it is shown how it varies for  $\mathbf{q}$  near to  $\mathbf{Q}$ . In the s-wave case the two are very nearly the same, but for d-wave they are quite different. This sets up a diagnostic where if we look at the ratio of  $T_1$  values for sites which depend very differently on  $\mathbf{q}$ , there will be a large expected difference between predicted behavior for s-wave and d-wave.

### *Comparison of RPA Calculations with $T_1$ Data*

The authors have calculated and discussed  $T_1$  behavior for a number of cases of parameter values with both s-wave and d-wave gap symmetry. The contrast between these two symmetries is best displayed by taking the ratio of  $T_1$  values for cases which have different degrees of dependence on fluctuations near  $\mathbf{Q}$ , as shown in Fig. 5.18. As was clearly illustrated by Takigawa et al., [44],  $T_{1ab}$  for  $^{63}\text{Cu}(2)$  is most strongly dependent on AFM fluctuations, with a lesser

dependence for  $T_{1c}$ , and very nearly zero dependence for the oxygen  $^{17}\text{O}(2,3)$  relaxation  $T_{1O}$  (for any axis).

To illustrate the foregoing effect, calculations and experimental data were presented for  $T_{1c}/T_{1ab}$  ( $^{63}\text{Cu}(2)$  in YBCO7) [40], which we reproduce in Fig. 5.19(a). Over a range of  $\sim 3$  orders of magnitude in relaxation rates, the variation of  $T_{1c}/T_{1ab}$  is relatively slight, but has a definite signature. The data shown are the low-field measurements of Martindale et al., [37] (squares) reviewed above, and similar low-field measurements of  $T_{1ab}$  combined with low-field NMR measurements (filled circles) and NQR ( $H = 0$ ) measurements (open circles) of  $T_{1c}$  [44], which give equivalent results. The theory curves plotted for s-wave ( $2\Delta_0/k_B T_c = 4$  (dotted line) and 8 (dashed line)) are seen to drop slightly, then remain flat, since there is no real distinction between the  $D_0(\mathbf{q})$  curves (Fig. 5.18). For the d-wave case (solid curve), however, the drop and then rise reflect clearly the difference in behavior of the respective  $D_0(\mathbf{q})$  curves in Fig. 5.18(a) and (b). The observed ratio in Fig. 5.19(a) is a very clear sign in favor of d-wave gap behavior, which appeared several years before d-wave symmetry was widely accepted for the cuprates.

The ratio  $T_{1O}$  for  $^{17}\text{O}(2,3)$  to  $T_{1c}$  in Fig. 5.19(b) is also clearly supportive of d-wave symmetry. The message here is somewhat muted, owing to the fact that no low-field  $^{17}\text{O}(2,3)$   $T_1$  data were available at the time, so the entire data base for the latter plot is 7–8 T NMR data [12]. The latter circumstance would only affect behavior at the low-temperature end, however, so the comparison with theory is for the most part justified.

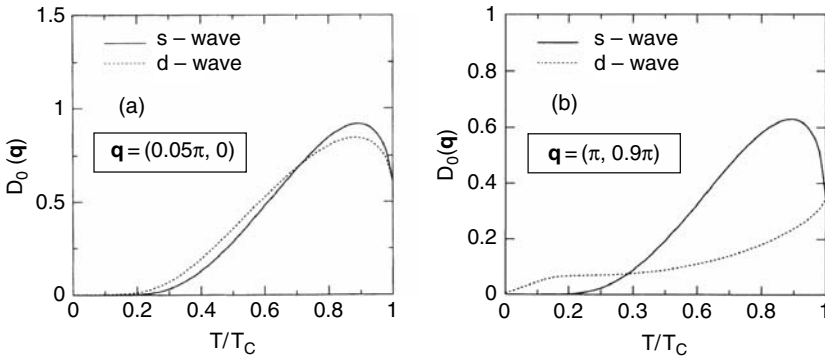


**Fig. 5.18.** (a) The quantity  $D_0(\mathbf{q})$ , defined in (5.7.7), characterizes the variation in intensity of low-energy fluctuations over the Brillouin zone. In part (a) this quantity is plotted vs.  $T/T_c$  at  $\mathbf{q} = (0.05\pi, 0)$  for s-wave and d-wave gaps as shown. Here and in part (b),  $2\Delta_0 = 3.52 k_B T_c$ , and broadening  $\Gamma = 0.3T_c$  has been used to control the coherence factor singularity. (b) The quantity  $D_0(\mathbf{q})$  is plotted for the same parameters as in part (a), except that  $\mathbf{q} = (\pi, 0.9\pi)$ . A sharp contrast between s-wave and d-wave behavior is seen to occur. Reprinted figures from N. Bulut and D. J. Scalapino, Phys. Rev. B45, 2371 (1992). Copyright 1992 American Physical Society

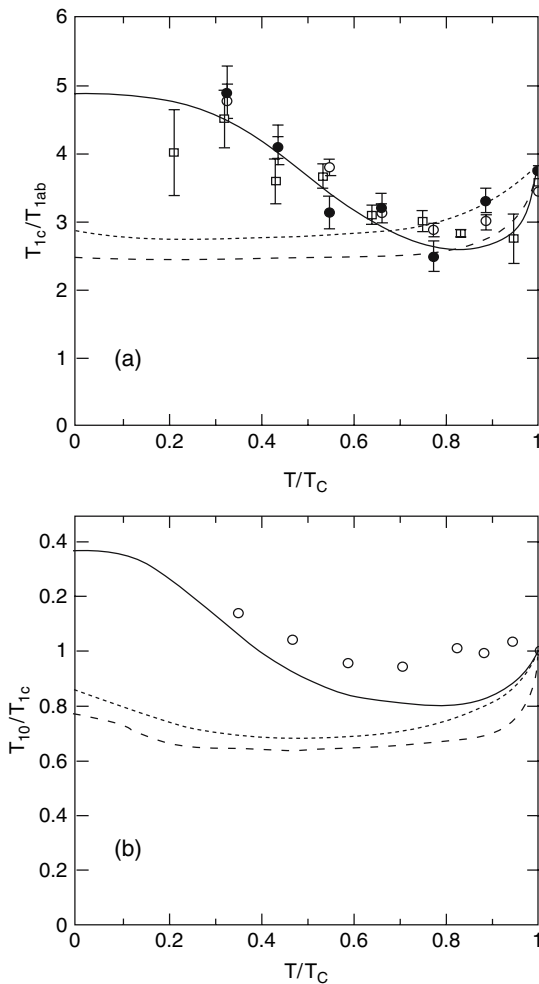


**Fig. 5.19.** (a) For  $^{63}\text{Cu}(2)$  in YBCO7, a plot of the ratio  $T_{1c}/T_{1ab}$  vs.  $T/T_c$  for temperatures in the superconducting state. The square symbols represent low-field data from Fig. 5.17 [37]. The circles are data from Takigawa et al., [44], where the open circles represent  $T_{1c}$  data taken using NQR ( $H = 0$ ) and the closed circles represent data taken in a  $c$ -axis field of 0.44 T. The data for  $T_{1ab}$  were taken in a transverse field of 0.44 T. See the text for an explanatory note on these measurements. The solid line is the calculated curve for a d-wave gap as described in the text, using  $2\Delta_0/k_B T_c = 8$ . The other lines represent calculations with an s-wave gap assuming  $2\Delta_0/k_B T_c = 4$  (dotted) and 8 (dashed), respectively. (b) The ratio of the  $^{17}\text{O}(2,3)$  relaxation time  $T_{1O}$  and  $T_{1c}$  (for  $^{63}\text{Cu}(2)$ ) is plotted vs.  $T/T_c$  as in (a), but with plotted data scaled to their value at  $T_c$ . The data are from Hammel et al., [12] and were measured in fields of 7–8 T. The calculated curves correspond to the same set of cases as in (a). Reprinted figures from N. Bulut and D. J. Scalapino, Phys. Rev. Lett. **68**, 706 (1992). Copyright 1992 American Physical Society

It is interesting to note that a simple modification of the analysis would make the displayed effect in Fig. 5.19(a) somewhat more dramatic. This is suggested by the method of  $T_1$  measurement employed by Takigawa et al., [44], in which they write

$$\frac{1}{T_{1ab}} = J_{ab} + J_c; \quad \frac{1}{T_{1c}} = 2 J_{ab}, \quad (5.7.8)$$

where the  $J_\alpha$ 's are terms corresponding to HF fluctuations along the  $\alpha$  axis.<sup>5</sup> With field applied  $\perp$  to the NQR principal axis to measure  $T_{1ab}$ , a complex set of terms occurs in the relaxation process. Thus,  $J_c(T)$  and  $J_{ab}(T)$  are actually measured separately. Compared with  $T_{1c}/T_{1ab}$ , a plot of  $J_{ab}/J_c$  [44] would show a more striking contrast between s-wave and d-wave.

Finally, it is interesting to simply compare an RPA calculation of  $T_{1c}(T)$  for  $T < T_c$  [41] with NQR data attributed to Takigawa, Smith, and Hults [44]. These results are shown in Fig. 5.20(a), where the experimental points are open circles and the calculation is shown as a solid line. The data points are seen to drop very steeply below  $T_c$ , then approach a  $T^3$  behavior (dashed line), as expected for a d-wave gap. The RPA calculation gives a very good account of this behavior [41].

### *RPA Theory for the NMR Shift below $T_c$*

Bulut and Scalapino also calculated the NMR shift behavior with their model [40, 41], which is simply given by

$$K_s(T) \propto \chi(\mathbf{q} \rightarrow 0, 0) = \frac{\chi_0(\mathbf{q} \rightarrow 0, 0)}{1 - U\chi_0(\mathbf{q} \rightarrow 0, 0)}. \quad (5.7.9)$$

There is also a temperature-independent Van Vleck shift term, which renders the zero of  $K_s(T)$  a bit uncertain. This has been subtracted off in the data plot of Fig. 5.20(b). The data shown are for  $^{63}\text{Cu}(2)$  by Barrett et al., [16] (crosses) and  $^{17}\text{O}(2,3)$  by Takigawa et al., [45, 46] (circles). All data are scaled to their total estimated excursion between  $T_c$  and 0 K. Theoretical curves are shown for  $U = 2t$  and several values of the d-wave gap parameter  $2\Delta_0/k_B T_c$ . As the authors note [41], the lowest-temperature value is very important here. If the curves had been least-squares fitted to the two sets of data, it appears that the dashed curve ( $2\Delta_0/k_B T_c = 6$ ) would have been an excellent fit.

The distinction between  $K_s(T)$  for s-wave and that for d-wave is that for d-wave the curve approaches  $T = 0$  with a finite slope, but with zero slope for s-wave [41]. The data are certainly consistent with a finite slope, although

---

<sup>5</sup> This is the same procedure as that used in the UM analysis of Sect. 5.1., where the  $U_\alpha$ 's defined there are the same as the present  $J_\alpha$ 's.

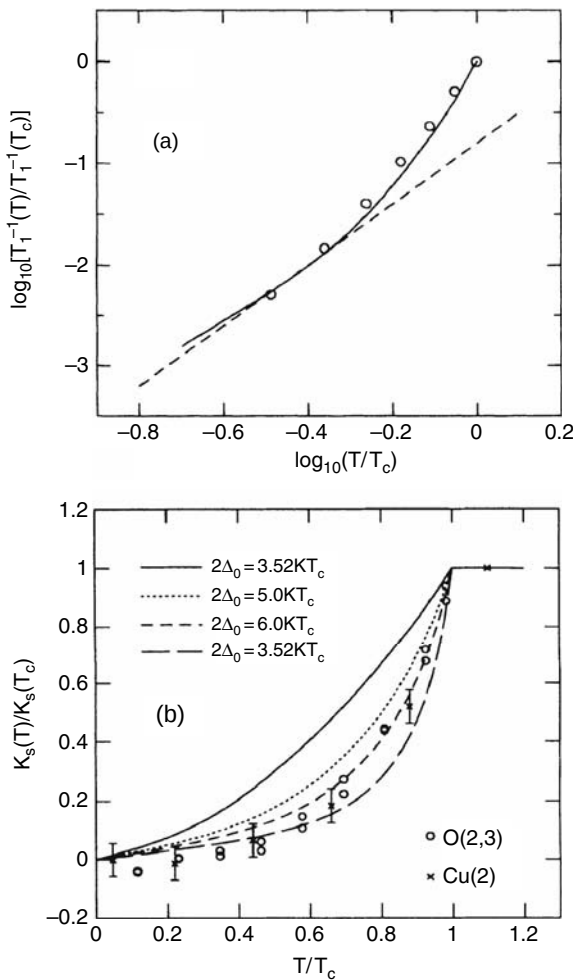


**Fig. 5.20.** (a) The  $c$ -axis relaxation rate  $T_{1c}$  for  $^{63}\text{Cu}(2)$ , scaled to its value at  $T_c$ , is plotted logarithmically vs.  $T/T_c$ . The data are attributed to Takigawa, Smith, and Hults [44]. The relaxation rate drops sharply below  $T_c$ , then falls very nearly as  $T^3$  (dashed line). The solid curve shows the RPA theory calculation for the d-wave case with  $U = 2t$  and  $2\Delta_0/k_B T_c = 8$ . (b) The behavior of the NMR shift  $K_s(T)$ , scaled to its value at  $T_c$ , is plotted for  $0 \leq T/T_c \leq 1$ . The crosses with error bars are  $^{63}\text{Cu}(2)$  data from Barrett et al., [16], and the open circles are  $^{17}\text{O}(2,3)$  data from Takigawa et al., [45, 46]. The lines plotted are calculations for a d-wave gap with  $U = 2t$  and various values of  $\Delta_0$  as shown. Reprinted figures from N. Bulut and D. J. Scalapino, Phys. Rev. B **45**, 2371 (1992). Copyright 1992 American Physical Society

the scatter is large enough so that s-wave is not ruled out. All in all, the shift results are a nice complement to the  $T_1$  data. The two together make a very strong case for d-wave symmetry.

### 5.7.2 $T_1$ and Spin-Spin Correlations below $T_c$ : The UM Analysis

In this final subsection we consider the behavior of  $T_1$  below  $T_c$  from another standpoint, one which does not employ any particular microscopic model of the spin dynamics, but relies only on the general formulation of the  $T_1$  process involving  $\chi''(\mathbf{q}, \omega)$  and the Mila-Rice HF Hamiltonian (3.3.2) (see Sect. 3.5.3). This, of course, is the basic premise of the Uldry-Meier analysis of cuprate  $T_1$  data presented in Sect. 5.1. These authors and co-workers have also employed this approach to discuss the behavior of spin-spin correlations above and below  $T_c$  and have come to two remarkable conclusions [47]. First, they find that in-plane spin-spin correlations vanish as  $T \rightarrow 0$  in a fashion roughly symmetrical to how they vanish at high temperatures. Secondly, they give evidence that it is only the in-plane correlations which vanish, while the  $c$ -axis correlations remain basically unchanged below  $T_c$ .

To review the UM formulation, relaxation of the  $k^{th}$  nuclear spin species quantized along the  $\alpha$  axis is written (see Sect. 5.1)

$$\frac{1}{kT_{1\alpha}(T)} = [{}^kV_\beta(T) + {}^kV_\gamma(T)] \tau_{eff}(T), \quad (5.7.10)$$

where  $(\alpha, \beta, \gamma)$  are a permutation of the axes (a,b,c) and  ${}^kV_\alpha(T)$  is expressed in terms of the HF constants and the correlation functions  $\mathcal{K}_{ij}^\alpha(T)$ . For example, for  $^{17}\text{O}(2,3)$  one has

$${}^{17}V_\alpha(T) = \frac{1}{2\hbar^2} C_\alpha^2 [1 + \mathcal{K}_{01}^\alpha(T)], \quad (5.7.11)$$

where we emphasize that the  $\mathcal{K}_{ij}^\alpha$  were allowed to be anisotropic. For YBCO7 it was found, for example, that the  $\mathcal{K}_{ij}^c$  were  $\sim 20\%$  larger than the  $\mathcal{K}_{ij}^{ab}$  (see Fig. 5.2(a)).

#### *Behavior of ab Plane Correlations*

In this same notation we also have (5.1.4)

$${}^{63}V_\alpha(T) = \frac{1}{4\hbar^2} [A_\alpha^2 + 4B^2 + 8A_\alpha B \mathcal{K}_{01}^\alpha(T) + 8B^2 \mathcal{K}_{12}^\alpha(T) + 4B^2 \mathcal{K}_{13}^\alpha(T)]. \quad (5.7.12)$$

Thus,

$$\frac{{}^{17}T_{1c}}{{}^{63}T_{1c}} = \frac{2 {}^{63}V_{ab}(T)}{{}^{17}V_a(T) + {}^{17}V_b(T)} \xrightarrow{\mathcal{K}_{ij} \rightarrow 0} \frac{A_{ab}^2 + 4B^2}{C_a^2 + C_b^2} \quad (5.7.13)$$

is purely a function of in-plane correlations, approaching the value on the right as they vanish.

Several sets of low-field data for  $^{17}T_{1c}/^{63}T_{1c}$  are plotted in Fig. 5.21(a) as a function of  $T/T_c$  for  $0 \leq T/T_c \leq 4.5$  for YBCO7 [17, 48, 49, 50] (see figure caption for details) and for Y248 [51]. Since the only temperature dependence for this ratio comes from the  $\mathcal{K}_{ij}(T)$ 's, what the figure shows is that correlations are small at the highest temperature, grow as  $T$  is reduced until they reach a peak value  $\mathcal{K}_{01}^{ab}(T_c) \sim -0.4$ , and then decline again toward zero at low temperatures. The dashed line in this plot shows the value of  $^{17}T_{1c}/^{63}T_{1c}$  for  $\mathcal{K}_{ij}^{ab} = 0$  (5.7.13), evaluated with numbers from the UM fit to YBCO7 data (Table 5.1). This line is seen to be in very good agreement with the high and low-temperature limiting values of the experimental  $T_1$  ratio.

The shaded triangles in Fig. 5.21(a) show the same plot for Y248, taken from the results of Bankay et al., [51]. There we see that the correlation effects are more than twice as great as in YBCO7 and do not seem to be very much affected by the spin pseudogap, which has quite a powerful effect on  $\tau_{eff}$  for this compound. It follows that the  $\mathcal{K}_{ij}^{ab}(T)$ 's are not much affected.

### *Behavior of c-axis Correlations*

The foregoing results show that the ab-plane correlations  $\mathcal{K}_{ij}^{ab}(T)$  are strongly peaked at  $T_c$  in these systems and vanish at low temperatures  $T \ll T_c$ . However, if one looks at the ratio  $T_{1c}/T_{1ab}$  for  $^{63}\text{Cu}(2)$ , the value of  $T_{1ab}$  is strongly dominated by  $c$ -axis fluctuations, for which  $^{63}V_\alpha(T)$  is markedly dependent on  $\mathcal{K}_{ij}^c(T)$ . What Uldry et al., found is that  $^{63}V_\alpha(T)$  behaves as though the  $\mathcal{K}_{ij}^c(T)$  do not change appreciably below  $T_c$  [47]. Data for  $T_{1c}/T_{1ab}$  vs.  $T/T_c$  are plotted in Fig. 5.21(b), showing the variation of this ratio for both YBCO7 and Y248 [51]. Both sets of data were measured in low magnetic fields. In the normal state  $T_{1c}/T_{1ab}$  is fairly flat for both of these compounds, with a value  $\sim 3.7$  for YBCO7 and  $\sim 3.3$  for Y248. Below  $T_c$  the data decline slightly, then rise to new maximum values, Y248 slightly higher than YBCO7.

To discuss these data we use

$$\frac{T_{1c}}{T_{1ab}} = \frac{1}{2} \left[ 1 + \frac{^{63}V_c(T)}{^{63}V_{ab}(T)} \right]. \quad (5.7.14)$$

Data for  $T_{2G}$ , to be defined and discussed in Chap. 6, suggest that  $c$ -axis correlations do not change much below  $T_c$  [47]. If that were true, then the  $T_1$  ratio in (5.7.14) will have the value  $\frac{1}{2}[1 + ^{63}V_c(T_c)/^{63}V_{ab}(T_c)]$  at  $T_c$  and the value  $\frac{1}{2}[1 + ^{63}V_c(0)/^{63}V_{ab}(T_c)]$  at  $T = 0$ . For YBCO7, these values are obtained from the fits and parameter plots from the original UM paper [11] (see Table 5.1 and Fig. 5.3). The resulting ratio values are plotted in Fig. 5.21(b) (open circles), where they are seen to be in good agreement with the YBCO7 data.

To evaluate  $T_{1c}/T_{1ab}$  for Y248 one needs a special procedure, because the magnitude of the correlations at  $T_c$  is not known from experimental data. The asymptotic, high-temperature value of  $T_{1c}/T_{1ab} \simeq 3.3$  for  $^{63}\text{Cu}(2)$  was obtained from the measurements of Bankay et al., [52]. However, it seems

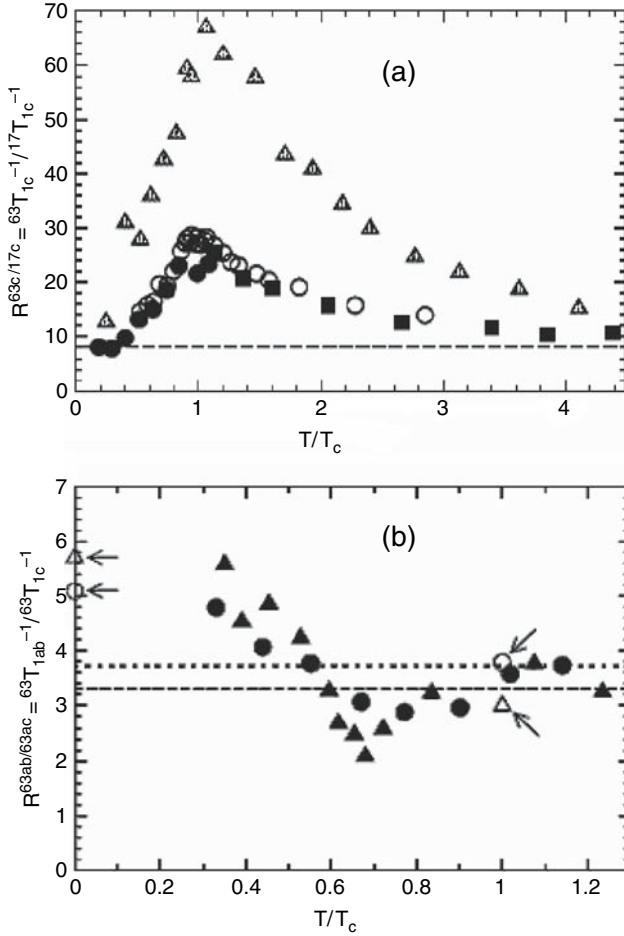


**Fig. 5.21.** (a) The ratio of  $^{17}\text{O}(2,3)$  to  $^{63}\text{Cu}(2)$   $T_{1c}$  values is plotted vs.  $T/T_c$  for YBCO (squares and circles) and for Y248 (*shaded triangles*). For YBCO7 the open circles are high-field data from Yoshinari et al., [48], and filled circles are low-field data from Martindale et al., [49]. The filled squares denote data points where  $^{63}\text{Cu}(2)$  data from Barrett et al., [50] are combined with  $^{17}\text{O}(2,3)$  data from Nandor et al., [17]. The Y248 data are high-field  $^{17}\text{O}(2,3)$  data combined with NQR data for  $^{63}\text{Cu}(2)$ , both from Bankay et al., [52]. The dashed line is the model prediction for vanishing transverse AFM correlations ( $\mathcal{K}_{01}^{ab} = 0$ ). (b) The ratio  $T_{1c}/T_{1ab}$  for  $^{63}\text{Cu}(2)$  is plotted vs.  $T/T_c$  for YBCO7 (*filled circles*) and for Y248 (*filled triangles*). The YBCO7 data are low-field data from Takigawa et al., [44] and the Y248 data are low-field data from Bankay et al., [52]. The dotted and dashed lines are normal state ratios from the same sources for YBCO7 and Y248, respectively. The open symbols are corresponding predictions from UM model calculations at  $T_c$  and at 0 K, which are obtained as described in the text. Reprinted figures from A. Uldry, M. Mali, J. Roos, and P. F. Meier, J. Phys. Condens. Matter **17**, L499 (2005). Copyright 2005 I.O.P

unlikely that this corresponds to  $\mathcal{K}_{ij}^\alpha \sim 0$ . From fit results for YBCO7 [11], if  $\mathcal{K}_{ij}^\alpha = 0$ , one has  $T_{1c}/T_{1ab} \simeq 2.75$ . For Y248, then, the values of  $\mathcal{K}_{01}^\alpha$  were estimated from the fit values for YBCO6.63, arguing that these two compounds have similar carrier densities and pseudogaps. Taking  $\mathcal{K}_{01}^{ab}(T_c) \simeq -0.53$  and  $\mathcal{K}_{01}^c(T_c) \simeq -0.61$  from data fits for YBCO6.63 [11], they obtained

$$\left. \frac{T_{1c}}{T_{1ab}} \right]_{T=T_c} \simeq 3.00; \quad \left. \frac{T_{1c}}{T_{1ab}} \right]_{T=0} \simeq 5.78. \quad (5.7.15)$$

These approximate values are plotted in Fig. 5.21(b) as open triangles, and are seen to correspond well with the data [47].

The point here is, of course, that these results give good evidence that the  $c$ -axis correlations do not decay at low temperatures. If the  $c$ -axis correlations decay to zero as  $T \rightarrow 0$ , then according to (5.7.14)  $T_{1c}/T_{1ab} \rightarrow 2.75$  in Fig. 5.21(b) for both compounds. This value is below the dashed and dotted lines and is not in good accord with the data.

Comparing this discussion with the analysis given by Bulut and Scalapino in Sect. 5.7.1, their Hubbard model gives a functional form for  $\chi''(\mathbf{q}, \omega)$  at low frequencies at  $T < T_c$  which they have used *in effect* to evaluate the  $\mathcal{K}_{ij}^\alpha(T)$  (see (3.5.17) and (3.5.18)), and thus the behavior of  $T_{1c}/T_{1ab}$  vs.  $T$ , etc. The major difference with the present analysis by Uldry et al., [47] is that  $\chi''(\mathbf{q}, \omega)$  for the Hubbard model is *isotropic and would not predict the anisotropic correlation effects seen here*. Further, the Hubbard model with  $d$ -wave symmetry does not inhibit AFM correlations in the superconducting state. As we have seen from the analysis of this subsection, only the  $c$ -axis correlations survive below  $T_c$ , with in-plane correlations declining to zero as  $T \rightarrow 0$ . Thus, with the simple analytic method pioneered by Uldry and Meier, important effects have been uncovered which might never have seen the light of day through the usual process of theoretical modeling.

## References

1. F. Mila, T.M. Rice, Physica C **157**, 561 (1989) 159, 161, 173
2. B.S. Shastry, Phys. Rev. Lett. **63**, 1288 (1989) 159
3. H. Monien, D. Pines, Phys. Rev. B **41**, 6297 (1990) 159, 199, 202
4. A.J. Millis, H. Monien, D. Pines, Phys. Rev. B **42**, 167 (1990) 159, 172, 173, 192
5. A.J. Millis, H. Monien, Phys. Rev. B **45**, 3059 (1992) 159, 172, 173, 174, 175, 178, 179, 192, 193
6. M. Horvatić, C. Berthier, Y. Berthier, et al., Phys. Rev. B **48**, 13848 (1993) 159
7. T. Auler, M. Horvatic, et al., Physica C **313**, 255 (1999) 160, 166, 179, 180, 181, 182, 183, 184
8. N. Bulut, D.W. Hone, et al., Phys. Rev. B **41**, 1797 (1990); Phys. Rev. Lett. **64**, 2723 (1990) 160, 187, 188, 189, 192, 194, 201
9. J.P. Lu, Q. Si, J.H. Kim, K. Levin, Phys. Rev. Lett. **65**, 2466 (1990) 160, 192, 195
10. C.M. Varma, Phys. Rev. Lett. **77**, 3431 (1996) 160, 196, 197
11. A. Uldry and P.F. Meier, Phys. Rev. B **72**, 094508 (2005) 160, 166, 208, 210
12. P.C. Hammel, M. Takigawa, et al., Phys. Rev. Lett. **63**, 1992 (1989) 161, 162, 189, 191, 199

13. R.E. Walstedt, W.W. Warren, Jr., et al., Phys. Rev. B**40**, 2572 (1989) 161, 162, 198
14. J.A. Martindale, P.C. Hammel, et al., Phys. Rev. B**57**, 11769 (1998) 161, 162
15. M. Takigawa, W.L. Hults, J.L. Smith, Phys. Rev. Lett. **71**, 2650 (1993) 161, 162, 166, 178,
16. S.E. Barrett, D.J. Durand, et al., Phys. Rev. B**41**, 6283 (1990) 162, 205, 206
17. V. Nandor, et al., Phys. Rev. B**60**, 6907 (1999) 162, 164, 166, 208, 209
18. V. Barzykin, D. Pines, Phys. Rev. B**52**, 13585 (1995) 164
19. D. Pines, C.P. Slichter, Phys. Rev. **100**, 1014 (1955) 166
20. F. Raffa, T. Ohno, et al., Phys. Rev. Lett. **81**, 5192 (1998) 169, 172
21. N. Curro, T. Imai, C.P. Slichter, B. Dabrowski, Phys. Rev. B**56**, 877 (1997) 169, 172
22. I. Tomeno, T. Machi, et al., Phys. Rev. B**49**, 15327 (1994) 169, 172
23. J.M. Tranquada, et al., Phys. Rev. B**46**, 5561 (1992) 175, 179, 193
24. L.P. Regnault, et al., Physica C **235-240**, 59 (1994); Physica B **213-214**, 48 (1995) 179
25. J. Rossat-Mignod, et al., Physica B **192**, 109 (1993) 179
26. B.J. Sternleib, et al., Phys. Rev. B**47**, 5320 (1993); Phys. Rev. B**50**, 12915 (1994) 179
27. M. Horvatić, C. Berthier, Y. Berthier, et al., Phys. Rev. B**48**, 13848 (1993) 179
28. M. Takigawa, P.C. Hammel, et al., Physica (Amsterdam) **162-164C**, 853 (1989) 191
29. Q. Si, J.H. Kim, J.P. Lu, K. Levin, Phys. Rev. B**42**, 1033 (1990) 192, 195
30. Q. Si, K. Levin, Phys. Rev. B**44**, 4727 (1991) 192
31. Q. Si, Y. Zha, K. Levin, J.P. Lu, Phys. Rev. B**47**, 9055 (1993) 192, 193, 194
32. Q. Si, J.P. Lu, K. Levin, Phys. Rev. B**45**, 4930 (1992) 192, 193, 194
33. C.M. Varma, Phys. Rev. B**73**, 155113 (2006) 194
34. C.M. Varma, P. Littlewood, et al., Phys. Rev. Lett. **63**, 1996 (1989) 195
35. R.E. Walstedt, B.S. Shastry, S.-W. Cheong, Phys. Rev. Lett. **72**, 3610 (1994) 198
36. B. Fauqué, et al., Phys. Rev. Lett. **97**, 197001 (2006) 199
37. J.A. Martindale, et al., Phys. Rev. Lett. **68**, 702 (1992) 199, 200, 203, 204
38. A.Z. Genack, A.G. Redfield, Phys. Rev. Lett. **31**, 1204 (1973) 199
39. G.B. Furman, S.D. Goren, Phys. Rev. B**68**, 064402 (2003) 199
40. N. Bulut, D.J. Scalapino, Phys. Rev. Lett. **68**, 706 (1992) 201, 203, 205
41. N. Bulut, D.J. Scalapino, Phys. Rev. B**45**, 2371 (1992) 201, 202, 205
42. J. Kirtley, C.C. Tsuei, et al., Nature (London) **373**, 225 (1995) 202
43. D.H. Wollman, D.J. van Harlingen, et al., Phys. Rev. Lett. **74**, 797 (1995) 202
44. M. Takigawa, J.L. Smith, W.L. Hults, Phys. Rev. B**44**, 7764 (1991) 202, 203, 204, 205, 206,
45. M. Takigawa, P.C. Hammel, R.H. Heffner, Z. Fisk, Phys. Rev. B**39**, 7371 (1989) 205, 206
46. M. Takigawa, P.C. Hammel, et al., Physica (Amsterdam) **162-164C**, 853 (1989) 205, 206
47. A. Uldry, M. Mali, J. Roos, P.F. Meier, J. Phys. Condens. Matter **17**, L499 (2005) 207, 208, 210
48. K. Yoshimura, T. Imai, et al., J. Phys. Soc. Japan **58**, 3057 (1989) 208, 209
49. J.A. Martindale, S.E. Barrett, et al., Phys. Rev. B**47**, R9155 (1993) 208, 209
50. S.E. Barrett, J.A. Martindale, et al., Phys. Rev. Lett. **66**, 108 (1991) 208, 209
51. M. Bankay, M. Mali, J. Roos, D. Brinkmann, Phys. Rev. B**50**, 6416 (1994) 208
52. M. Bankay, M. Mali, et al., Phys. Rev. B**46**, R11228 (1992) 208, 209

*This page intentionally blank*

## Dynamic Susceptibility Studies for the Cuprates

In Chap. 3 and 5 we saw how the dynamic susceptibility has come to play a pivotal role in interpreting cuprate spin-lattice relaxation data and rationalizing the sharp contrasts in  $T_1$  behavior among sites in and near the  $\text{CuO}_2$  planes. The principal driving force in all of the magnetic phenomenology of the cuprates is clearly the AFM fluctuation peak at or near  $\mathbf{Q} = (\pi, \pi)$ , which occurs in varying degrees of dominance depending in an inverse fashion on the degree of carrier doping. This scenario appears to be a unique property of doped Mott insulators.

A second consequence of strong AFM fluctuation effects is the indirect spin-spin coupling between neighboring nuclear spins which is thereby induced. This effect was recognized early on by Pennington et al., [1], shortly after which the Pennington-Slichter (PS) theory of indirect spin-spin coupling appeared, formulating this effect in terms of the static,  $\mathbf{q}$ -dependent susceptibility  $\chi'(\mathbf{q}, 0)$ . Equally important was the recognition that these couplings were responsible for a Gaussian spin-echo decay ( $T_{2g}$ ) process which, with due care, could be measured experimentally [2]. In the first section of this chapter we review the PS formulation and survey a range of experimental cuprate results and interpretations.

The importance of indirect spin-spin couplings for cuprate magnetism research is that  $T_{2g}(T)$  offers a second method of characterizing  $\chi(\mathbf{q}, \omega)$ .  $T_{2g}$  has been shown (and we document in Sect. 6.1) to be a fairly direct measure of the key parameter  $\chi'(\mathbf{Q})$ . It soon became *de rigueur* to measure  $T_{2g}$  as well as the NMR shift and  $T_1$  in a cuprate NMR study. In this chapter we illustrate why this is the case.

The connection between  $\chi''(\mathbf{q}, \omega)$  and  $\chi'(\mathbf{q}, 0)$  is the rather tenuous one through the Kramers-Kronig (KK) relation. It is, of course, not tenuous in principle, but difficult to implement experimentally, because it requires the entire frequency spectrum of  $\chi''(\mathbf{q}, \omega)$ . In theoretical modeling,  $T_{2g}$  through the KK relation becomes a constraint on model parameters. For example, Bulut and Scalapino have extended their calculations of dynamical properties using a small-U Hubbard model to the case of indirect spin-spin coupling ( $T_{2g}$ )

in the superconducting state. When compared with the data of Ohsugi et al., [3], the result was a dramatic confirmation of d-wave gap structure below  $T_c$  for Y248. We review these developments at the end of Sect. 6.1.

For a purely experimental implementation of the KK relation we turn to the case of optimally doped LSCO:  $x \sim 0.15$ . For this system there has been an INS characterization of  $\chi''(\mathbf{q}, \omega)$  for effectively all  $\mathbf{q}$  values (in the first BZ) and for all frequencies for which there is a substantial contribution. Moreover, the latter characterization is in absolute units, leading to a direct comparison between INS and  $T_1$  data with no adjustable parameters. The story of this first-ever quantitative juxtaposition of quantitative INS and NMR data is recounted in detail in Sect. 6.2. A closely-related  $T_2$  study for both  $^{63,65}\text{Cu}$  and  $^{17}\text{O}$  is included as well, where a successful implementation of the KK integral has been reported. The points where INS and NMR data are clearly incompatible is also an interesting part of the story.

An interesting interconnection between  $T_1$ ,  $T_{2g}$ , and the dynamic susceptibility components has been created by the dynamic scaling theories of Pines and co-workers. This topic is addressed in Sect. 6.4, where in the limit of long AFM correlation lengths  $\xi$  the two parameters  $\xi(T)$  and the spin fluctuation frequency  $\omega_{sf}(T)$  appear to control the dynamical properties accessible to the NMR probe. In this context a high-temperature investigation of  $^{63}\text{Cu}(2)$  static and dynamic NMR/NQR properties of  $\text{YBa}_2\text{Cu}_4\text{O}_8$  (Y248) by Curro et al., [4] has given evidence for a sharply-defined crossover temperature ( $\sim 500\text{ K}$ ) for the dynamical exponent ( $z = 1 \rightarrow 2$ ) in this system. These interesting developments are reviewed in detail, as well as suggestions for extension to other systems.

## 6.1 The Indirect Spin-Spin Coupling Theory of Pennington and Slichter

Indirect couplings between nuclear spins are very strong in the cuprates [1]. As was first demonstrated by Pennington and Slichter [2], these can be formulated in terms of the real part of the dynamic susceptibility  $\chi'(\mathbf{q}, 0)$ .  $\chi'(\mathbf{q}, 0)$  can, in turn, be expressed in terms of  $\chi''(\mathbf{q}, \omega)$ , so the estimation of  $\chi'(\mathbf{q}, \omega)$  ( $\omega = 0$ ) through measurements of the spin-echo  $T_2$  make the indirect couplings a powerful element in the NMR methodology for solids. In this section we give the derivation of the Pennington-Slichter result, which is straightforward, after which various applications of this result will be presented throughout the chapter.

There are indirect couplings between any pair of neighboring nuclei in (or near) the  $\text{CuO}_2$  plane. We shall begin with the pertinent example of interactions among the  $^{63,65}\text{Cu}$  nuclear spins. Although  $T_1$  can be formulated in terms of  $\chi''(\mathbf{q}, \omega)$  having the dimension of inverse energy (see discussion in Sect. 3.5), here we will use susceptibilities per mole, since  $\chi'(\mathbf{q}, \omega)$  becomes the measurable uniform, static susceptibility at  $\omega = 0$ . We calculate the indirect coupling

of a  $^{63}\text{Cu}$  with surrounding  $^{63,65}\text{Cu}$  spins, an effect which is mediated via the bath of fluctuating electronic spins  $\mathbf{S}_i$ . It is driven by the HF coupling tensor

$$\mathcal{H}_{HF} = \sum_{\alpha, i} \left[ A_{\alpha} I_{i\alpha} S_{i\alpha} + B \sum_{j(nn)} I_{i\alpha} S_{j\alpha} \right], \quad (6.1.1)$$

where  $\sum_{j(nn)}$  is taken over the four nearest-neighbor spins to the site  $i$ . Through this HF Hamiltonian a spin polarization is created in the local environment by a nuclear spin  $\mathbf{I}_i$  located at  $\mathbf{R}_i$ . The HF energy (6.1.1) can be written as an effective field  $H_{i\alpha}(\mathbf{R})$  which this nucleus exerts on spin moments  $-g_{\alpha}\mu_B S_{\alpha}(\mathbf{R})$  in the vicinity. The field is given by

$$H_{i\alpha}(\mathbf{R}) = \frac{I_{i\alpha}}{g_{\alpha}\mu_B} F_{\alpha\alpha}(\mathbf{R}, \mathbf{R}_i), \text{ with } F_{\alpha\alpha}(\mathbf{R}, \mathbf{R}_i) = [A_{\alpha}\delta_{\mathbf{R}, \mathbf{R}_i} + B \sum_{j(nn)} \delta_{\mathbf{R}, \mathbf{R}_j}]. \quad (6.1.2)$$

The effect of  $H_{i\alpha}(\mathbf{R})$  on the surrounding medium can be calculated in terms of  $\chi'(\mathbf{q}, 0)$ , which we denote  $\chi'_{\alpha}(\mathbf{q})$ . The  $\omega = 0$  component is used, because in a metallic environment nuclear spin motion is very slow on the time scale of electronic spin fluctuations. However, the field driving  $\chi'_{\alpha}(\mathbf{q})$  is the  $\mathbf{q}$ -component of  $H_{i\alpha}(\mathbf{R})$ . One may write the Fourier transform  $H_{i\alpha}(\mathbf{q}) = \sum_k \exp(-i\mathbf{q} \cdot \mathbf{R}_k) H_{i\alpha}(\mathbf{R}_k)$  in the form

$$H_{i\alpha}(\mathbf{q}) = \frac{I_{i\alpha}}{g_{\alpha}\mu_B} e^{-i\mathbf{q} \cdot \mathbf{R}_i} F_{\alpha\alpha}(\mathbf{q}), \text{ with } F_{\alpha\alpha}(\mathbf{q}) = [A_{\alpha} + 2B (\cos q_x + \cos q_y)]. \quad (6.1.3)$$

$H_{i\alpha}(\mathbf{q})$  then induces a  $\mathbf{q}$ -component of spin moment

$$\mathcal{S}_{\alpha}(\mathbf{q}) = -\frac{1}{N_A g_{\alpha}\mu_B} H_{i\alpha}(\mathbf{q}) \chi'_{\alpha}(\mathbf{q}), \quad (6.1.4)$$

where we divide  $\chi'(\mathbf{q})$  by Avogadro's number for an atomic susceptibility. The inverse Fourier transform of  $\mathcal{S}_{\alpha}(\mathbf{q})$  gives the resulting spin polarization in the vicinity of  $\mathbf{R}_i$ , i.e.

$$\mathcal{S}_{\alpha}(\mathbf{R}) = \sum'_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{R}} \mathcal{S}_{\alpha}(\mathbf{q}) = -\frac{\hbar I_{i\alpha}}{N_A g_{\alpha}^2 \mu_B^2} \sum'_{\mathbf{q}} e^{i\mathbf{q} \cdot (\mathbf{R} - \mathbf{R}_i)} \chi'_{\alpha}(\mathbf{q}) F_{\alpha\alpha}(\mathbf{q}), \quad (6.1.5)$$

where  $\sum'_{\mathbf{q}}$  is a normalized sum over the Brillouin zone.

The interaction energy with a second nucleus  $\mathbf{I}_j$  may now be obtained by inserting (6.1.5) into (6.1.1), where we use the notation of (6.1.2) to find

$$\sum_{\alpha} a_{\alpha}(i, j) I_{i\alpha} I_{j\alpha} = \sum_{\alpha} I_{j\alpha} \sum_{\mathbf{R}_k} \mathcal{S}_{\alpha}(\mathbf{R}_k) F_{\alpha\alpha}(\mathbf{R}_k, \mathbf{R}_j). \quad (6.1.6)$$

Substituting from (6.1.5) then gives the general result [5]

$$a_\alpha(i, j) = \frac{1}{N_A g_\alpha^2 \mu_B^2} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot (\mathbf{R}_j - \mathbf{R}_i)} \chi'_\alpha(\mathbf{q}) F_{\alpha\alpha}(\mathbf{q})^2. \quad (6.1.7)$$

Under suitable conditions the spin-spin interactions in (6.1.6) and (6.1.7) can be measured via the spin-echo decay time ( $T_2$ ) process, to be discussed in Sect. 6.1.3. The parameter controlling this process is the second moment contribution of the interaction (6.1.7). A useful relation for calculating the second moment of the line as well as the Gaussian decay time  $T_{2g}$  of the spin echo may be derived using (6.1.7). This result, given independently by Takigawa [6] and by Thelen and Pines [7], is

$$\sum_j a_\alpha(i, j)^2 = \frac{1}{(N_A g_\alpha^2 \mu_B^2)^2} \left[ \sum_{\mathbf{q}} [\chi'_\alpha(\mathbf{q}) F_{\alpha\alpha}(\mathbf{q})^2]^2 - \left[ \sum_{\mathbf{q}} \chi'_\alpha(\mathbf{q}) F_{\alpha\alpha}(\mathbf{q})^2 \right]^2 \right]. \quad (6.1.8)$$

### 6.1.1 Some General Properties of the Indirect Spin-Spin Coupling

We adopt a notation where  $\mathbf{q}$  is dimensionless and  $\mathbf{R}_i = (n_{xi}, n_{yi})$  in units of  $a$ , where  $n_{xi}, n_{yi}$  are integers. We shift the origin of the  $\mathbf{q}$  sum to  $\mathbf{Q}$ , i.e.  $\mathbf{q} = \mathbf{p} + (\pi, \pi)$ . Then  $\chi'_\alpha(\mathbf{p})$  is a symmetric function, where  $\sum_{\mathbf{p}}' \rightarrow (1/2\pi)^2 \int_{-\pi}^{\pi} dp_x \int_{-\pi}^{\pi} dp_y$ , and  $F_{\alpha\alpha}(\mathbf{p}) = [A_\alpha - 2B(\cos p_x + \cos p_y)]$ . The exponential factor in (6.1.7) reduces to  $\cos(n_x p_x) \cos(n_y p_y)$ , since the sine terms cancel by symmetry, where  $n_x = n_{xj} - n_{xi}$ , etc. Thus, (6.1.7) becomes

$$a_\alpha(i, j) = \frac{(-1)^{(n_x + n_y)}}{N_A g_\alpha^2 \mu_B^2} \sum_{n'_x = n_x - 2}^{n_x + 2} \sum_{n'_y = n_y - 2}^{n_y + 2} C_\alpha(n'_x, n'_y) G_\alpha(n'_x, n'_y), \quad (6.1.9)$$

where

$$G_\alpha(n'_x, n'_y) = \frac{1}{\pi^2} \int_0^\pi dp_x \int_0^\pi dp_y \chi'_\alpha(\mathbf{p}) \cos(n'_x p_x) \cos(n'_y p_y), \quad (6.1.10)$$

and where the  $C_\alpha(n'_x, n'_y)$  are functions of  $A_\alpha$  and  $B$ .

Some general properties of  $a_\alpha(i, j)$  are as follows:

- Terms in  $\chi'(\mathbf{q}, 0)$  which are independent of  $\mathbf{q}$  give no contribution to  $a_\alpha(i, j)$ .
- The essential range function of  $a(i, j)$  is the Fourier transform of the peak function  $\chi'_\alpha(\mathbf{q})$ .
- A sign reversal on moving between  $nn$  sites results from the the AFM nature of the fluctuations.

- The range function depends only on the magnitudes of the  $n_{x,y}$  and is invariant on exchange of  $n_x$  and  $n_y$ .
- Therefore  $a_\alpha(i, j)$  is symmetric about the  $x$  and  $y$  axes, and also about the  $x = \pm y$  axes.

### 6.1.2 The Gaussian model of Indirect Spin-Spin Coupling in YBCO

In the MM follow-up to MMP [8], a Gaussian model was suggested for  $\chi''(\mathbf{q}, \omega)$ . Citing this example, Imai et al., [9] made use of this model in their interpretation of data for  $T_1$  and  $T_{2g}$  (see below for definition of  $T_{2g}$ ). More recently, Auler et al., [10] employed this model for similar purposes, citing INS studies which showed a Gaussian-like shape with a width essentially independent of temperature. Their interpretation of  $T_1$  data on this basis was presented and discussed in Sect. 5.3.

INS data provide an important characterization of  $\chi''(\mathbf{q}, \omega)$ , which is then used to interpret NMR data. An important question regarding INS data is to what extent they are dependent on the frequency scale. Does a peak in  $\chi''(\mathbf{q}, \omega)$  at or near  $\mathbf{Q}$  with a certain measured width at  $\omega = 10$  meV have the same shape and width at an NMR frequency four orders of magnitude lower? With the limitations of current spectroscopic techniques one cannot answer this question experimentally. Many discussions of NMR  $T_1$  interpretation tacitly assume that the INS results will still be valid at NMR frequencies. We address this question in various contexts throughout this chapter.

For the purposes of the present discussion we adopt the Gaussian shape and width for the AFM peak given by Auler et al.,:

$$\chi'_\alpha(\mathbf{q}) = \frac{g_\alpha^2}{4} \chi'_{AF} e^{-(q_x^2 + q_y^2)\xi^2/4}, \quad (6.1.11)$$

with  $\xi \simeq 1.3$ , where we place the origin at  $\mathbf{Q} = (\pi, \pi)$  and we denote  $\chi'(\mathbf{Q}) = \chi'_{AF}$ . Inserting this into (6.1.10), a simplification occurs, where we can write  $G_\alpha(n'_x, n'_y) = (g_\alpha^2/4) \chi'_{AF} g(n_x) g(n_y)$ , with

$$g(n) = \frac{1}{\pi} \int_0^\pi dp e^{-p^2 \xi^2/4} \cos(np) \approx \frac{1}{\sqrt{\pi} \xi} e^{-n^2/\xi^2}. \quad (6.1.12)$$

In (6.1.12) the result on the far right is obtained by extending the upper integration limit to  $\infty$ . Since  $\exp(-\pi^2 \xi^2/4) \simeq 0.015$ , we suggest that this is a reasonable approximation. Inserting this expression for  $G_\alpha(n'_x, n'_y)$  into (6.1.9), we find, with  $n_x = n_{xj} - n_{xi}$ , etc.,

$$\begin{aligned}
a_\alpha(i, j) = & (-1)^{(n_x+n_y)} \frac{\chi'_{AF}}{\pi N_A \xi^2 g_\alpha^2 \mu_B^2} e^{-(n_x^2+n_y^2)/\xi^2} \{A_\alpha^2 + 4B^2 \\
& - 4A_\alpha B e^{-1/\xi^2} [\cosh(2n_x/\xi^2) + \cosh(2n_y/\xi^2)] \\
& + 8B^2 e^{-2/\xi^2} \cosh(2n_x/\xi^2) \cosh(2n_y/\xi^2) \\
& + 2B^2 e^{-4/\xi^2} [\cosh(4n_x/\xi^2) + \cosh(4n_y/\xi^2)]\}. \quad (6.1.13)
\end{aligned}$$

Equation (6.1.13) is used below to calculate indirect coupling energies for YBCO6.9 and to discuss results which have appeared in the literature. Before that, however, we make a brief digression to introduce spin echo decay measurements.

### 6.1.3 Measuring Indirect Spin-Spin Coupling via Spin-Echo Decay

Under suitably restrictive assumptions, it is possible to get good estimates of the indirect spin-spin coupling (6.1.7) by measuring spin-echo decay times. We give here a brief review of some of the essential points of spin-echo decay, followed by a discussion of results from the literature in the next subsection.

We consider spin-echo decay for the specific problem of  $^{63,65}\text{Cu}(2)$  NMR in the  $\text{CuO}_2$  planes of a cuprate superconductor. If the  $^{63,65}\text{Cu}$  isotopes are labelled A and B, where the A spins are under observation, then the nuclear spin-spin coupling has the general form

$$\mathcal{H}_{II} = \mathcal{H}_{II}^{AA} + \mathcal{H}_{II}^{AB} + \mathcal{H}_{II}^{BB}. \quad (6.1.14)$$

For cases of orthorhombic symmetry or higher, the latter terms can be written

$$\mathcal{H}_{II}^{AA} = \sum_{i>j} [\alpha_{ij} I_{zi}^A I_{zj}^A + \beta_{ij} I_{xi}^A I_{xj}^A + \gamma_{ij} I_{yi}^A I_{yj}^A], \text{ and } \mathcal{H}_{II}^{AB} = \sum_{i>j} \alpha_{ij} I_{zi}^A I_{zj}^A, \quad (6.1.15)$$

where we have taken  $z$  to be the quantization axis. For  $\mathcal{H}_{II}^{AB}$  the  $x$  and  $y$  terms have been omitted, because they are non-secular and have no measurable effects. Whether or not the  $x$  and  $y$  terms for  $\mathcal{H}_{II}^{AA}$  are secular, i.e. physically viable, is a matter of some discussion.

In cases where there is no detuning of neighboring  $A$  spins, i.e., where locally, the Zeeman splitting  $\gamma_A(1+K)H$  as well as quadrupolar splittings are homogeneous, then the  $x$  and  $y$  terms are technically viable. However, if the  $zz$  coefficient  $\alpha_{ij}$  is much larger than  $\beta_{ij}$  and  $\gamma_{ij}$  (a realistic case as we shall see below), then “flip-flop” processes such as  $|m_A, m_B\rangle \rightarrow |m_A+1, m_B-1\rangle$  may become severely inhibited and the transverse terms become de facto non-secular. Below, a simple test is suggested to determine the effectiveness of the dynamical terms.

For the moment we shall assume the flip-flop terms to be inoperative. This is a simple limiting case for which the spin-echo decay process has been calculated in Appendix A.1. Approximating the decay function with a Gaussian  $\exp(-(2\tau)^2/2T_{2g}^2)$ , then the echo decay time constant is found to be

$$\frac{1}{T_{2g}} = \sin(\theta_2/2) \left[ \frac{c_{63}}{8} \sum_j \alpha_{ij}^2 \right]^{1/2}, \quad (6.1.16)$$

where  $c_{63} \simeq 0.69$ , and the sum is over all neighbors. The dependence on refocussing pulse angle  $\theta_2$  suggests an interesting test for the spin dynamics of the sample. If the spins are completely static on the time scale of the echo sequence, then  $T_{2g}$  should become correspondingly long when  $\theta_2$  is small. If  $T_{2g}$  does not change a great deal over a range of values for  $\theta_2$ , it probably means that there is an appreciable degree of flip-flop motion taking place among the spins.

In applying (6.1.16) to actual measurements of  $\sum_j \alpha_{ij}^2$ , it is clearly necessary to be able to flip over nearly all of the spins with the  $\theta_2$  pulse. This is an important constraint on experimental technique. For cuprates this means that one will probably have to employ only the  $(-1/2 \leftrightarrow 1/2)$  transition, and possibly work at low fields in addition in order to narrow the line.

#### 6.1.4 Behavior and Interpretation of Indirect Couplings in YBCO and Y248

There have been a number of measurements of  $T_{2g}$  for both YBCO and Y248 in the literature, with much discussion of its behavior as compared with  $T_1$ . Since they are both driven, at least in part, by AFM fluctuations, these relaxation times are reflections of the same underlying quasiparticle physics. Thus, the advent of  $T_{2g}$  as an additional characterization of cuprate hole dynamics was a most welcome development.

##### *Results Given by Pennington and Slichter*

In their original paper formulating the indirect couplings, expounded in the previous subsection, PS [2] presented calculations of coupling coefficients  $a_\alpha(i, j)$  as well as of  $T_{2g}$  for fully oxygenated YBCO7. They calculated their range function using the MMP Lorentzian form

$$\chi'(\mathbf{q}) = \chi_0 \left[ 1 + \frac{(\xi/\xi_0)^2}{1 + (\mathbf{q} - \mathbf{Q})^2 \xi^2} \right] \quad (6.1.17)$$

centered on  $\mathbf{Q}$ . The  $\xi^2$  factor gives only a rough normalization for  $\chi'(\mathbf{q})$ , since  $\sum_{\mathbf{q}} \chi'(\mathbf{q})$  depends on  $\ln(\xi)$ . The resulting relaxation time is found to vary  $1/T_{2g} \propto \xi$  [2]. The parameters and assumptions for various calculations of  $T_{2g}$  discussed here are shown in Table 6.1. Adopting the MMP estimate [11]  $\xi = 2.5a$ , the half-width of the AFM peak in the PS calculations with (6.1.17) is 0.4. Also from (6.1.17),  $\chi'(\mathbf{Q}) = 1.66 \times 10^{-3} \text{ emu/mol Cu}(2)$ . With values of  $A_c$  and  $B$  as shown in Table 5.1, PS find a value of  $1/T_{2g}$  which is just slightly smaller than their experimental number, which clearly validates their formulation of the indirect spin-spin coupling.

**Table 6.1.** Models, data, and results for c-axis indirect coupling values of  $1/T_{2g}$  are presented from various sources for different doping levels in YBCO. The first line gives the original results of Pennington and Slichter with a Lorentzian model. HF parameters vary only slightly between calculated results given. Experimental data in the final column corresponds generally to 100 K. Under “Source”, Imai and Auler are first authors, as are Bulut and Itoh. The Takigawa reference is [6]. For Imai et al., and Auler et al., the estimated values of  $1/T_{2g}$  have been made using (6.1.13) and direct summation to give  $\sum_j a_c(i, j)^2$ . For the Takigawa estimate, which was made with a Lorentzian model, the PS result is simply scaled to the larger value of  $\chi'(\mathbf{Q})$  shown. The units of parameters given are as follows:  $A_c$  and  $B$  ( $10^{-6} \text{ eV}$ );  $\chi'(\mathbf{Q})$  ( $10^{-3} \text{ emu/mol}$ );  $1/T_{2g}$  ( $\text{ms}^{-1}$ ). These results are discussed extensively in the text

| System   | Source                | $\chi'(\mathbf{q})$ Form | H.W. ( $a^{-1}$ ) | $A_c$ | $B$  | $\chi'(\mathbf{Q})$ | $(1/T_{2g})_{est}$ | $(1/T_{2g})_{exp}$ |
|----------|-----------------------|--------------------------|-------------------|-------|------|---------------------|--------------------|--------------------|
| YBCO7    | PS[2]                 | Lorentzian               | 0.40              | -1.53 | 0.38 | 1.66                | 5.26               | 7.7                |
| YBCO7    | Bulut/Itoh            | Hubbard RPA              | 0.5               | -1.53 | 0.38 | 1.23                | 9.0                | 11.1               |
| YBCO7    | Itoh ( $c_{63} = 1$ ) | Hubbard RPA              | 0.5               | -1.53 | 0.38 | 1.23                | 10.8               | 12.9               |
| YBCO6.9  | Imai[9]               | Gaussian                 | 0.37              | -1.77 | 0.45 | 3.28                | 9.2                | 9.6                |
| YBCO6.9  | Auler[10]             | Gaussian                 | 1.28              | -1.56 | 0.39 | 1.41                | 7.5                | 11.5               |
| YBCO6.63 | Takigawa              | Lorentzian               | 0.40              | -1.53 | 0.38 | 6.14                | 19.5               | 18.4               |

### *Effects of Transverse Coupling and of Dipolar Fields*

Before proceeding with discussion of experimental data, we note in passing that transverse and dipolar coupling contributions to  $\mathcal{H}_{zz}$  are much smaller and can be ignored for most purposes. The dipolar coupling coefficient for quantization axis  $\perp$   $\text{CuO}_2$  plane is simply  $\alpha_c^{dip}(i, j) = \hbar\gamma^2/R_{ij}^3$ , which has the value  $908 \text{ s}^{-1}$  for  $nn$   $^{63}\text{Cu}(2)$ . The corresponding second moment value is less than 6% of the estimated indirect coupling value calculated above. Moreover, it has a constant positive sign for all in-plane neighbors, so that its effects tend to cancel when combined with the staggered indirect coupling. We shall ignore the dipolar terms from this point forward. The transverse indirect coupling terms are also much smaller than the c-axis contribution, giving a second moment only 15% of the latter effect using  $A_{ab} \sim 0.31$  in the units of Table 6.1, with  $B$  having the same value as for the c-axis terms. As far as we are aware, no effort has been made to measure the transverse terms, and we shall not discuss them further.

### *Comparison of the PS Results with Other Models and Data*

Throughout the derivation of indirect spin-spin coupling given above [2], it is assumed that the resulting spin-echo decay process will be Gaussian in form or nearly so. Itoh et al. have tested this hypothesis for the case of NQR studies of  $^{63}\text{Cu}(2)$  in Y248 [12]. Their results are plotted in Fig. 6.1(a) and (b) for several temperatures. After corrections for  $T_1$  effects (see Appendix A.3), it is seen that these decay curves exhibit nearly perfect Gaussian character over two orders of magnitude. Some discussion of the origin of such Gaussian behavior, which is very widespread in  $T_{2g}$  studies, is presented in Sect. 6.3.

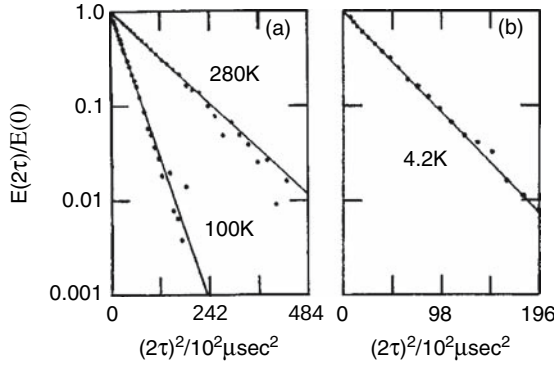


**Fig. 6.1.** (a) and (b) Spin echo decay curves, corrected for  $T_1$  effects, are plotted semilogarithmically vs.  $(2\tau)^2$ , showing nearly perfect Gaussian behavior over two orders of magnitude of decay at several temperatures. These are data for  $^{63}\text{Cu}(2)$  in  $\text{YBa}_2\text{Cu}_4\text{O}_8$ . Reprinted figures from Y. Itoh, H. Yasuoka, et al., *J. Phys. Soc. Japan* **61**, 1287 (1992). Copyright 1992 Physical Society of Japan

In the second line of Table 6.1 we list the calculated result of Bulut and Scalapino (BS) based on their small- $U$  Hubbard model calculations [13] along with experimental numbers from Itoh, Yasuoka et al., [12]. BS calculated the indirect coupling using the same model and parameters they had applied to the  $T_1$  problem [14, 15], finding good agreement with experimental data with an AFM peak width  $\sim 25\%$  greater than that used by PS. Itoh et al., also tested the proportionality of  $^{63}\text{Cu}(2)$  second moment to the concentration of  $^{63}\text{Cu}$  by measuring a sample which contained 100%  $^{63}\text{Cu}$ . The result, shown on the third line of Table 6.1, is within experimental error of the expected increase  $1/T_{2g} \propto (c_{63})^{1/2}$ . The BS calculated result scaled in this fashion is shown for comparison. Itoh et al. [12] also measured the behavior of  $T_{2g}$  in the superconducting state of Y248. The latter results and the BS model calculations for this case are discussed in the next subsection.

We make further comparisons with the results in Table 6.1 with calculations using (6.1.13) based on the parameters provided by Auler et al., [10]. Results obtained with a Gaussian peak for  $\chi'(\mathbf{q})$  and other parameters from Auler et al., [10] are listed in line five of the table. The INS-derived peak width is more than three times that used by PS. The value of  $(1/T_{2g})_{est}$  is substantially larger than the PS value with a slightly smaller value for  $\chi'(\mathbf{Q})$ . Although this is a satisfactory result, it is puzzling that it does not give the rather larger relaxation rate which they quote, and from which the value given for  $\chi'(\mathbf{Q})$  was supposedly derived [10]. The origin of this discrepancy is not understood.

In line four of Table 6.1 are listed the results of a similar calculation based on (6.1.13) as well as the HF coupling,  $\chi'(\mathbf{Q})$ , and peak width parameters given by Imai et al., [9], on which the calculation is based. The estimated value of  $1/T_{2g}$  is in good agreement with the experimental value given. A result

reported by Takigawa [6] is given in the bottom line of the table. Parameter values were stated in [6] for the Lorentzian model with a range of peak widths. Choosing the peak width used by PS for the same model with the same HF parameter values, we simply scale the PS result to the larger value of  $\chi'(\mathbf{Q})$  given in [6] to yield the value of  $(1/T_{2g})_{est}$  stated in the table, which is in good agreement with the experimental value given for YBCO6.63. The greatly enhanced AFM fluctuations in YBCO6.63 are clearly reflected in a shorter decay time  $T_{2g}$ .

Before continuing to discuss the significance of these results, we address the question of how the results for  $1/T_{2g}$  scale with the correlation length.

### ***Scaling of $T_{2g}$ with $\chi'(\mathbf{q})$ Parameters***

There appears to be an interesting difference between Lorentzian and Gaussian models of  $\chi'(\mathbf{q})$  which has to do with their dependence on the correlation length parameter  $\xi$ . For the Gaussian model as prescribed by Auler et al., [10], we find that the second moment  $\propto \sum_j \alpha(i, j)^2$  varies roughly as  $\xi^{-1}$ . From (6.1.16) it follows that  $T_{2g} \sim \xi^{1/2}$ . In contrast, PS note that  $T_{2g} \propto \xi^{-1}$  for their Lorentzian model. However, the latter model (see (6.1.17)) included a prefactor  $\propto \xi^2$  multiplying a peak function of unit amplitude, whereas the Gaussian has none. *The  $\xi^2$  prefactor by itself accounts for the stated variation of  $T_{2g}$  with  $\xi$ .* Without the prefactor effect, then, the PS result is that  $T_{2g}$  is essentially independent of  $\xi$ .

We next consider whether it is possible to account for the foregoing behaviors using the expression (6.1.8) for the second moment. While under some circumstances it may be possible to deduce how  $\sum_j \alpha_{ij}^2$  scales with  $\xi$  using (6.1.8), there is no simple answer to this question in general for two reasons. First, if  $F_{\alpha\alpha}(\mathbf{q})$  contains transferred HF couplings, the cosine factors do not scale in any simple way. Second, in the case of a Lorentzian form for  $\chi'(\mathbf{q})$ , the sum  $\sum_{\mathbf{q}} \chi'(\mathbf{q})$  does not converge at the boundaries, so that the integration limits become  $\xi$ -dependent. This problem is particularly severe for small values of  $\xi$ .

Nonetheless we shall consider what sort of results (6.1.8) gives for  $\mathbf{q}$ -independent HF couplings. Such a calculation is presented in Appendix A.2 for the case of a Gaussian susceptibility, with the result

$$\sum_j \alpha_{ij}^2 = \frac{1}{2\pi\xi^2} \left[ 1 - \frac{2}{\pi\xi^2} \right]. \quad (6.1.18)$$

Thus, as  $\xi$  declines, the leading term gives  $T_{2g} \propto \xi$ . However, at small values of  $\xi$  the correction term in the brackets becomes increasingly important. For  $\xi \sim 1.3$ , the correction term increases  $T_{2g}$  by  $\sim 25\%$ . We suggest that the  $\mathbf{q}$ -dependent HF couplings also contribute to the behavior mentioned above for YBCO, where  $T_{2g} \propto \xi^{1/2}$ .

For the Lorentzian case, with  $\chi'(\mathbf{q}) = \chi'(\mathbf{Q})/(1+q^2\xi^2)$ , the leading term in (6.1.8) gives  $T_{2g} \propto \xi$  as with the Gaussian case. However, the second term gives

a somewhat larger correction than in (6.1.18), so that  $\sum_j \alpha_{ij}^2$  levels off and may even diminish at low values of  $\xi$ . It is plausible that over a modest range of  $\xi$  values  $\sum_j \alpha_{ij}^2$  may be rather flat, leading to the  $\xi$ -independent behavior noted, in effect, by PS. Therefore, it appears that the contrast between Gaussian and Lorentzian susceptibilities may be accounted for in this simple fashion.

A second and equally important conclusion which we draw from this discussion is that the results for  $T_{2g}$  do not depend strongly on  $\xi$  or on the choice of Gaussian or Lorentzian for the shape of the AFM peak in  $\chi'(\mathbf{q})$ . For this reason it will also be difficult to extract information from  $T_{2g}$  data on either of these points. At the same time, the results in Table 6.1 show that  $T_{2g}$  can be analyzed to yield semi-quantitative results for  $\chi'(\mathbf{Q})$ , even if the width and detailed character of the associated AFM peak are not well established.

### *Comparing the Temperature Variation of $T_{2g}$ with that of $T_1$*

The relatively weak dependence of  $T_{2g}$  on the width of the AFM peak in  $\chi'(\mathbf{q})$  leads to an interesting contrast between echo decay times and  $T_1$  processes. While  $1/T_1T$  is given by sums of  $\chi''(\mathbf{q}, \omega)$  over all of  $\mathbf{q}$ -space,  $1/T_{2g}$  is very nearly proportional to  $\chi''(\mathbf{Q})$ , i.e. to the staggered susceptibility.  $T_1$  is, of course, also sensitive to the staggered susceptibility, since it measures the area under the AFM peak in  $\chi''(\mathbf{q}, \omega)$  at  $\mathbf{Q}$ . But  $T_1$  for  $^{63}\text{Cu}(2)$  has major contributions from the rest of the Brillouin zone as well, much of which collapses in the presence of a pseudogap. We see the result of this in Fig. 6.2 from Takigawa [6]. The curve for  $1/T_{2g}$  indicates that the staggered susceptibility is rising fairly rapidly in a Curie-Weiss-like fashion.  $T_1$  for the  $^{63}\text{Cu}(2)$  rises below 300 K at a similar rate. When the spin pseudogap sets in around 200 K, however,  $1/T_1T$  goes over a maximum and then begins a steep descent which indicates collapsing behavior for  $\chi''(\mathbf{q}, \omega)$  over much of the BZ. The fact that  $1/T_{2g}$  is immune to the pseudogap decline suggests that  $\chi'(\mathbf{Q})$  is made up from parts of the Fermi surface which are not gapped. A related result is presented in the next subsection, where  $1/T_2$  for Y248 does not decay in the superconducting state, presumably because contributions to  $\chi'(\mathbf{Q})$  are not affected by the superconducting gap either.

Curie-Weiss behavior for  $1/T_{2g}$  is also found in YBCO7 [9, 10], though with rather smaller increases between 300 K and  $T_c$ . It would be, of course, most enlightening to be able to compare such results with INS data on the same systems, including temperature dependences. While the INS characterizations are not easy to perform, the cuprates provide an ideal test bed for comparison of results for the dynamic susceptibilities. We shall see this in more detail in Sect. 6.3 with the system LSCO.

Takigawa also made an effort to apply the scaling theory of Sokol and Pines [16] to the susceptibility behavior of YBCO6.63 [6]. The scaling effect may be seen in Fig. 6.2, where just at the upper end of the temperature range the ratio  $T_1T/T_{2g}$  approaches a constant value. Effects such as this have become a major branch of the study of cuprate magnetism and will be reviewed at some length in Sect. 6.4.

## 6.2 The Bulut-Scalapino Calculation of $1/T_{2g}$ for $T < T_c$

Bulut and Scalapino (BS) used their small- $U$  Hubbard model of spin dynamics to treat both  $T_1$  (Sect. 5.7) and  $T_{2g}$  in the superconducting state [13]. In the latter case they found a major distinction between the cases of s-wave and d-wave pairing. We first describe their calculation, and then review the experimental  $T_{2g}$  data of Itoh, Yasuoka et al., [12] on  $\text{YBa}_2\text{Cu}_4\text{O}_8$  (Y248) which has been compared with the BS theory.

### *Model Calculations of Bulut and Scalapino: $T_{2g}$ in the Normal State*

The BS calculations of  $T_{2g}$  used much the same parameter values as employed in related work on  $T_1$  (see Sect. 5.4) [14, 15], where they used the RPA formula

$$\chi'(\mathbf{q}) = \frac{\chi_0(\mathbf{q})}{1 - U\chi_0(\mathbf{q})} \quad (6.2.1)$$

for the real part of the dynamic susceptibility  $\chi'(\mathbf{q})$  at  $\omega = 0$ . They give for the noninteracting susceptibility  $\chi_0(\mathbf{q} \rightarrow 0) = 0.214t^{-1}$ , where  $t$  is the hopping integral giving band energies  $\mathcal{E}_{\mathbf{q}} = -2t[\cos q_x + \cos q_y] - \mu$ . The chemical potential was set so that the band occupation  $\langle n \rangle = 0.86$ , very near the critical value for instability (see [15] and Sect. 5.4).

The enhanced curve of  $\chi'(\mathbf{q})$  from the BS model is shown in Fig. 6.3(a) for the path in  $\mathbf{q}$ -space shown in the inset. We determine the molar value of  $\chi'(Q)$

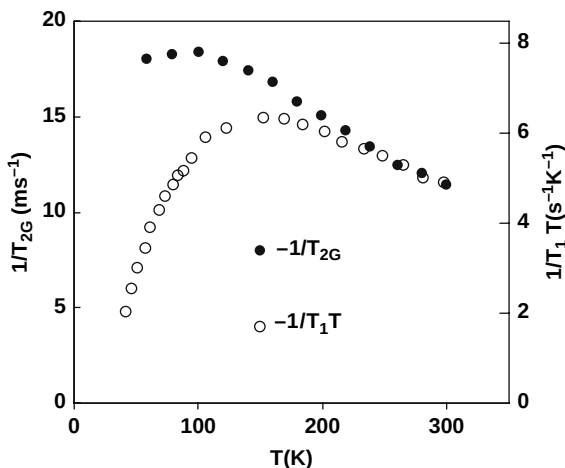


**Fig. 6.2.** Measured values of  $1/T_{2g}$  and  $1/T_1 T$  for  $^{63}\text{Cu}(2)$  in YBCO6.63 are plotted vs. temperature. The data have been scaled to coincide near room temperature, where they show similar behavior. Reprinted figure from M. Takigawa, , Phys. Rev. B49, 4158 (1994). Copyright 1994 American Physical Society

as follows. From discussion of NMR shift calculations in [15] the  $\mathbf{q} = 0$  Stoner enhancement is given as 1.75. Equating their c-axis susceptibility result to  $\chi_c = 1.18 \times 10^{-4}$  emu/mol Cu(2) from Table 2.4, we find  $\chi_0(0) = 6.74 \times 10^{-5}$  emu/mol Cu(2). Relative to that value, the peak value in Fig. 6.3(a) is enhanced by a factor  $\sim (3.8/0.214)$ , giving the estimate  $\chi'(\mathbf{Q}) \simeq 1.23 \times 10^{-3}$  emu/mole Cu(2). The latter value is within  $\sim 15\%$  of the result obtained by taking  $t = 0.1$  eV [15]. The AFM peak half-width of  $\sim 0.5$  (Table 6.1) is also taken from Fig. 6.3. The latter results apply in the vicinity of 100 K.

BS also calculated the temperature variation of  $1/T_{2g}$ , both in the normal state up to 300 K and below  $T_c$  down to essentially zero temperature. Their results as given are shown as the dashed line in Fig. 6.3(b), where they are seen to fall just below the YBCO7 data from Itoh et al., [12] (filled circles). The open circles in the same figure are a plot of measured values of  $1/T_{2g}$  for  $^{63}\text{Cu}(2)$  in Y248 also taken from [12]. The latter data have been compared with the BS calculations (solid lines) from [13], which have been scaled to coincide with the experimental data in the region around 100 K<sup>1</sup>. The result is a dramatic comparison of  $T_{2g}$  data with the s and d-wave BS model calculation [13].

### *The Superconducting State: A Dramatic Success for d-Wave*

The normal-state calculation gives a reasonable account of the Y248 data for  $1/T_{2g}$  in Fig. 6.3. In the superconducting state, these data, combined with the BS calculations, give a very dramatic confirmation of d-wave pairing symmetry. The effect of superconducting pairing on the susceptibility curve is shown in Fig. 6.3(a) where calculated susceptibility curves at  $T = 0.8T_c$  are shown for both s-wave (dashed line) and d-wave (dotted line). The contrast between these two is attributed by BS to nodes in the d-wave energy gap which simply allow contributions to  $\chi'(\mathbf{Q})$  to persist into the superconducting state. This is very likely related to the continued c-axis spin correlations below  $T_c$  which were demonstrated by Uldry et al., [17], as was discussed in Sect. 5.7. It may also be related to the fact that  $\chi'(\mathbf{Q})$  is immune to the pseudogap in the normal state, exhibiting Curie-Weiss behavior down to  $T_c$ . Thus, the pseudogap and the superconducting gap have similar character in this respect.

---

<sup>1</sup> Since the Y248 data were obtained using NQR, the original (dotted) curve was first rescaled by  $\sqrt{2}$  to reflect the enhanced NQR relaxation rate (see Appendix A.2.1 for a discussion of this effect). Following that, rescaling with the Stoner factor has been done using (6.2.1) as follows. It is presumed that the temperature dependence of  $\chi'(\mathbf{Q})$  is driven by that of  $\chi_0(\mathbf{Q})$ . From [13] it was determined that the enhancement at the peak of the curve in Fig. 6.3(a) is  $\simeq 5.4$  at  $T = 100$  K. Using that fact and (6.2.1) to recover  $\chi_0(\mathbf{Q})$  as a function of  $T$ , the dotted curve with an adjusted value of  $U$  was plotted as the solid curve in Fig. 6.3(b). For the region below  $T_c$ , the original curves from [13] were simply rescaled to meet the normal-state curve at  $T = 82$  K.

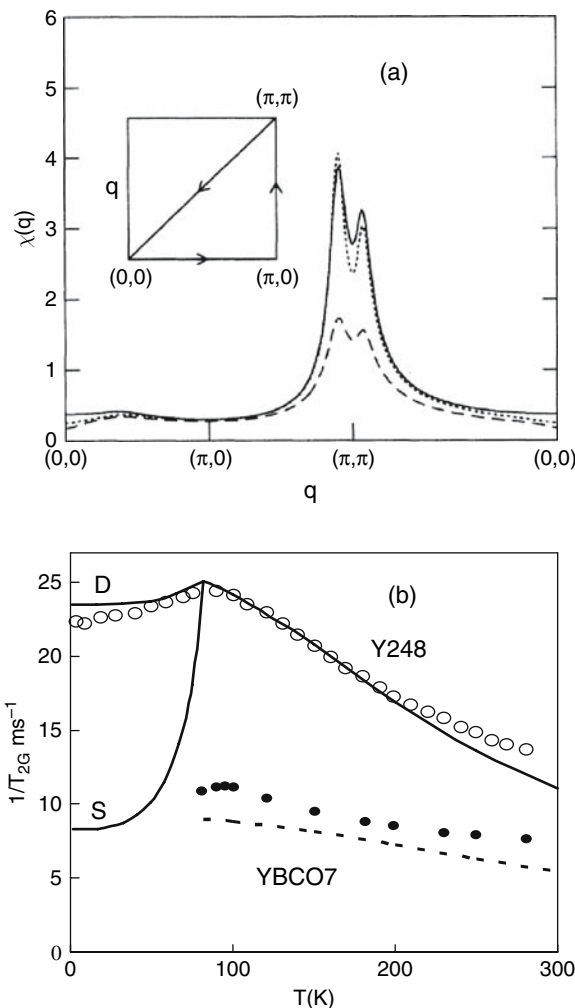


**Fig. 6.3.** (a) The enhanced susceptibility  $\chi'(q)$  obtained with (6.2.1) [13] is plotted for the path in  $q$ -space shown in the inset. The solid curve shows behavior at  $T \sim 100$  K, while the dashed and dotted curves show behavior for s-wave and d-wave pairing, respectively, at  $T = 0.8 T_c$ . See text and part (b) of this figure for discussion of this effect. (b) NMR measurements of  $1/T_{2g}$  for YBCO7 (dots) and NQR measurements for Y248 (open circles) by Itoh et al., [12] are plotted vs. temperature. The dotted line shows the normal-state calculations of Bulut and Scalapino [13] for  $^{63}\text{Cu}(2)$  NMR in YBCO7. The solid curves are determined as follows. For the normal state the dotted line is scaled by  $\sqrt{2}$  for the NQR case, then the enhancement is re-calculated using (6.2.1) to match the experimental curve near 100 K. For  $T < T_c$  the curves from [13] are simply scaled to meet the normal-state curve at  $T_c = 82$  K. See text for additional discussion

The present results along with the dramatic  $T_1$  effects discussed in Sect. 5.7 constituted a very strong case for d-wave pairing several years before it was widely accepted by the high- $T_c$  community. To summarize, we have seen in this section and the last that the formulation of indirect spin-spin coupling in terms of  $\chi'(\mathbf{q})$  by Pennington and Slichter opened up a very important new avenue of approach for the characterization of the AFM enhancement peaks as well as of  $\chi'(\mathbf{Q})$ .

### 6.3 Coordinated Interpretation of NMR and INS Data for LSCO

In Sect. 4.4 we discussed data for the NMR shift, uniform susceptibility, and spin-lattice relaxation time  $T_1$  for  $^{63}\text{Cu}$  in LSCO: $x$ , for  $x$  ranging over the superconducting region,  $0.06 \leq x \leq 0.25$ . This system was seen to exhibit a peculiar sort of pseudogap effect, which strongly affects the susceptibility even at the peak of the  $T_c$  curve, but allows the  $^{63}\text{Cu}$   $T_1$  curves to follow a Curie-Weiss-like behavior down to temperatures very close to  $T_c$ . Here, we look at another aspect of the LSCO system which came about, because this system emerged as being unique among the cuprates in having received a very thorough characterization of  $\chi''(\mathbf{q}, \omega)$  by means of INS. The detailed geometry of the four mildly incommensurate peaks near  $(\pi, \pi)$  has been scanned in great detail over a wide range of frequencies. As a consequence, LSCO became a classic “test bed” for the theoretical relationship between NMR and  $\chi''(\mathbf{q}, \omega)$ . We first review the theoretical basis for such an investigation.

The fluctuation-dissipation theorem relation between spin-fluctuation-generated  $T_1$  processes in a metallic environment and the dissipative term  $\chi''(\mathbf{q}, \omega)$  of the dynamical susceptibility, as recounted in Sect. 3.5, had been known for many decades [18] before it was tested using experimental INS data for  $\chi''(\mathbf{q}, \omega)$ . The latter test was conducted via  $T_1$  measurements for  $^{63}\text{Cu}$  and  $^{17}\text{O}$  (both planar and apical) in LSCO:0.15 [19] and was based on the INS data of Cheong et al., [20] and Mason et al., [21]. Such an enterprise – to correlate two pieces of experimental data using an “exact” theoretical relationship<sup>2</sup> – may not seem well motivated at the outset. However, this relationship had not been tested experimentally before. Furthermore, it led to the uncovering of some interesting limitations, among which is the clash between INS and NMR data for the case of planar  $^{17}\text{O}$  [19], which we review below.

In this section we review the circumstances of the latter test, which call into question the usual assumption that INS results may safely be extrapolated to NMR frequencies, which are lower by a factor  $\sim 10^4$ . Additional INS data which have appeared since that time may throw some new light on the

---

<sup>2</sup> This relationship is very nearly exact under the assumption that spin hyperfine processes are predominant. However, it has not yet been determined how important the orbital relaxation rates are for the cuprates (see Sect. 5.6).

situation, as well. We shall also review indirect spin-spin coupling measurements for LSCO:0.15, interpreted with values of  $\chi'(\mathbf{q})$  which were calculated from the measurements of  $\chi''(\mathbf{q}, \omega)$  using the Kramers-Kronig relation [22]

$$\chi'(\mathbf{q}) = \frac{2}{\pi} \int_0^\infty d\omega \chi''(\mathbf{q}, \omega) / \omega. \quad (6.3.1)$$

From (6.3.1) one sees that such a procedure requires data for  $\chi''(\mathbf{q}, \omega)$  over a wide range of frequencies. Since that time, such high-frequency data have actually appeared in the literature [23]. The latter data will be taken into account in reviewing this calculation. For the  $T_2$  processes we come to a similar conclusion as with  $T_1$ , namely there is a successful account of the  $^{63}\text{Cu}$  data with (or without) discommensurations, but not for the planar  $^{17}\text{O}$  (see Sect. 6.3.2).

### 6.3.1 Review of INS Data for Optimally-Doped LSCO

We first set the stage with a brief review of relevant INS data for LSCO:x, with  $x \sim 0.15$ . It seems that of all the cuprate compounds, LSCO alone was available in large, uniform crystals with homogeneous oxygen content. Conveniently enough,  $\chi''(\mathbf{q}, \omega)$  is a quantity which can be measured directly by means of INS. The principal difficulty is that INS measurements can only be made at frequencies several orders of magnitude higher than those at which NMR data are recorded. We examine the available INS data with that problem in mind.

INS data for  $\chi''(\mathbf{q}, \omega)$  at energies of a few  $m\text{V}$  are shown in Fig. 6.4. In part (a) we see data for scans through two of the four incommensurate peaks located at  $(\pi, \pi) \pm \delta(0, \pi)$  and  $(\pi, \pi) \pm \delta(\pi, 0)$ , where  $\delta = 0.245$  for  $\text{La}_{1.86}\text{Sr}_{0.14}\text{CuO}_4$  [21]. The peaks are seen to be well resolved, with relatively little difference between behavior near  $T_c = 35\text{ K}$  and that at  $4.6\text{ K}$ . There is, however, an increase in intensity at the point between the peaks at higher energy. That trend is also visible in the lower-energy scans from Thurston et al., [24] in part (b) of Fig 6.4, where at  $\omega = 1.5\text{ meV}$  the peaks are completely resolved, while) at  $4.0\text{ meV}$  there is already some filling in of the space between peaks. The incommensurability varies with composition,  $\delta \simeq 2x$  [20], but it shows no measureable variation with energy at the lowest energies scanned [24].

From available INS results for LSCO, then, it does not appear that discommensurations will vanish at lower (i.e. at NMR) frequencies, although the point remains at issue. At higher frequencies, however, early work showed the discommensurations fading into a single broad peak by  $\omega = 15\text{ meV}$  [20]. That this trend would continue to higher energies was verified by studies to above  $200\text{ meV}$  carried out at ISIS [23]. In that study, results for LSCO:x,  $x = 0.14$ , were compared with the undoped antiferromagnet  $\text{La}_2\text{CuO}_4$ , both  $\mathbf{q}$ -scans and energy spectra. For LSCO:0.14, discommensurations are not visible

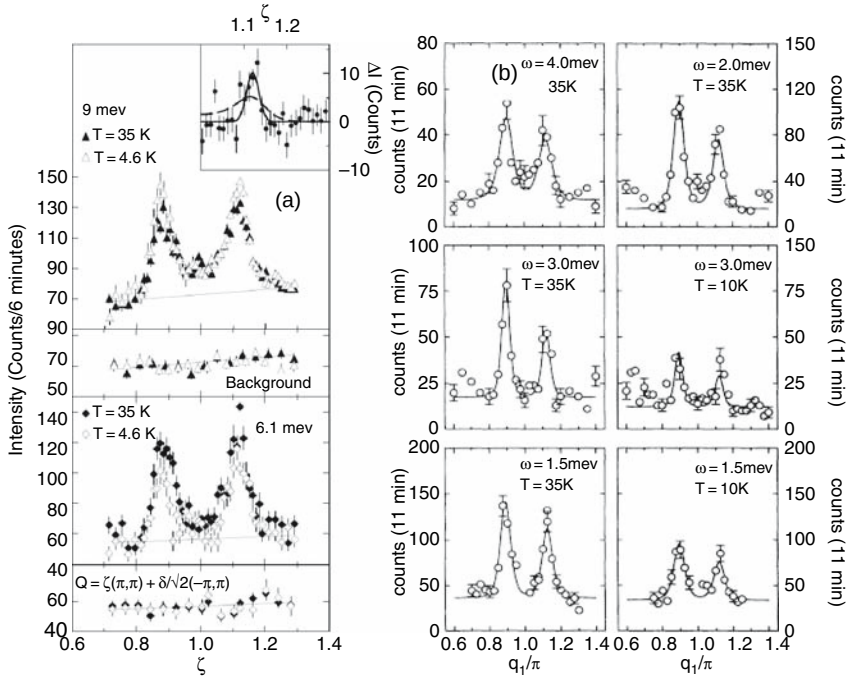


**Fig. 6.4.** (a) INS  $q$ -scans along the path shown at the bottom of the figure are plotted for  $T \sim T_c$  and for  $T \ll T_c$  for the two scattering energies shown [21]. These data show the well-resolved incommensurate peaks and a relatively small difference in scattering intensity for the two temperatures. The inset shows the difference in intensity measured for the two temperatures at 9 meV. Note the small, but definite increase in intensity between the peaks between 6 meV and 9 meV. Reprinted figure from T. E. Mason, G. Aeppli, H. Mook, Phys. Rev. Lett. **68**, 1414 (1992). Copyright 1992 American Physical Society. (b) INS data at energies  $\omega \leq 4.0$  meV, showing very well-resolved incommensurate peaks with no measurable variation of the discommensuration  $\delta$  with  $\omega$ . These authors find  $\delta = 0.22$  for  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ . They also find relatively small variation of intensity with temperature below  $T_c$ . Reprinted figure from T. R. Thurston, P. M. Gehring, G. Shirane, et al., Phys. Rev. B **46**, 9128 (1992). Copyright 1992 American Physical Society

in the lowest energy scans (25-50 meV) reported [23], nor any above that. The resolution in  $q$ -space may be somewhat marginal for this purpose, although the AFM (Bragg?) peak at 295 K for  $\text{La}_2\text{CuO}_4$  showed a width  $\Delta q \sim 0.25$  r.l.u.

We display three composite data plots from Hayden et al., [23], namely the equal-time spin correlation function  $S(\mathbf{q}) = \int_{-\infty}^{\infty} d\omega \chi''(\mathbf{q}, \omega)$ , the zero-frequency susceptibility  $\chi'(\mathbf{q}) = (2/\pi) \int_0^{\infty} d\omega \chi''(\mathbf{q}, \omega) / \omega$ , and the local susceptibility  $\chi''(\omega) = \sum_{\mathbf{q}} \chi''(\mathbf{q}, \omega)$ . These quantities have been computed from the results of the spallation-source study [23]. The local susceptibilities are shown in Fig. 6.5(a) and (b), where it is noteworthy that the results are plot-

ted in absolute units, and where in (b), reactor-based results are included below  $\sim 25 \text{ meV}$ . Below we shall compare these data with the absolute susceptibility results which were used to calculate  $T_1$  in [19]. The results in Fig. 6.5(a) and (b) show that the effect of doping is to concentrate  $\chi''(\mathbf{q}, \omega)$  at energies below  $50 \text{ meV}$  (as compared with  $\text{La}_2\text{CuO}_4$ ), and that the peak seen at  $22 \text{ meV}$  is a “new energy scale” for this superconductor [23]. This energy is also a rough upper limit for the appearance of discommensurations. The solid line plotted in panel (b) is

$$\chi'' = \frac{\Gamma\omega}{(\Gamma^2 + \omega^2)}, \quad (6.3.2)$$

with  $\Gamma = 22 \pm 5 \text{ meV}$ .

The equal-time correlation function  $S(\mathbf{q})$  and the zero-frequency susceptibility  $\chi'(\mathbf{q})$  obtained with (6.3.1) in [23] are shown in Fig. 6.5 for the undoped ((c) and (d)) and the doped ((e) and (f)) cases, respectively. Owing to the near-constant width of  $\chi''(\mathbf{q}, \omega)$  in  $\mathbf{q}$ -space for LSCO:0.14 [23], there is very little difference between  $S(\mathbf{q})$  and  $\chi'(\mathbf{q})$ . The associated energy integrals have been carried out for  $\omega$  ranging from 15 to  $150 \text{ meV}$ . The central peak in Fig. 6.5(e) and (f) has an HWHM of  $\kappa = 0.26(5) \text{ \AA}^{-1}$ , which is just slightly larger than the incommensurate splitting. (See below for definition of  $\kappa$ .) Since the Kramers-Kronig integral favors low energies, one wonders whether there would be visible incommensurate peaks in  $\chi'(\mathbf{q})$  if the reactor-based intensity (e.g. that which gives the open circles in Fig. 6.5(b)) were included in the calculation of  $\chi'(\mathbf{q})$ . As noted below, such a contribution might be appreciable for indirect spin-spin coupling with the planar  $^{17}\text{O}$ .

### *The Calibrated Susceptibility for $T_1$ Calculations in LSCO*

In order to discuss  $T_1$  behavior in LSCO we need two main ingredients. The first is a calibrated susceptibility function  $\chi''(\mathbf{q}, \omega)$  for vanishing  $\omega$ , with detailed  $\mathbf{q}$ -dependence, and the second is a measured HF tensor or a near approximation thereto. We begin with the calibrated susceptibility, which was used earlier in [19], but originated with the measurements of Mason et al., [21]. The absolute calibration to these was presented in [25], but had also been used, it seems, in the paper by Hayden et al., [23]. We shall recount here the calibration used in [19]. Some careful checking finds that the latter result leads to a value for the initial slope of  $\chi''(\omega)$  in Fig. 6.5(b) within 10% or less of the plotted value.

The low-energy INS data for  $\chi''(\mathbf{q}, \omega)$ , part of which is displayed in Fig. 6.4(a), may be represented in the normal state by the function

$$\left. \frac{\chi''(\mathbf{q}, \omega)}{\omega} \right]_{\omega \rightarrow 0} = \frac{K_0 \mathcal{A}^2 \theta[\Gamma_c - \Gamma_n(\mathbf{q})]}{\Gamma_n(\mathbf{q})^2}, \quad (6.3.3)$$

where  $\Gamma_n(\mathbf{q}) = \mathcal{A}^2[\kappa^2 + R(\mathbf{q})]$ , with

$$R(\mathbf{q}) = \frac{1}{8\pi^2 a_L^2 \delta^2} \{[(q_x - q_y)^2 - \pi^2 \delta^2]^2 - [(q_x + q_y)^2 - \pi^2 \delta^2]^2\}. \quad (6.3.4)$$

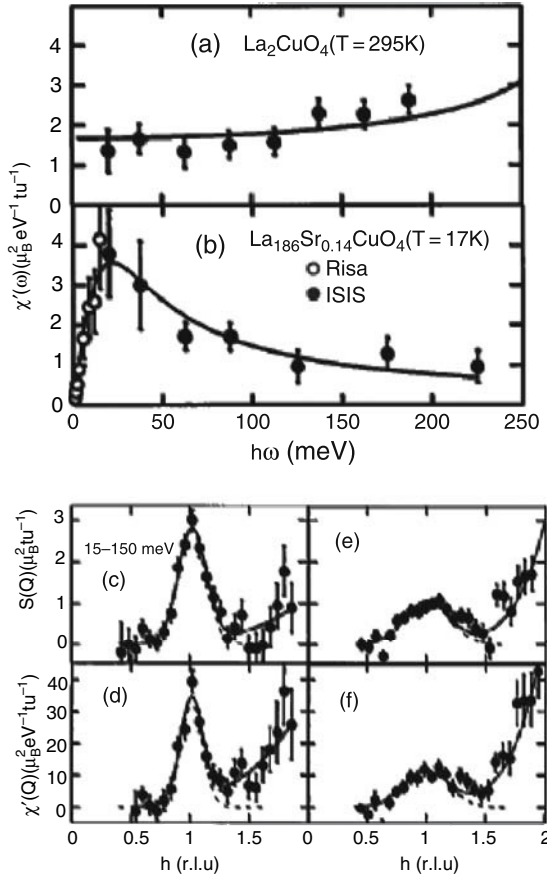


**Fig. 6.5.** (a) and (b) The local susceptibilities  $\chi''(\omega)$  for  $\text{La}_2\text{CuO}_4$  (295 K) and LSCO:0.14 (17 K), derived from the data presented in [23], are plotted as a function of energy  $\hbar\omega$ . As compared with  $\text{La}_2\text{CuO}_4$ , the effect of doping is seen to concentrate the amplitude at low energies, giving a peak at  $\sim 22 \text{ meV}$ . Below that point are plotted data from earlier reactor-based studies [21], which serve to determine the initial slope used for  $T_1$  calculations. (c) and (e) are the equal-time spin correlation functions  $S(\mathbf{q})$  defined in the text, for  $\text{La}_2\text{CuO}_4$  and LSCO:0.14, respectively. (d) and (f) are zero-frequency susceptibilities  $\chi'(\mathbf{q})$  obtained with (6.3.1) in a similar fashion. For LSCO:0.14 ((e) and (f)) these quantities are nearly indistinguishable, since the width of  $\chi''(\mathbf{q}, \omega)$  shows very little dependence on energy [23]. In (c)–(f) the rise in intensity to the right is caused by phonons, where the suggested behavior of the quasiparticle properties is indicated by dashed lines. Although the spallation source resolution width is not as good as in reactor-based studies, it is clearly well below the peak widths found for LSCO:0.14 in (e) and (f). Reprinted figures from S. M. Hayden, G. Aeppli, H. Mook, et al., Phys. Rev. Lett. **76**, 1344 (1996). Copyright 1993 American Physical Society

Here  $a_L = 3.8\text{\AA}$  is the  $\text{CuO}_2$  lattice constant and  $\delta = 0.245$  is the discommensuration [21]. The other quantities in (6.3.3) are

- The constant  $\mathcal{A}^2 = 3.858\text{ eV}\text{\AA}^2$  comes from a form used to fit INS data at finite values of  $\omega$  [21].
- The peak width parameter  $\kappa = [(0.034)^2 + 31.35(k_B T)^2]^{1/2}\text{\AA}^{-1}$  is also from an expression used to fit data over a range of  $\omega$  values, but is stated here for  $\omega = 0$ . In this expression  $k_B T$  is to be entered in units of eV. We note that this representation of  $\kappa$  has been updated [25] from what was used in [19]. The two expressions give very similar values for temperatures of 100 K or less.
- The calibration obtained using acoustic phonons [25] gives  $K_0 \mathcal{A}^2 \simeq 2.5\mu_B^2$ .
- The function  $\theta[p] = 1$  if  $p > 0$  and 0 otherwise. In (6.3.3)  $\Gamma_c$  is taken to be an estimated maximum magnon energy  $\sim 0.3\text{ eV}$ .

The foregoing function describes  $\chi''(\mathbf{q}, \omega)$  in  $\mathbf{q}$ -space as having four incommensurate peaks located at  $(\pi, \pi) \pm (0, \pi)\delta$  and  $(\pi, \pi) \pm (\pi, 0)\delta$ . These peaks have calibrated widths given by  $\kappa$ . As stated, the function has units of  $\mu_B^2/\text{eV}^2$  per formula unit. This is the initial slope of  $\chi''(\mathbf{q}, \omega)$ , determined by INS data at energies of just a few meV. From the standpoint of INS methodology, it is supposed that this function would apply in the energy range in which it was determined and to all energies below that as well.

As we shall see below, however, there is a problem with this interpretation in connection with the  $T_1$  data for the planar  $^{17}\text{O}$ , which will be discussed in Sect. 6.3. We note here that there is also a second problem with using INS measurements as a calibration of  $\chi''(\mathbf{q}, \omega)$  for NMR frequencies. This has to do with the behavior in the superconducting state. We know from  $T_1$  measurements for  $^{63}\text{Cu}$  in LSCO (as well as those for other superconductors at  $T < T_c$ ) that the effective value of  $\chi''(\mathbf{q}, \omega)$  declines typically by a large factor. For LSCO  $1/T_1$  drops by a factor  $\sim 100$  at a temperature of 4.2 K relative to its value in the normal state [3]. The INS data for  $\chi''(\mathbf{q}, \omega)$  as given by Thurston et al., for example, shows no decline whatever below  $T_c$ , particularly at the lowest energies tested  $\hbar\omega \sim 1.5\text{ meV}$ . As the latter authors have commented [24], this is a situation for which "further theory is required". It seems, then, that we do not always understand when the INS results will apply at NMR frequencies and when they do not.

### *NMR Shift and Susceptibility Analysis for LSCO*

Below, we apply the calibrated expression (6.3.3) for  $\chi''(\mathbf{q}, \omega)$  to  $T_1$  data for  $^{63}\text{Cu}$  and planar  $^{17}\text{O}$  in LSCO. For this purpose, The numbers are similar to those for YBCO given in Chap. 3, but need, of course, to be established independently. Working from the  $^{63}\text{Cu}$  shift results of Ohsugi et al. [3], it is first noted that  $K_c(T)$  is constant at  $\sim 1.20\%$  well into the superconducting state. Similar to YBCO, then, we have  $A_c + 4B \simeq 0$ . Next,  $K_c^{vv}$  is slightly smaller than that ( $\simeq 1.28\%$ ) for YBCO. Thus, the crystal-field energies for

**Table 6.2.** Compilation of parameters related to the analysis of  $^{63}\text{Cu}$  and planar  $^{17}\text{O}$  NMR shifts and susceptibilities for LSCO:0.15 at  $T = 300\text{ K}$ . These quantities are defined and discussed in the text. The units are as follows: NMR shifts: %; susceptibilities:  $10^{-6}\text{ emu/mol}$ ; HF constants: kOe/spin. The HF constants are defined by (3.3.2). They will have their proper energy units when multiplied by  $10^3\hbar\gamma_{17,63}$

| $g_{ab}$ | $g_c$ | $K_{ab}^{vv}$ | $K_c^{vv}$ | $K_{ab}^s$ | $\chi_{ab}^{vv}$ | $\chi_c^{vv}$ | $\chi_{ab}^s$ | $\chi_c^s$ | $B$ | $A_{ab}$ | $A_c$ | $K_a^{17}$ | $K_b^{17}$ | $K_c^{17}$ | $C_a$ | $C_b$ | $C_c$ |
|----------|-------|---------------|------------|------------|------------------|---------------|---------------|------------|-----|----------|-------|------------|------------|------------|-------|-------|-------|
| 2.06     | 2.27  | 0.27          | 1.20       | 0.41       | 19.1             | 85.1          | 145           | 177        | 76  | 19       | -304  | 0.274      | 0.162      | 0.214      | 108   | 64    | 77    |

LSCO are a bit higher and the g-factors slightly smaller as well. Estimated values are given in Table 6.2. From the  $K_\alpha^{vv}$  tensor we use the effective orbital HF shift coefficient  $\alpha_{orb} = 141(\text{emu/mol})^{-1}$  given with (2.3.5) for YBCO. This leads to the Van Vleck susceptibility components given in Table 6.2.

The Van Vleck susceptibility tensor is combined with the estimate  $\chi_{dia} \approx -99 \times 10^{-6}\text{ emu/mol}$  [26, 27] to extract the spin susceptibility tensor from

$$\chi_\alpha^{expt} = \chi_\alpha^s + \chi_\alpha^{vv} + \chi_{dia}. \quad (6.3.5)$$

The powder average susceptibility was found to be  $98 \times 10^{-6}\text{ emu/mol}$  (300 K) [19], a value within 5% of those given by Ishida et al., [28] and Johnston [29]. Since  $\chi_\alpha^s \propto g_\alpha^2$  [18], we define a quantity  $\chi_0^s$  with the relation  $\chi_\alpha^s = (g_\alpha^2/4)\chi_0^s$ . This leads to the expression for the powder average spin susceptibility  $\frac{1}{3}(\chi_c^s + 2\chi_{ab}^s) = 1.137\chi_0^s$  using g-values from the table. With (6.3.5) and the numbers given, we find  $\chi_0^s = 137.1 \times 10^{-6}\text{ emu/mol}$ . The values for  $\chi_\alpha^s$  in Table 6.2 follow immediately. These are essentially the susceptibility results given in [19]. Note that the spin susceptibilities are substantially larger than those found for YBCO7 (Table 3.4).

We now can extract the  $^{63}\text{Cu}$  spin HF constants for LSCO:0.15. The shift coefficient for  $K_{ab}^s \simeq 0.41\%$  (300 K) [3] is  $K_{ab}^s/\chi_{ab}^s = 28.3(\text{emu/mol})^{-1}$ . Using (2.3.4) this gives  $A_{ab} + 4B = \hbar\gamma_{63} 325\text{ kOe/spin}$ . From studies of undoped  $\text{La}_2\text{CuO}_4$  [30] we take the result  $A_{ab} - 4B = -286\text{ kG/spin}$ . Combining the latter two relations leads to  $A_{ab}$  and  $B$  as given in Table 6.2, as well as the estimate  $A_c = -4B = -304\text{ kG/spin}$ . All results are summarized in Table 6.2. We believe that these slightly smaller numbers than used in [31] give a more realistic outcome.

The corresponding values  $C_\alpha$  for the planar  $^{17}\text{O}$  were derived from room-temperature NMR shift measurements and reported in [19]. The shift measurements, which have been corrected for orbital background shifts  $K_{a,b,c}^{orb} = (0.046, 0.008, -0.027)$  (in %, from Takigawa et al., [32]), and their corresponding HF constant values are listed in Table 6.2.

### *Evaluation of $T_1$ for $^{63}\text{Cu}$ and $^{17}\text{O}$ from INS Data*

With HF couplings from Table 6.2, we can now evaluate  $T_1$  for  $^{63}\text{Cu}$  and  $^{17}\text{O}$  in LSCO:0.15 using the INS susceptibility data embodied in (6.3.3). Relaxation rates were calculated for  $^{63}\text{Cu}$  with (3.5.11) and for  $^{17}\text{O}$  with (3.5.14) [19].

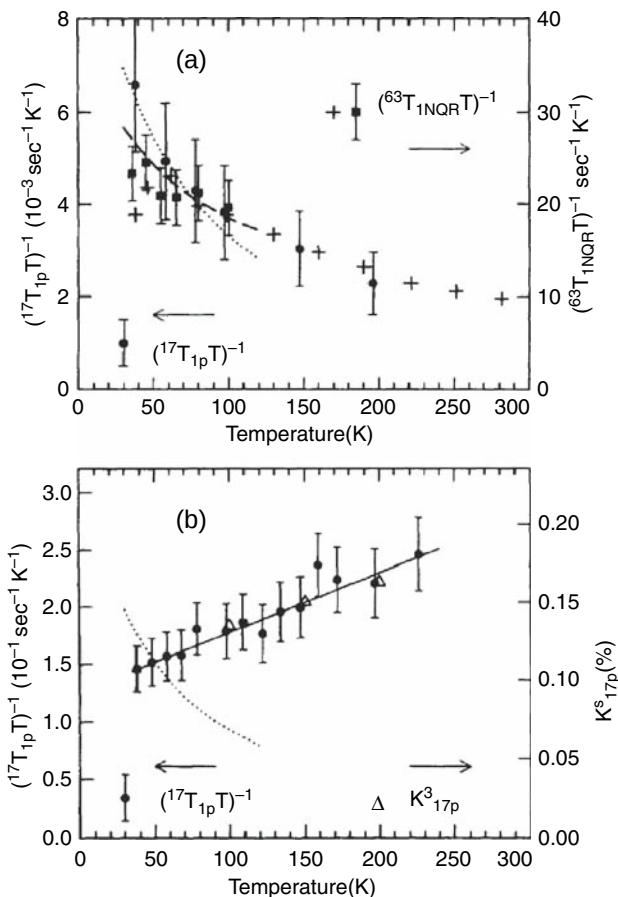


**Fig. 6.6.** (a) Data for  $1/T_1T$  are plotted vs.  $T$  for  $^{63}\text{Cu}$  (filled squares, +': right-hand scale) and for apical  $^{17}\text{O}$  (dots: left-hand scale) in LSCO:0.15 [19]. The data plotted as +'s are from Imai et al. [33]. The dotted curve is a plot of the calculated rate based on INS data given with (6.3.3) and HF constants from [19]. See text for discussion of expected behavior with HF constants from Table 6.2. (b)  $1/T_1T$  data (dots) are plotted vs.  $T$  for planar  $^{17}\text{O}$  in LSCO:0.15 [19]. Also plotted are data points for the c-axis NMR shift  $K_{17p}^s$  (open triangles), which have been scaled to coincide with the relaxation data (right-hand scale). The calculated behavior for  $1/T_1T$  based on INS data given with (6.3.3) and HF constants from Table 6.2 is shown as a dotted line. See text for discussion of these results. Reprinted figures from R. E. Walstedt, B. S. Shastry, S.-W. Cheong, Phys. Rev. Lett. **72**, 3610 (1994). Copyright 1994 American Physical Society

Experimental data plotted as  $1/T_1T$  for both  $^{63}\text{Cu}$  and the apical  $^{17}\text{O}$  in LSCO:0.15 are shown in Fig. 6.6(a).  $^{63}\text{Cu}$  NQR data are plotted as filled squares, while some earlier data from Imai et al., [33] are plotted as “+” symbols. These data sets are in very good accord where they overlap. In addition, data for the apical  $^{17}\text{O}$  scaled to coincide with the  $^{63}\text{Cu}$  data between 100 K and 200 K are shown as dots with error bars. Since the apical  $^{17}\text{O}$  is relaxed purely by local HF contact with one Cu-site spin, it is expected to behave roughly like the  $^{63,65}\text{Cu}$ . Owing to a very weak HF coupling, the latter data (i.e.  $^{17}T_1$ ) are in the seconds range at 50 K, while the corresponding numbers for  $^{63}\text{Cu}$  are in the sub-millisecond region. The apical oxygen appears to be diverging at the lowest temperatures a bit faster than the  $^{63}\text{Cu}$ , but they otherwise show a very similar temperature dependence.

The calculated values of  $1/T_1T$  for the  $^{63}\text{Cu}$  based on INS data for  $\chi''(\mathbf{q}, \omega)$  are shown as a dotted line cutting through the data plot at a rather steep angle [19]. With very limited parameter adjustability, the agreement between INS data and the  $^{63}\text{Cu}$  relaxation rate is quite satisfactory. However, our current estimate of the HF parameters, i.e.  $B$  in particular in Table 6.2, is somewhat smaller than that used in [19]. The latter values would therefore lead to estimates of  $1/T_1T \sim 30\%$  smaller than those plotted in the figure. We suggest that this would give a somewhat more realistic result, although it would clearly show that some other mechanism – presumably from a “background” contribution to  $\chi''(\mathbf{q}, \omega)$ , which cannot be seen with INS – becomes important at higher temperatures.

In Fig. 6.6(b) are plotted  $1/T_1T$  data for the planar  $^{17}\text{O}$  (dots: left-hand scale) scaled with three NMR shift data points (open triangles: right-hand scale). Thus,  $1/T_1T$  follows the susceptibility curve as was found for YBCO6.63 (Figs. 4.4 and 4.9), in behavior which is typical of a spin pseudogap. On the other hand, the calculated  $1/T_1T$  curve based on INS data and (3.5.14), shown as a dotted line, has the correct magnitude, but varies with temperature in a fashion which is totally incompatible with the NMR data.

The magnitude of the INS-based estimates of  $1/T_1T$  is generally correct for both nuclear spin species, verifying in part the extrapolated use of INS data at such low frequencies. What appears to be the case for the planar  $^{17}\text{O}$ , however, is that the discommensurations do not appear to hold up at the very low NMR frequencies<sup>3</sup>. With the same parameters for  $\chi''(\mathbf{q}, \omega)$ , except that  $\delta \sim 0$ , the planar  $^{17}\text{O}$  curve would drop by more than an order of magnitude. It follows, then, that the  $^{17}\text{O}$  relaxation process is completely dominated by

---

<sup>3</sup> The decay of the discommensurations at low frequencies implies, of course, that there is another energy scale in the problem where this happens. We must point out that there is no other evidence for such an effect. Moreover, such a crossover to commensurate fluctuations has been suggested to imply an instability in the system as well (C. Varma, private communication). We only wish to emphasize that the discommensurations observed in INS studies lead to predicted NMR effects which are not found.

a broad background term in  $\chi''(\mathbf{q}, \omega)$  which covers most of the BZ and which has the pseudogap (NMR shift-like) temperature dependence.

In [19] it was suggested that a two-band model of quasiparticle dynamics may be the answer to the  $^{17}\text{O}$   $T_1$  problem. However, in view of all of the negative discussion of that option in earlier chapters, such a possibility seems to be quite out of the question at this point. On the other hand, just how the discommensurations disappear and below what energy scale this happens are just as much a mystery now as they were in 1994. To this we must add the discrepancy which occurs in the superconducting state, where INS shows only a modest decline in the vicinity of  $\mathbf{Q} = (\pi, \pi)$  [21, 24]. Before concluding from this discrepancy with NMR data that there is some problem in principle here, however, one must verify that this is not a sample-dependent effect.<sup>4</sup>

### 6.3.2 Interpretation of $^{63}\text{Cu}$ and $^{17}\text{O}$ $T_2$ Data with INS Data for $\chi'(\mathbf{q})$

In Sect. 6.1 the interpretation of spin-echo decay ( $T_{2g}$ ) measurements with the purely static indirect coupling term  $\mathcal{H}_{zz}$  (see Appendix A.1) was discussed in some detail. This technique has been applied widely to cuprate NMR/NQR measurements. Here we consider the case of LSCO:0.15, for which we shall use the INS-derived calibration of  $\chi''(\mathbf{q}, \omega)$ , along with the Kramers-Kronig relation (6.3.1), to obtain quantitative estimates of  $\chi'(\mathbf{q})$ . The latter data, combined with HF constants from Table 6.2, are used for the indirect coupling calculation.

Spin echo decay in LSCO:0.15 presents a number of complications which did not occur in the “static” cases discussed in Sect. 6.1. The effects of  $T_1$  fluctuations, both direct and indirect (i.e., of neighbors), are quite important. Moreover, there is strong evidence that like-spin  $^{63,65}\text{Cu}$  neighbors in the  $m = \pm\frac{1}{2}$  states are fluctuating among themselves on the time scale of  $T_2$ , changing the nature of the problem in a fundamental way.

The planar  $^{17}\text{O}$  also present a different and unique situation, in that  $T_2$  is dominated by the  $^{63,65}\text{Cu}$ - $^{17}\text{O}$  indirect spin-spin coupling term, which is time-modulated by the  $^{63,65}\text{Cu}$   $T_1$  processes. The  $^{17}\text{O}$ - $^{17}\text{O}$  coupling term is reckoned to be negligibly small. The somewhat different methodology needed to treat these cases was reported in [31]. The techniques used there will be reviewed briefly here in the course of discussing the  $T_2$  data for LSCO:0.15 and its interpretation.

#### $^{63,65}\text{Cu}$ $T_2$ Data and Simulations of Nuclear Spin Fluctuations

Spin-echo decay measurements for  $^{63,65}\text{Cu}$  were carried out on a partially oriented powder sample of LSCO:0.15 containing  $\sim 30\%$   $^{17}\text{O}$  [31] at  $T \simeq 100\text{ K}$ . The measurements were made on the  $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$  transition in a field of 7 T. Decay curves were measured for  $^{63}\text{Cu}$  with several levels of refocussing

<sup>4</sup> The author thanks T. E. Mason for an informative discussion of this point.

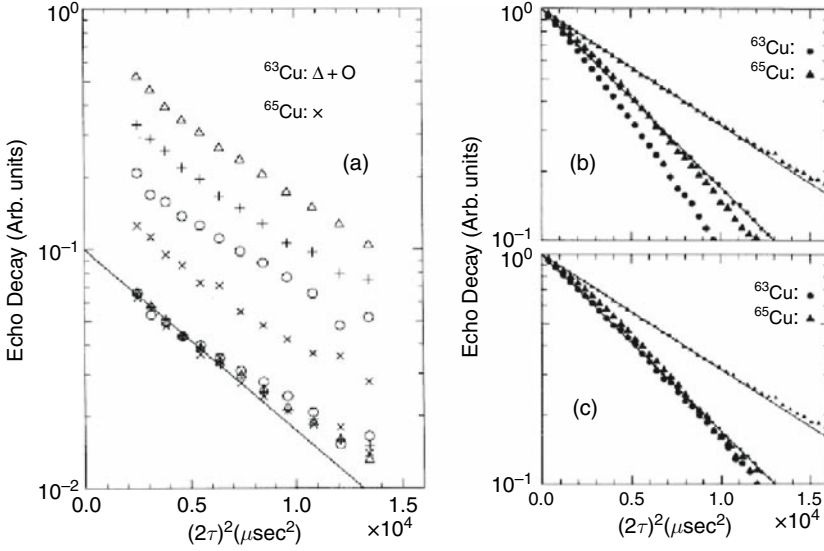


**Fig. 6.7.** (a) Spin echo decay curves for  $^{63,65}\text{Cu}$  taken on the  $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$  transition in a field of 7 T at a temperature of 100 K. Data for different refocussing pulses have been displaced vertically for clarity. Conditions are as follows: Full power,  $\theta_2 \simeq \pi$  ( $^{63}\text{Cu}$ :  $\Delta$ ). Power down 10 db,  $\theta_2 \simeq 3\pi/4$  ( $^{63}\text{Cu}$ :  $+$ ). Power down 10 db,  $\theta_2 \simeq \pi/4$  ( $^{63}\text{Cu}$ :  $\circ$ ). Full power,  $\theta_2 \simeq \pi$  ( $^{65}\text{Cu}$ :  $\times$ ). The curvature is thought to be caused by a distribution of indirect coupling strengths. The bottom curve is a composite of all the data. The solid line is the estimated Gaussian decay with  $T_{2g} = 75.6 \mu\text{s}$ . These data have all been corrected for direct  $T_1$  effects as described in the text. (b) and (c) Simulated decay curves obtained with random-number selection techniques as described in [31]. Small dots and triangles show static decay curves for  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ , respectively, where the decay is caused by a single  $\pi$  pulse. The solid lines show pure Gaussian decay. For (b) the large triangles and dots show how the decay curves are modified if random transitions simulating  $T_1$  relaxation effects are included. For (c) the large triangles and dots show results for when both  $T_1$  fluctuations and flip-flop transitions between the  $\pm\frac{1}{2}$  levels for  $^{63,65}\text{Cu}$  are included as described in the text. Reprinted figures from R. E. Walstedt, S.-W. Cheong, Phys. Rev. B **51**, 3163 (1995). Copyright 1995 American Physical Society

pulse as well as for  $^{65}\text{Cu}$  with  $\theta_2 \simeq \pi$ . The echo decay data obtained are shown in Fig. 6.7(a) [31].

The decay data shown have been corrected for direct  $T_1$  relaxation effects using results from Appendix A.3. The essence of the procedure is as follows. Direct  $T_1$  relaxation effects result in a factor  $\exp(-2\tau/T_{1E})$  multiplying the spin echo decay function. The value of  $T_{1E}$  depends on the  $T_1$  process of the nuclei observed, i.e. on its anisotropy and on the transition being excited. Defining  $W_\alpha$  to be the contribution to  $1/T_1$  from fluctuations along the  $\alpha$  axis,

then the relaxation rate with field along the  $z$  axis becomes  $1/T_{1z} = W_x + W_y$ . For arbitrary half-integral spin the  $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$  transition echo decay rate for isotropic spin-lattice relaxation is  $1/T_{1E} = (I + \frac{1}{2})^2/T_1$ . For the anisotropic case this becomes

$$\frac{1}{T_{1Ez}} = \frac{[I(I+1) - 3/4]}{T_{1z}} + \frac{1}{2T_{1x}} + \frac{1}{2T_{1y}}, \quad (6.3.6)$$

in terms of  $T_1$  values measured along the three axes. For axial symmetry with  $I = \frac{3}{2}$  this becomes  $1/T_{1Ez} = 3/T_{1z} + 1/T_{1xy}$  in an obvious notation. With known values of  $T_{1\alpha}$  for LSCO:0.15, this formula gives  $T_{1Ec} = 90\mu\text{s}$  for  $^{63}\text{Cu}$  and  $80\mu\text{s}$  for  $^{65}\text{Cu}$ . The corresponding correction factors have been applied to the echo decay data in Fig. 6.7(a).

The decay curves in Fig. 6.7(a) have been shifted vertically for clarity. At the bottom of the figure is a composite plot of all four curves, which shows that they are very nearly indistinguishable. This is a remarkable result in the sense that the decay is independent of  $\theta_2$  and is also the same for both isotopes, whose  $\gamma$  values differ by  $\sim 7\%$ . The first effect shows that there is considerable amount of “flip-flop” motion taking place, and the second can be rationalized by means of the latter effect combined with the effect of  $T_1$  fluctuations [31]. We give here a brief account of these mechanisms, which were presented in detail in [31].

In order to take account of the foregoing effects in a calculation of spin echo decay, the decay process has been simulated with a model where the spin in question is coupled to neighbor spins with a set of randomly chosen coefficients. The coefficients are scaled to give a second moment adjusted at first to produce the observed value of  $1/T_{2g}$  (line drawn in Fig. 6.7(a)) in a static decay process for  $^{63}\text{Cu}$ . In a statistical simulation of such a static echo decay this yields the small dots in Fig. 6.7(b) for  $^{63}\text{Cu}$  and small triangles for  $^{65}\text{Cu}$ . Straight lines representing precise Gaussian decay functions are drawn for comparison. Note that the  $^{65}\text{Cu}$  spin echo decays much more slowly than the  $^{63}\text{Cu}$ . This is because the 31% abundant  $^{65}\text{Cu}$  has only half as many “like-spin” neighbors with which to relax the echo [31].

The next step is to introduce the “indirect  $T_1$  effects” by allowing the neighbor spins to execute random transitions between  $m$  levels at the correct rate dictated by magnetic dipole coupling  $T_1$  processes. The result of this is shown as large dots ( $^{63}\text{Cu}$ ) and large triangles ( $^{65}\text{Cu}$ ) in Fig. 6.7(b). The decay constant  $1/T_{2g}$  for  $^{63}\text{Cu}$  is increased by  $\sim 15\%$  by the  $T_1$  fluctuations, but for  $^{65}\text{Cu}$  the increase is nearly three times as much. This is because the number of neighbor spins relaxing the  $^{65}\text{Cu}$  is increased by about a factor of six, whereas the increase for  $^{63}\text{Cu}$  is much smaller. Now the  $^{63}\text{Cu}$  are relaxing  $\sim 10\%$  faster than the  $^{65}\text{Cu}$ .

The final step is to initiate flip-flop transitions between the  $\pm\frac{1}{2}$  levels of both isotopes. That these are actually taking place is evidenced by the absence of change in the decay curve with  $\theta_2$  in Fig. 6.7(a). Since the  $(\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2})$  transitions undergo severe first-order quadrupolar broadening, flip-flop transitions

are only allowed for the  $\pm\frac{1}{2}$  levels. Estimates from the indirect interaction calculations suggest that flip-flops are present on a time scale of about  $50\mu s$ . Introducing these into the simulation then gives the decay curves shown in Fig. 6.7(c) (large dots and triangles). The  $^{65}\text{Cu}$  decay time increases slightly, but the  $^{63}\text{Cu}$  increases by more than 10%, so that the two now very nearly coincide. Evidently, the flip-flops give a slightly greater “narrowing” effect for like spins than for unlike spins. In any case, now the decay times are nearly the same for both isotopes, as was observed. Quite coincidentally, they are both now equal to the initially estimated static decay time for  $^{63}\text{Cu}$  within just a small error. We do not believe that there is any simple way to obtain this result except by simulation [31].

### Indirect Coupling Calculations for $^{63}\text{Cu}$

Having determined a reasonable experimental estimate of  $1/T_{2g}$  for the  $^{63}\text{Cu}$  in LSCO:0.15, we could now compare that number with calculations based on an evaluation of  $a_\alpha(i, j)$  with (6.1.7), the HF parameters from Table 6.2, and  $\chi'(\mathbf{q})$  calculated with INS data for  $\chi''(\mathbf{q}, \omega)$  using the Kramers-Kronig relation (6.3.1). This kind of calculation was reported in [31], using the form (6.3.3) for  $\chi''(\mathbf{q}, \omega)$  at all energies. Below, we display the latter results and then make a critical commentary on how this evaluation should be modified in the light of more recent INS data, particularly the high-energy spallation source results [23].

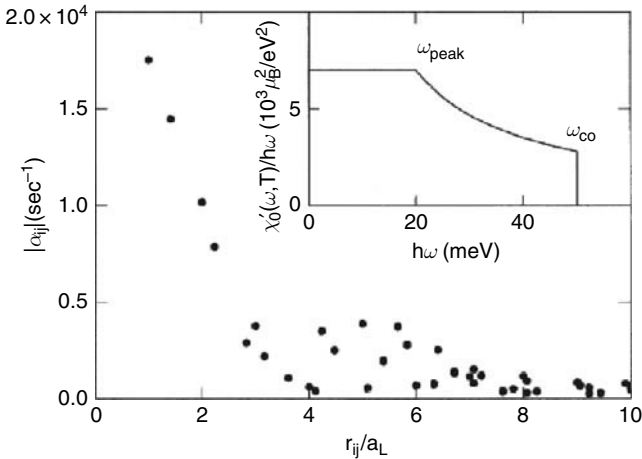


**Fig. 6.8.** The calculated range function  $\alpha_{ij}$  for the “zz” indirect coupling terms among the  $^{63,65}\text{Cu}$  is shown as filled circles vs.  $r_{ij}$ . Only coefficients greater than 2% of the  $nn$  value are included in the plot. The inset shows the coefficient from (6.3.7) which occurs in the KK integral, adjusted to yield the measured value of  $T_2$ . Reprinted figures from R. E. Walstedt, S.-W. Cheong, Phys. Rev. B **51**, 3163 (1995). Copyright 1995 American Physical Society

In [31] the same basic expression (6.1.9) was used for the coefficients, where the Kramers-Kronig integral of the expression

$$\chi''(\mathbf{q}, \omega) = \frac{\chi_0''(\omega, T) \kappa^4(\omega, T)}{[\kappa^2(\omega, T) + R(\mathbf{q})]^2}, \quad (6.3.7)$$

in the same notation as (6.3.3), is used for  $\chi'_\alpha(\mathbf{q})$ . In this expression, one has  $\kappa^2(\omega, T) = \kappa_0^2 + a_L^2[(k_B T/E_T)^2 + (\hbar\omega/E_\omega)^2]$ , with  $\kappa_0 = 0.034 \text{ \AA}^{-1}$  and  $E_T = E_\omega = 47 \text{ meV}$  [25]. For the low-frequency region ( $\omega < 20 \text{ meV}$ ), the function  $\chi''(\omega, T)$  can be represented as linear in  $\omega$  and declining with temperature as  $1/T^2$  [25]. It was found that the KK integral up to  $20 \text{ meV}$  was insufficient to account for  $1/T_{2g}$ , so the integral was extended, with  $\chi''(\omega, T) = \text{constant}$ , up to a cutoff for an evaluation at  $T = 100 \text{ K}$ . Adjusting the cutoff to obtain the experimental value of  $1/T_{2g}$ , it was found to be  $\omega_{co} \simeq 50 \text{ meV}$ .

The range function  $\alpha_{ij}$  for the  $^{63}\text{Cu}$  coupling ( $\mathcal{H}_{zz}$ ) calculated as described is displayed in Fig. 6.8(a), where the KK integrand  $\chi''(\omega, T)/\omega$  is shown in the inset. Since there are usually four neighbors at each value of  $r_{ij}$ , this figure shows that the indirect coupling second moment is dominated by 15–20 neighbor nuclei.

It is interesting to consider what modification would be made to this analysis in the light of high-frequency  $\chi''(\mathbf{q}, \omega)$  data [23] (Fig. 6.5), which were not available at the time [31] was submitted. There are two main differences if one envisions using the data of Fig. 6.5. First, to the extent that discommensurations survived in  $\chi'(\mathbf{q})$ , they would no doubt be greatly diminished in importance with data from Fig. 6.5, which would be represented by a single peak with amplitude varying as  $\Gamma\omega/(\Gamma^2 + \omega^2)$  with  $\Gamma = 22 \pm 5 \text{ meV}$ . This is probably of little significance for the  $^{63,65}\text{Cu}$ , but it will figure in our discussion of  $^{17}\text{O}$  below. Second, the Lorentzian gives a broader “spectrum” of contributions, extending out to  $150 \text{ meV}$  and beyond. Interestingly, if one performs the KK integral for these two cases, the results agree within a few percent. Thus, the new data [23] corroborate the earlier result for  $^{63,65}\text{Cu}$  [31].

### ***T<sub>2</sub> Decay of the Planar $^{17}\text{O}$ at 100 K***

The planar  $^{17}\text{O}$  spin-echo decay data at  $100 \text{ K}$  are displayed in Fig. 6.9. This decay curve cannot be characterized in a simple way, a circumstance resulting, we believe, from the nature of the sample. Whereas only a modest percentage of field-oriented sample material contributed to the Cu NMR signals, the  $^{17}\text{O}$  second-order quadrupolar shifts are negligibly small. As a result, essentially all of the poorly-aligned sample material contributes to the planar  $^{17}\text{O}$  line. We therefore treat the system as a random powder. Furthermore, quite unexpectedly, the dipolar spin-spin coupling alone accounts for the decay curve in Fig. 6.9. Its peculiar character, with a long tail of low amplitude, is caused by the “magic angle” region of phase space where  $3\cos^2\theta - 1 \sim 0$ . The corresponding subset of nuclei relax very slowly.

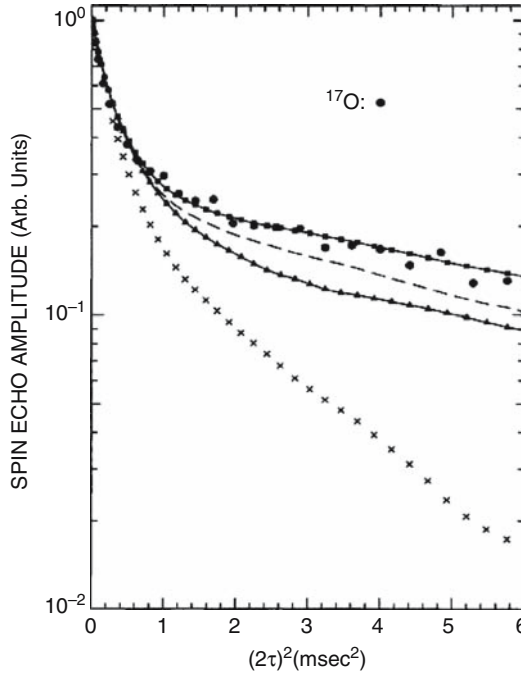


**Fig. 6.9.** Experimental data for the  $^{17}\text{O}$  spin echo decay at 100 K (*filled circles*) are plotted vs.  $(2\tau)^2$ . The field is oriented along the  $c$  axis. A simulated decay curve calculated with the combined effects of dipolar and indirect coupling calculated as for the  $^{63,65}\text{Cu}$  is shown as “ $\times$ ” symbols. A simulated decay curve with purely dipolar couplings modulated by  $T_1$  processes alone is plotted with filled triangles connected by a solid line. The same calculation with both  $T_1$  modulation and dynamic flip-flop transitions between the  $\pm\frac{1}{2}$  levels of the  $^{63,65}\text{Cu}$  neighbors, shown as filled squares connected by a solid line, is seen to be in good accord with the data [31]. Reprinted figures from R. E. Walstedt, S.-W. Cheong, Phys. Rev. B **51**, 3163 (1995). Copyright 1995 American Physical Society

There is, however, more to the story than just those simple points. On evaluating the indirect coupling terms for the planar  $^{17}\text{O}$ , it was found that the  $^{17}\text{O}$ – $^{17}\text{O}$  terms were small, but that there was a sizeable  $^{63,65}\text{Cu}$ – $^{17}\text{O}$  term, which gives an unlike spin indirect second moment  $\langle\Delta\omega^2\rangle_{AB}^I = 1.5 \times 10^7 \text{ s}^{-2}$  [31], larger than the corresponding dipolar term  $\langle\Delta\omega^2\rangle_{AB}^{\text{dip}} = 6.25 \times 10^6 \text{ s}^{-2}$  (98% of which is contributed by the two  $nn$   $^{63,65}\text{Cu}$  spins). This unlike-spin second moment is expected to dominate the  $^{17}\text{O}$  spin-echo decay, because of its time-modulation by the  $^{63,65}\text{Cu}$   $T_1$  processes. Thus, for a crystal of unique orientation one has  $1/T_{2\text{O}} = \langle\Delta\omega^2\rangle_{AB} T_{1\text{Cu}}$ .

The calculation of the powder-average decay curve, including indirect couplings evaluated as for the  $^{63,65}\text{Cu}$  case above, leads to the decay curve plotted with “ $\times$ ” symbols in Fig. 6.8(b). This is widely at variance with the

experimental data. The difficulty, we surmise, is again related to the assumed discommensurations at NMR frequencies. If  $\delta \rightarrow 0$  in  $R(\mathbf{q})$  (6.3.4), the indirect coupling drops by a large factor and its contribution to  $\langle \Delta\omega^2 \rangle_{AB}$  becomes negligibly small. *This inconsistency with discommensurations is on the same scale as the estimate of  $T_1$  in Fig. 6.6(b).* It again suggests that the discommensurations in the INS data ((6.3.3) and (6.3.4)) are not “seen” at NMR frequencies.

There is yet another small surprise in the interpretation of Fig. 6.9. If one takes the dipolar second moment in the foregoing formula, i.e.  $1/T_{2O} = \langle \Delta\omega^2 \rangle_{AB}^{dip} T_{1Cu}$ , averaged over all orientations, one finds the curve plotted with small triangles in Fig. 6.8(b), not quite in quantitative agreement with the data. The final curve, plotted with filled squares, is only obtained when one includes the  $50 \mu s$ -rate flip-flops between the  $\pm \frac{1}{2}$  levels. These, we recall, were important in interpreting the  $^{63,65}\text{Cu}$   $T_2$  decay curves as well.

In the end, however, the most astonishing result is the total abnegation of indirect spin-spin coupling for the planar oxygen nuclei.

## 6.4 The Sokol-Barzykin-Pines Scaling Theory of $\chi(q, \omega)$

A large body of work has grown up around the discussion of scaling theories in the normal state of YBCO, Y248, and LSCO by Pines and co-workers [16, 34] and Moriya et al., [35]. We offer here a brief summary of NMR/NQR results and interpretation in terms of the theories mentioned. Although a great deal has been done, there seem to be important questions which remain unresolved as well. The details of these theoretical models go beyond the scope of this book, so we shall focus here on predicted behavior and experimental tests thereof. In the interest of presenting a compact account of this subject, many interesting experimental details have been omitted. The interested reader is referred to the literature cited for a more detailed account of these matters.

### 6.4.1 Phase Diagram and Basic Relationships for $T_1$ , $T_{2g}$

To facilitate discussion we display the basic phase diagram presented by Barzykin and Pines (BP) [34] in Fig. 6.10, which refers specifically to  $\text{YBCO}_y$  (see also the paper by Sokol and Pines (SP) [16]). For the superconducting phases ( $6.45 \leq y \leq 7.0$ ) the important regions are labelled “quantum critical” (QC), “quantum disordered” (QD), and “no scaling”, which was formerly termed the “overdamped” (OD) region [16]. These terms refer, of course, to the behavior of the AFM fluctuations in the system, which are generally assumed to control the static and dynamic magnetic properties. One of the key parameters is a temperature-varying correlation length  $\xi$ , which is dimensionless in units of the lattice constant  $a$ . In the QC region,  $\xi \gg 1$  but grows shorter with increasing temperature, until at  $\xi \sim 2$  there is a crossover labelled  $T_{cr}$  to the OD region, in which  $\xi$  is of the order of 1 or less. At higher

temperatures and doping levels the AFM fluctuations cease to be a controlling factor and the system reverts to a normal Fermi liquid. The temperature  $T_*$  which marks the boundary between QC and QD will be defined below.

It is useful to note that the phase boundary in Fig. 6.10 is similar to the phase boundary between regions I and II of the phase diagram proposed by Varma (see Fig. 4.19). The implied physical significance of these phase boundaries may also be quite different in detail [36].

In Fig. 6.10,  $T_{cr}$  has also been identified with a maximum in the uniform susceptibility by BP, and data points shown in Fig. 6.10 for  $T_{cr}$  have derived from NMR shift data. Large error bars reflect the flatness of such maxima. Below, we review an effort to locate  $T_{cr}$  more precisely with NQR studies of  $T_1$  and  $T_2$  of  $^{63}\text{Cu}(2)$  in Y248. From the behavior of  $^{89}\text{Y}$  NMR shift data, Han et al., [37] have determined that the equivalent oxygen level of Y248 in the  $\text{YBCO}_y$  family is at YBCO6.8. On that basis, BP suggest that  $T_{cr}$  for Y248 should occur at  $\sim 500\text{ K}$ .

Although drawn for YBCO, the phase diagram structure shown in Fig. 6.10 is presumed to apply to all cuprates. The superconducting region lies within the QD region. A system doped to the right of the  $T_{cr}$  line has no pseudogap and lies in the OD region at all temperatures. If there are AFM fluctuations in the OD region, they are assumed to obey mean-field behavior [35] as opposed to QC behavior. We now define the behavior of  $\chi(\mathbf{q}, \omega)$  according to the BP model [16, 34].

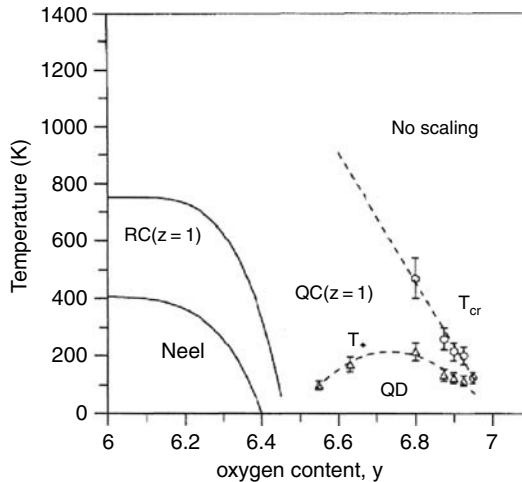


**Fig. 6.10.** Phase diagram from Barzykin and Pines [34] for magnetic scaling behavior in the YBCO family of cuprates. In the superconducting phases there are three regions identified, the quantum critical (QC:  $z=1$ ), the quantum disordered (QD:  $z=1$ ), and the “no scaling” (or overdamped OD:  $z=2$ ). Definition and measurement of the phase boundaries is discussed in the text. Reprinted figure from V. Barzykin, D. Pines, Phys. Rev. B **52**, 13585 (1995). Copyright 1995 American Physical Society

To consider the SP-BP model, AFM correlations are characterized by the correlation length  $\xi$  and the low-frequency fluctuation energy scale  $\omega_{sf}$ , both of which may vary with temperature. These energy and length scales are related by the *dynamical exponent*  $z$ , thus  $\omega_{sf} \sim \xi^z$ . In this connection it is also useful to employ the MMP model susceptibility [4, 11, 16]

$$\chi(\mathbf{q}, \omega)_{MMP} = \frac{\xi^2 \chi_0}{1 + q^2 \xi^2 - i\omega/\omega_{sf}} \quad (6.4.1)$$

as was employed by PS in their indirect coupling calculation [2]. Then, taking the simplified forms

$$\frac{1}{T_1 T} \sim \int d^2 q \left[ \frac{\chi''(\mathbf{q}, \omega)}{\omega} \right]_{\omega \rightarrow 0}, \quad \frac{1}{T_{2g}} \sim \int d^2 q \chi'(\mathbf{q}, 0)^2, \quad (6.4.2)$$

one finds the relations

$$\frac{1}{T_1} \sim \frac{T}{\omega_{sf}}, \quad \frac{1}{T_{2g}} \sim \xi. \quad (6.4.3)$$

Without paying much attention to the approximations involved, we apply (6.4.3) to different parts of the phase diagram. In the overdamped,  $z = 2$  region, we have  $\omega_{sf}^{-1} \sim \xi^2$ , leading to  $T_1 T / T_{2g}^2 \sim \text{constant}$ , which was the scaling prediction of Moriya et al., [38]. On this basis it was suggested that  $T_1 T / T_{2g}^2$  is approximately constant for YBCO7 [6, 16] (however, see further discussion of this point below). At high temperatures BP suggest  $\omega_{sf} \sim T$ , so that  $T_1 \sim \text{constant}$  and  $T_{2g} \sim T^{1/2}$ , which is at least a semiquantitative description of the data of Imai et al., [9].

The point here is that across the  $T_{cr}$  line in Fig. 6.10 the behavior is expected to be qualitatively different. Moreover, the approximations for (6.4.2) and (6.4.3) are better in that  $\xi \gg 1$ . Thus, with  $z = 1$ ,  $\omega_{sf}^{-1} \sim \xi$  and one expects that  $T_{2g}/T_1 T \sim \text{constant}$ . Again, at high  $T$ ,  $\omega_{sf} \sim T$ , so with (6.4.3) one again expects  $T_1 \sim \text{constant}$  [34]. An interesting example of the latter behavior is seen in the LSCO data of Ohsugi et al., [3] shown in Fig. 6.11. The behavior of  $T_1 T$  vs.  $T$  is such that the curve is linear at high temperatures for all compositions of LSCO: $x$  up to  $x = 0.24$ . Lest one suppose that  $x = 0.24$  is “overdoped” (or OD), however, it is noteworthy that at low temperatures  $1/T_1 T$  for LSCO:0.24 is more than twice as great as for YBCO7 [3]. What is quite remarkable, however, is that for  $x = 0.075$  the linear behavior of  $T_1 T$  in Fig. 6.11 extrapolates nearly to the origin;  $T_1$  is almost perfectly constant from  $\sim 75$  K up to 300 K.

The latter figure also illustrates the QC-QD boundary  $T_*$ , which is the point at which the data for  $T_1 T$  break away from the linear high- $T$  behavior.  $T_*$  is seen to range from  $\sim 50$  K to  $\sim 100$  K over the range of compositions tested.

We note in passing that the behavior of  $T_1 T$  in Fig. 6.11 suggests that the  $^{63,65}\text{Cu}$  relaxation process over this range of temperature and concentrations is dominated by a single mechanism, namely the contribution of the AFM

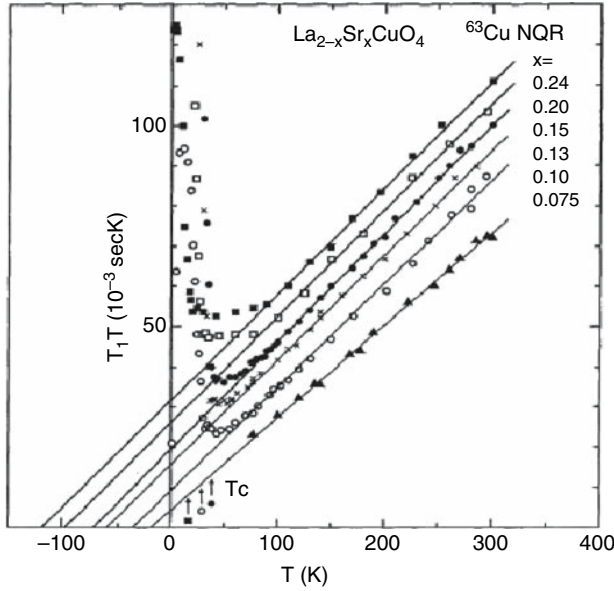


**Fig. 6.11.** Plot of  $T_1T$  data vs.  $T$  for compositions of LSCO: $x$ , with  $x$  ranging over the superconducting phase [3]. These data exhibit the high-temperature limiting behavior of the SP model [16], where  $T_1T$  goes asymptotically as  $\omega_{sf} \sim T$ . Reprinted figure from S. Ohsugi, Y. Kitaoka, K. Ishida, G-q. Zheng, and K. Asayama, *J. Phys. Soc. Japan* **63**, 700 (1994). Copyright 1994 Physical Society of Japan

peak(s) in the vicinity of  $(\pi, \pi)$ . That viewpoint, however, is not quite consistent with the behavior seen in Fig. 6.6(a), where it appears from the INS data employed there that by room temperature the relaxation will be dominated by a “background” term not resolvable with INS. This discrepancy remains to be analyzed and understood.

As for the behavior of  $T_{2g}$  in LSCO, the variation of  $T_1T/T_{2g}^n$ ,  $n = 1$  or  $2$ , was examined in some detail in a study where the indirect  $T_1$  corrections to spin echo decay discussed in Sect. 6.3 were carefully evaluated [39]. It was found for LSCO:0.15 that  $T_1T/T_{2g}$  is constant well within the errors and  $T_1T/T_{2g}^2$  was not, clearly placing this system in the QC category. Interestingly, a similar evaluation for YBCO7 found that QC behavior for this system was favored as well [39], contrary to the conclusion mentioned earlier [16]. In much of the literature, the indirect  $T_1$  corrections to  $T_{2g}$  have not been taken account of. Note, however, the work of Keren et al., [40].

#### 6.4.2 The Dynamical Crossover Study by Curro et al: Y248

A very interesting piece of experimental work regarding the  $z = 1$  to  $z = 2$  crossover is that of Curro et al., [4], who performed a temperature scan of the dynamics on the system Y248. To our knowledge, no other such test of the

$T_{cr}$  boundary has been reported. Y248 is an excellent system for such a test, because it is stable (i.e. does not lose oxygen) for temperatures well beyond 700 K. This study reported  $T_1$  and  $T_{2g}$  data up to the latter temperature. In order to perform such a study it was necessary to use a random powder sample, since no known epoxy resin would be stable at such high temperatures. Thus,  $T_1$  and  $T_{2g}$  were measured using NQR and the NMR shift was measured using the powder-pattern NMR spectrum. Stray magnetic fields had to be shielded out of the sample space to a fraction of a Gauss, because they disturb the NQR spin echo decay function. Finally, the authors examined and corrected for the indirect  $T_1$  modifications of  $T_{2g}$  described in Sect. 6.3 for LSCO [31].

One stimulus for the Y248 study discussed here was the conjecture by Barzykin and Pines [34] that the Y248 system would exhibit a crossover transition at  $T \sim 500$  K. The  $^{63}\text{Cu}(2)$   $T_1$  data from Y248 exhibited a curve of  $T_1 T$  vs.  $T$  very similar to one of the lightly-doped compounds in Fig. 6.11 with  $T_* \sim 200$  K, but showed no feature at 500 K [4]. The  $T_{2g}$  data, on the other hand, showed a definite kink near 500 K, as may be seen in Fig. 6.12. Also shown in that figure are data (open circles) from a previous study by Corey et al., [41] which are in excellent accord, but extend only to  $\sim 450$  K.

In Fig. 6.13  $T_1$  and  $T_{2g}$  data for  $^{63}\text{Cu}(2)$  are combined to make plots of both  $T_1 T / T_{2g}$  (upper panel) and  $T_1 T / T_{2g}^2$  (lower panel), using the data described.

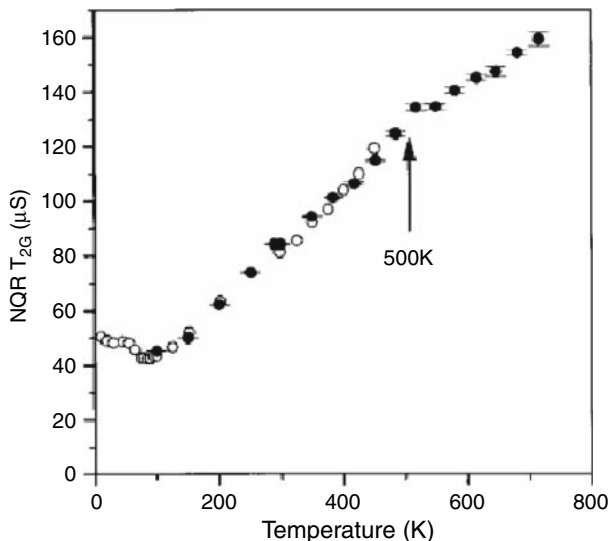


**Fig. 6.12.** Plot of measured  $T_{2g}$  for  $^{63}\text{Cu}(2)$ , taken on the NQR line of Y248. Data from the study of the dynamical crossover in Y248 by Curro et al. [4] are shown as solid circles. The open circles are from a previous study by Corey et al., [41]. Note the abrupt change of slope at 500 K. Reprinted figure from N. Curro, T. Imai, C.P. Slichter, and B. Dabrowski, Phys. Rev. B **56**, 877 (1997). Copyright 1997 American Physical Society

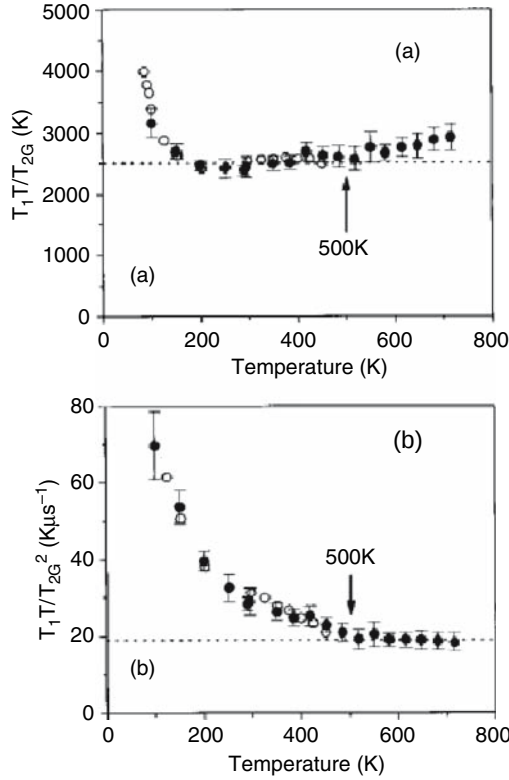


**Fig. 6.13.** Data for  $T_1$  and  $T_{2g}$  for  $^{63}\text{Cu}(2)$  in Y248, plotted as  $T_1 T / T_{2g}$  vs.  $T$  (a) and as  $T_1 T / T_{2g}^2$  vs.  $T$  (b) (closed circles). The (a) panel shows the scaling (QC:  $z=1$ ) regime extending from  $T^* \sim 200$  K to  $T_{cr} \simeq 500$  K. The (b) panel shows the onset of the non-scaling (OD:  $z=2$ ) regime at  $\simeq 500$  K. The earlier data of Corey et al., [41] are shown as open circles. Reprinted figures from N. Curro, T. Imai, C.P. Slichter, and B. Dabrowski, Phys. Rev. B **56**, 877 (1997). Copyright 1997 American Physical Society

The upper panel data show that once past  $T^* \sim 200$  K,  $T_1 T / T_{2g}$  remains very nearly constant up to the crossover  $T_{cr} \simeq 500$  K, as expected for QC behavior. Above that point it veers upward very slightly. In the lower panel, the ratio  $T_1 T / T_{2g}^2$  is plotted with the same data. Up to 500 K the latter ratio is seen to execute a downward path, levelling off at 500 K just where the putative entry into the OD phase should occur. This seems about as clear-cut a crossover as one could expect. Moreover, these data show that the transition from QC to OD behavior is relatively sharp.

The foregoing identification of the crossover was also corroborated by NMR shift data, which indicate (Fig. 6.14) a flat maximum in the uniform susceptibility in the vicinity of 500 K. These data do not locate the crossover as

precisely as the dynamical plots, but they are consistent with the results in Fig. 6.13.

The authors have also developed a procedure to observe the crossover directly in terms of  $\xi(T)$ . Using, first, (6.4.3) with the coefficient adjusted to give the BP predicted value  $2.0\text{\AA}$  at the crossover, they find the bottom curve in Fig. 6.15 (triangles). Secondly, they have adopted the exact solution for the susceptibility of a Heisenberg AFM given by Sokol, Singh, and Elstner (SSE) [42] to give a second estimate of the  $\xi(T)$  curve, where the latter workers also suggested that this would be a reasonable approximation to the behavior of lightly-doped cuprates at high temperatures [4]. The latter susceptibility is given by

$$\chi(\mathbf{q}, \omega, T)_{SSE} = \frac{\chi_0(T)[1 + \theta(T)]}{1 + \theta(T)\gamma(\mathbf{q}) + i\Gamma_q\omega}, \quad (6.4.4)$$

where  $\gamma(\mathbf{q}) = \frac{1}{2}[\cos q_x + \cos q_y]$ ,  $\theta(T) = 4\xi^2(T)/[1 + 4\xi^2(T)]$ , and  $\Gamma_q$  is a fluctuation rate which is not required for  $\chi'(\mathbf{q}, 0)$  (and thus  $T_{2g}$ ). In using (6.4.4) to interpret the  $T_{2g}$  data, the value of  $\chi_0(T)$  was taken from the NMR shift measurements, the known HF constants were used, and the second moment was calculated using the full expression (6.1.8). The only unknown parameter  $\xi(T)$  is then extracted from the  $T_{2g}$  data in Fig. 6.12. These values are plotted in Fig. 6.15 as open circles. According to this determination,  $\xi = 1.4$  at the crossover temperature, somewhat less than the BP estimate. If the de-

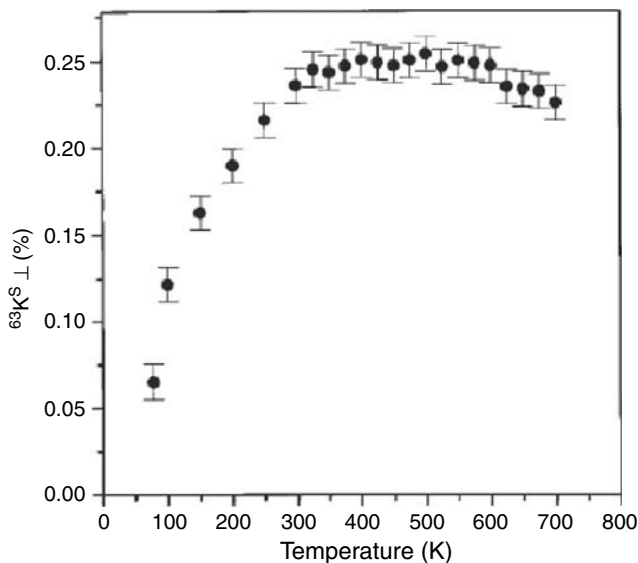


**Fig. 6.14.** The  $^{63}\text{Cu}(2)$  NMR shift is plotted vs. temperature, showing the maximum of the uniform susceptibility at  $T_{cr} \sim 500\text{ K}$ , in agreement with the plot of  $T_{2g}$  (Fig. 6.12). Reprinted figure from N. Curro, T. Imai, C.P. Slichter, and B. Dabrowski, Phys. Rev. B **56**, 877 (1997). Copyright 1997 American Physical Society

termination using (6.4.3) is adjusted to give  $\xi = 1.4$  at 500 K, then the curve with filled squares results, which is remarkably similar to the exact solution by SSE.

In all three of the plotted curves for  $\xi(T)$  vs.  $T$  there is a definite point very near to 500 K which one would naturally associate with a transition from one type of behavior to another, even if there had been no theoretical prediction of such a point. With the SSE susceptibility (6.4.4), however, there is a remarkably large change in the slope of the curve at  $T_{cr}$ , giving very dramatic evidence of the dynamical crossover.

In conclusion, it seems that the QC,  $z = 1$  behavior for AFM fluctuations is clearly established for Y248 as well as for LSCO [39]. For Y248, the present work finds a clear-cut crossover transition at  $T \simeq 500$  K. In the case of LSCO there is evidence for a crossover curve from susceptibility [43, 44] as well as Hall effect data [34, 45]. It appears quite possible that a crossover curve for LSCO could also be established using  $T_1 T / T_{2g}^n$  plots as was done with Y248. Measurements would probably have to be done with single-crystal samples and conducted in an oxygen atmosphere in order to maintain sample integrity at

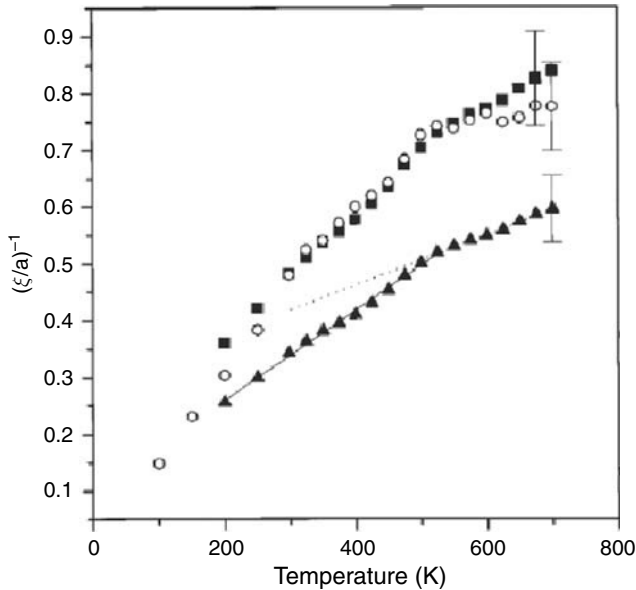


**Fig. 6.15.** Values of correlation length  $\xi(T)$  derived from the data for  $T_{2g}$  in Fig. 6.12 as follows: Triangles are from (6.4.3) with coefficient adjusted to give  $\xi = 2.0$  at  $T = 500$  K. Open circles are from the SSE exact solution ([42]), where  $\chi_0(T)$  is derived from the shift data in Fig. 6.14. Closed squares are from (6.4.3) with the coefficient adjusted to give  $\xi = 1.4$  at  $T = 500$  K. See text for interpretation of this result. Reprinted figure from N. Curro, T. Imai, C. P. Slichter, and B. Dabrowski, Phys. Rev. B **56**, 877 (1997). Copyright 1997 American Physical Society

elevated temperatures (e.g. see [46]). It would be interesting and important to investigate the *sharpness of the crossover transition* in this fashion, since the present work has shown that this could be a very interesting issue [4].

## References

1. C.H. Pennington, D.J. Durand, C.P. Slichter, Phys. Rev. B**39**, 274 (1989) 213, 214
2. C.H. Pennington, C.P. Slichter, Phys. Rev. Lett. **66**, 381 (1991) 213, 214, 219, 220, 244
3. S. Ohsugi, Y. Kitaoka, K. Ishida, G.-q. Zheng, K. Asayama, J. Phys. Soc. Japan **63**, 700 (1994) 214, 232, 233, 244, 245
4. N. Curro, T. Imai, C.P. Slichter, B. Dabrowski, Phys. Rev. B**56**, 877 (1997) 214, 244, 245, 246
5. D. Pines, C.P. Slichter, Phys. Rev. **100**, 1014 (1955) 216
6. M. Takigawa, Phys. Rev. B**49**, 4158 (1994) 216, 220, 222, 223, 244
7. D. Thelen, D. Pines, Phys. Rev. B**49**, 3528 (1994) 216
8. A.J. Millis, H. Monien, Phys. Rev. B**45**, 3059 (1992) 217
9. T. Imai, C.P. Slichter, et al., Phys. Rev. B**47**, 9158 (1993) 217, 220, 221, 223, 244
10. T. Auler, M. Horvatic et al., Physica C **313**, 255 (1999) 217, 220, 221, 222, 223
11. A.J. Millis, H. Monien, D. Pines, Phys. Rev. B**42**, 167 (1990) 219, 244
12. Y. Itoh, H. Yasuoka, et al., J. Phys. Soc. Japan **61**, 1287 (1992) 220, 221, 224, 225, 226
13. N. Bulut, D.J. Scalapino, Phys. Rev. Lett. **67**, 2898 (1991) 221, 224, 225, 226
14. N. Bulut, D.J. Scalapino, Phys. Rev. Lett. **68**, 706 (1992) 221, 224
15. N. Bulut, D.J. Scalapino, Phys. Rev. B**45**, 2371 (1992) 221, 224, 225
16. A. Sokol, D. Pines, Phys. Rev. Lett. **71**, 2813 (1993) 223, 242, 243, 244, 245
17. A. Uldry, M. Mali, J. Roos, P.F. Meier, J. Phys. Condens. Matter **17**, L499 (2005) 225
18. T. Moriya, J. Phys. Soc. Japan **18**, 516 (1963) 227, 233
19. R.E. Walstedt, B.S. Shastry, S.-W. Cheong, Phys. Rev. Lett. **72**, 3610 (1994) 227, 230, 232, 233
20. S.-W. Cheong, G. Aeppli, T.E. Mason et al., Phys. Rev. Lett. **67**, 1791 (1991) 227, 228
21. T.E. Mason, G. Aeppli, H. Mook, Phys. Rev. Lett. **68**, 1414 (1992) 227, 228, 229, 230, 231, 232
22. A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1983) 228
23. S.M. Hayden, G. Aeppli, H. Mook et al., Phys. Rev. Lett. **76**, 1344 (1996) 228, 229, 230, 231, 232
24. T.R. Thurston, P.M. Gehring, G. Shirane et al., Phys. Rev. B**46**, 9128 (1992) 228, 232, 236
25. G. Aeppli, T.E. Mason et al., Science **278**, 1432 (1997) 230, 232, 240
26. K. Ishida et al., J. Phys. Soc. Japan **60**, 2351 (1991) 233
27. B. Batlogg, in *Physics of High-Temperature Superconductors*, ed S. Maekawa and M. Sato, Springer Series in Solid-State Sciences, Vol. 106 (Springer-Verlag, Berlin, 1992), p. 219 233
28. K. Ishida et al., J. Phys. Soc. Japan **60**, 3516 (1991) 233
29. D.C. Johnston, J. Magn. Magn. Mater. **100**, 219 (1991) 233
30. T. Imai, C.P. Slichter, et al., Phys. Rev. Lett. **70**, 1002 (1993) 233
31. R.E. Walstedt, S.-W. Cheong, Phys. Rev. B**51**, 3163 (1995) 233, 236, 237, 238, 239, 240, 241, 242
32. M. Takigawa, A.P. Reyes, P.C. Hammel, Phys. Rev. B**43**, 247 (1991) 233
33. T. Imai et al., J. Phys. Soc. Japan **59**, 3846 (1990) 234, 235
34. V. Barzykin, D. Pines, Phys. Rev. B**52**, 13585 (1995) 242, 243, 244, 246, 249
35. T. Moriya, Prog. Theor. Phys. **28**, 371 (1962) 242, 243
36. C.M. Varma, Phys. Rev. B**73**, 155113 (2006) 243
37. Z.P. Han, R. Dupree et al., Phys. Rev. Lett. **69**, 1256 (1992) 243

- 38. T. Moriya, Y. Takahashi, K. Ueda, Phys. Rev. Lett. **59**, 2905 (1990) 244
- 39. R.E. Walstedt, S-W. Cheong, Phys. Rev. B**53**, R6030 (1996) 245, 249
- 40. A. Keren, H. Alloul, P. Mendels, Y. Yoshinara, Phys. Rev. Lett. **78**, 3547 (1997) 245
- 41. R.L. Corey, N. Curro, et al., Phys. Rev. B**53**, 5907 (1996) 246, 247
- 42. A. Sokol, R.P. Singh, N. Elstner, Phys. Rev. Lett. **46**, 4416 (1990) 248, 249
- 43. D.C. Johnston, Phys. Rev. Lett. **62**, 957 (1989) 249
- 44. T. Nakano et al., Phys. Rev. B**49**, 16000 (1994) 249
- 45. H.Y. Hwang, B. Batlogg, H. Takagi et al., Phys. Rev. Lett. **72**, 2636 (1994) 249
- 46. R.E. Walstedt, S.-W. Cheong, Phys. Rev. B**64**, 014404 (2001) 250

# A

---

## Appendices

### A.1 Some Basic Properties of Spin Echoes

We give in this appendix a brief discussion of the behavior of two-pulse spin echoes. For the original derivations of spin echo phenomena see the paper by Hahn [1]. A shorter exposition by this author discussed some special topics having to do with echo studies in solids [2]. A brief list is (i) echo behavior with phase variation between the pulses, (ii) the “area theorem” (see also below), (iii) computer simulation of echo profiles (of which Fig. 2.3 is an example), and (iv) the cancellation of spurious transient signals in echo studies using a four-step phasing sequence for the two excitation pulses.

We begin with a basic derivation of the two-pulse echo, so that the amplitude dependence on pulse rotation angles, as well as the basic phenomenology of the  $T_2$  process are illustrated. At the same time the basic principle of spin-echo double resonance (SEDOR) can be illustrated. In the final subsection we derive the Gaussian echo decay time  $T_{2g}$  associated with the indirect nuclear spin-spin couplings first investigated in the cuprates by the Slichter group [3] and formulated conveniently in terms of  $\chi'(\mathbf{q})$  by Pennington and Slichter [4].

#### A.1.1 Basic Derivation of the Two-Pulse Spin Echo.

Spin echoes are generally observable with spin systems where the echo decay time is long enough so that two excitation pulses can be applied at some minimal pulse spacing, after which the echo signal can be detected following the “dead time” of the receiver. Another requirement for echo generation which is often overlooked is that the observed nuclei must be subject to a quasi-static broadening effect which is greater than any homogeneous or dynamic broadening. This circumstance can come about through an internal distribution of shifts, HF fields, EFG values, quasi-static interactions with other spin systems or through the application of an inhomogeneous field. If you have a homogeneously broadened NMR line relaxed by fluctuating like-spin couplings or by

$T_1$ , you may be able to see the free-induction signal, but the echo will be very elusive.

Supposing these conditions are met, let us consider the application of *rf* pulses to excite an echo. For simplicity, we shall suppose the excitation pulses to be of negligible length. One imagines, then, a very large rotating magnetic field  $H_1$  (at a suitable frequency) applied for just an instant, during which the magnetization of the nuclei nutates at  $\omega_1 = \gamma H_1$  away from its equilibrium position along the  $z$  axis. At time  $t_{w1}$  the magnetization has rotated by  $\theta_1 = \omega_1 t_{w1}$ , creating a magnetization component  $M_0 \sin \theta_1$  along the  $x$  axis.

Following the first pulse, the spins are allowed to precess freely for a time  $\tau$ , during which time the transverse magnetization decays quickly to zero. The associated free-induction signal is typically too short to be observed. This decay time is labelled  $T_2^*$ , being either the inverse of the width  $\Delta$  of the distribution  $P(\Delta_i)$  of static frequencies being excited or in a broad line  $T_2^* \sim \pi/\omega_1$ . We consider our typical nuclear spin  $\mathbf{I}_i$  to be subject to a local, static frequency perturbation  $\Delta_i$ . We also introduce one source of echo relaxation perturbations, namely the spin-spin coupling term

$$\mathcal{H}'_{II}(i) = \sum_j \alpha_{ij} I_{zi} I'_{zj} = \Omega_i I_{zi}, \quad (\text{A.1.1})$$

where the resulting local frequency perturbation  $\Omega_i = \sum_j \alpha_{ij} m'_j$  contributes to the precession frequency between *rf* pulses. The perturbation  $\Omega_i$  could come from like or unlike spins, and could be fluctuating or static, with results which vary enormously depending on the details.

We shall proceed with the calculation assuming the  $\Omega_i$ 's are static, and then comment on other possible cases. During the interval between the first and second pulses, spin  $\mathbf{I}_i$  will precess around the  $z$  axis, where in the rotating frame, the transverse component of spin  $i$  in the  $xy$ -plane precesses through an angle  $(\Delta_i + \Omega_i)\tau$ , where  $\Delta_i$  and  $\Omega_i$  are as defined above. To capture the effects of these motions we follow the development in the rotating frame<sup>1</sup> of the density matrix  $\rho^*(t)$  which obeys the equation of motion [5]

$$i \frac{d\rho^*}{dt} = [\mathcal{H}^*, \rho^*], \quad (\text{A.1.2})$$

where starred quantities have been transformed into the rotating frame. For simplicity we drop the star notation, noting that the rest of the calculation will take place in the rotating frame. The initial value of density matrix is  $\rho_0 I_x$ , where  $\rho_0 \propto \sin \theta_1$ . During the interval  $\tau$  between pulses and during time interval  $t - \tau$  following the second pulse, spin  $\mathbf{I}_i$  will precess through the angles

$$\beta_{1i} = (\Delta_i + \Omega_i)\tau \quad \text{and} \quad \beta_{2i} = (\Delta_i + \Omega_i)(t - \tau), \quad (\text{A.1.3})$$

---

<sup>1</sup> The rotating frame is a reference frame rotating at the frequency of the applied *rf* pulses.

respectively, where at time  $\tau$  a second pulse of *rf* field  $H_1$  is applied, rotating the spins through angle  $\theta_2$ . The  $\theta_2$  pulse is known as the “refocussing pulse”. At time  $t - \tau$  following the latter pulse, the density matrix may be written

$$\frac{\rho(t)}{\rho_0} = \langle \exp(i\beta_{2i}I_{zi}) \exp(i\theta_2I_y) \exp(i\beta_{1i}I_{zi}) I_{xi} \exp(-i\beta_{1i}I_{zi}) \exp(-i\theta_2I_y) \exp(-i\beta_{2i}I_{zi}) \rangle_i, \quad (\text{A.1.4})$$

where the brackets  $\langle \rangle_i$  indicate an average over the entire sample. In (A.1.4) only the exponential operators which survive in the echo amplitude calculation, i.e. in  $Tr(I_x\rho(t))$ , are kept.

At this point we make some remarks about the potential effects of the broadening terms  $\beta_{1,2i}$  in (A.1.4). These terms can always be divided into separate operators  $\exp(iI_{zi}\Delta_i t) \exp(iI_{zi}\Omega_i t)$ , where the effect of the static  $\Delta_i$ 's is particularly simple. If the  $\Omega_i$  terms are static and unaffected by the  $\theta_2$  pulse, then they have no effect and will simply disappear from the calculation. If they are like-spin terms and are affected by the  $\theta_2$  pulse, then they cause an echo relaxation process. In the next subsection we develop expressions for the  $\theta_2$ -dependent relaxation time  $T_{2g}$  for the Gaussian relaxation from indirect spin-spin coupling in cuprates [4].

If the  $\Omega_i$  terms are from unlike spins, then there is a series of possible effects. If, for example, an *rf* pulse is applied to the  $\mathbf{I}'$  spins so that their  $m'_j$  values (and thus the  $\Omega_i$ 's) change, then the echo will undergo a potentially observable effect known as *spin echo double resonance* (SEDOR). SEDOR has undergone various applications to solid-state science [6, 7], but we shall not discuss this technique further. If the unlike-spin  $\Omega_i$ 's are fluctuating in time, then there will be an associated echo relaxation process of a character which depends on whether the fluctuations are slow, fast, or intermediate. If the fluctuations are fast or slow, then some estimate of their effects can be obtained with perturbation methods. If they are intermediate in speed, then the effects could be very large and treatment would have to be improvised on a case-by-case basis. In the case where the  $\Omega_i$ 's are time-dependent between the *rf* pulses, then it is easy to show that the  $\Omega_i\tau$  etc. in (A.1.3) would simply be replaced by

$$\Omega_i\tau \rightarrow \int_0^\tau \Omega_i(t)dt. \quad (\text{A.1.5})$$

We now proceed to obtain a general expression for the echo signal from the foregoing expressions. In (A.1.4) only the exponential operators which survive in the echo calculation have been kept. These exponential operators are processed using the relation

$$\exp(i\phi I_\gamma) I_\alpha \exp(-i\phi I_\gamma) = I_\alpha \cos \phi \mp I_\beta \sin \phi, \quad (\text{A.1.6})$$

where the second term is negative if  $(\alpha, \beta, \gamma)$  is a positive permutation of (x,y,z) and positive otherwise.

Following development of  $\rho(t)$  using (A.1.6), we keep only the terms in  $I_{xi}$ , which form the principal component of the echo. The corresponding signal amplitude can then be written

$$\mathcal{E}(t) = \frac{1}{2} \mathcal{E}_0 \langle (1 + \cos \theta_2) \cos(\beta'_{1i} + \beta_{2i}) - (1 - \cos \theta_2) \cos(\beta'_{1i} - \beta_{2i}) \rangle_i, \quad (\text{A.1.7})$$

where  $\beta'_{1i}$  is defined below. The echo signal at  $t = 2\tau$  arises only from the second term, which becomes

$$\frac{\mathcal{E}(t)}{\mathcal{E}_0} = (1 - \cos \theta_2) \sum_i P(\Delta_i) \cos \left( \Delta_i(t - 2\tau) + \sum_j \alpha_{ij} [m_j \tau - m'_j(t - \tau)] \right), \quad (\text{A.1.8})$$

where  $m'_j$  (defining  $\beta'_{1i}$ ) is the value of  $m_j$  following the operation  $e^{i\theta_2} I_{zj} e^{-i\theta_2}$ . We shall make use of this in Sect. A.2.

The average over the distribution of  $\Delta_i$  values gives the time profile of the echo, which has its maximum at  $t = 2\tau$ . The two terms in the cos argument ( ) in (A.1.8) are very different in character. The  $\Delta_i$  term vanishes at  $t = 2\tau$ , but is otherwise large and rapidly varying. The second, relaxation term is a slowly varying perturbation. In a reasonable approximation we evaluate the second term at  $t = 2\tau$  and separate it from the first one and remove it from the sum as a relaxation factor  $f_r(2\tau) = \langle \cos[\sum_j \alpha_{ij} (m_j - m'_j)] \rangle_j$ , where the  $\langle \rangle_j$  brackets indicate a second, independent averaging process. (A.1.8) is then rewritten as

$$\mathcal{E}(t) = C \sin \theta_1 (1 - \cos \theta_2) f_r(2\tau) \sum_i P(\Delta_i) \cos[\Delta_i(t - 2\tau)], \quad (\text{A.1.9})$$

where the average over the  $\Delta_i$ 's gives the echo shape function, and where we have inserted  $\sin \theta_1$  to give the full dependence on pulse angles.

We now make some observations on the echo expression (A.1.9). First, we recount the *area theorem* for spin echoes. Although not developed in detail in this derivation (see [2]), an echo excited from a distribution  $g(\omega)$  of NMR/NQR frequencies is an integral of that distribution over excitation factors, giving an echo proportional to

$$\int_{-\infty}^{\infty} d\omega g(\omega) \sin \theta_1 (1 - \cos \theta_2) \cos[(\omega - \omega_0)(t - 2\tau)], \quad (\text{A.1.10})$$

where the distribution  $P(\Delta_i)$  is effectively replaced by  $g(\omega)$ . If we integrate the area under the echo, i.e. over a range  $-\Delta t \leq t - 2\tau \leq \Delta t$  which includes all possible nonzero echo amplitude, this produces delta function in frequency so that

$$\int_{2\tau - \Delta t}^{2\tau + \Delta t} \mathcal{E}(t) dt = 2\pi C f_r(2\tau) g(\omega_0) [\sin \theta_1 (1 - \cos \theta_2)]_{\omega_0}, \quad (\text{A.1.11})$$

where if the pulse angles are frequency-dependent, they are evaluated at  $\omega_0$ , which is the frequency of the  $rf$  pulses. Thus, the area under the echo is very precisely proportional to  $g(\omega_0)$ , with a resolution which does not depend on  $H_1$  (in principle), but on the time  $2\Delta t$  over which the integration can take place. In general the resolution of  $g(\omega_0)$  is very good. In practice, the smaller  $H_1$  is, the better the resolution which is obtained.

### A.1.2 Modelling Spin-Echo Decay

Secondly, as an example of spin-echo decay, we consider the form which  $f_r(2\tau)$  from (A.1.9) takes in the limit where the  $m_j$ 's are from unlike spins and are fluctuating rapidly. We therefore consider the quantities  $\Omega_i(t)$  to be stochastic variables, where

$$f_r(2\tau) = \left\langle \cos \left[ \int_0^\tau \Omega_i(t) dt - \int_\tau^{2\tau} \Omega_i(t) dt \right] \right\rangle_i. \quad (\text{A.1.12})$$

The two integrals over time are equivalent under the average over  $i$ , so we expand the cosine, assuming the sine terms to vanish on averaging. Expanding the remaining cosines in power series and keeping just the first two terms we find

$$F_r(2\tau) \simeq 1 - \int_0^\tau dt \int_0^\tau dt' \langle \Omega_i(t) \Omega_i(t') \rangle_i + \dots. \quad (\text{A.1.13})$$

Taking the indicated average  $\langle \rangle_i$  generates a correlation function which we write as  $\langle \Omega_i^2 \rangle_i C(|t - t'|)$ , where  $\int_0^\infty C(t) dt = \tau_c \ll \tau$ . The first expansion term is therefore linear in  $\tau$  so that the decay function may be approximated as

$$f_r(2\tau) \simeq e^{-2\tau/T_{2\Omega}}, \quad \text{with } 1/T_{2\Omega} = \langle \Omega_i^2 \rangle \tau_c. \quad (\text{A.1.14})$$

The foregoing is an example of exponential spin-echo decay with a rapidly modulated perturbation. Another such effect is echo decay through spin-lattice interactions. This is discussed in some detail in Appendix A.2.1. In the next subsection we give an example of Gaussian spin-echo decay through modulation of like-spin interactions by the refocussing ( $\theta_2$ ) pulse, which is widely encountered in cuprate NMR studies.

## A.2 The Gaussian Decay Time $T_{2g}$ for Indirect Spin-Spin Coupling

The following calculation of spin-echo decay applies to magnetic dipole transitions excited between any pair of HF energy levels for which  $m = \langle I_z \rangle$  (suitably chosen) is a reasonably good quantum number, i.e. a  $\Delta m = \pm 1$  transition. Examples are (i) any high-field transition with quadrupolar splittings or (ii) a zero-field NQR splitting. For NQR lines with, e.g.  $I = 3/2$ , the excitation

pulses excite two transitions simultaneously ( $\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$ ) with their separate signals. We shall be considering the decay of only one of these signals at a time, though the calculation will apply to both.

We henceforward consider only the echo amplitude  $\mathcal{E}(2\tau)$  given by (A.1.8), which can be expanded as a power series in  $(2\tau)^{2n}$ , where we keep only the  $\tau^2$  term:

$$\mathcal{E}(2\tau) \approx \mathcal{E}_0(1 - \cos \theta_2) \left\langle 1 - \frac{\tau^2}{2} \left[ \sum_j \alpha_{ij}(m'_j - m_j) \right]^2 \right\rangle_i. \quad (\text{A.2.1})$$

In squaring the sum  $\sum_j \alpha_{ij}(m'_j - m_j)$  the cross terms will average to zero. In the diagonal terms the quantity  $(m'_j - m_j)^2$  will equal 1 with a probability  $\sin^2(\theta_2/2)$  and will be zero otherwise. (A.2.1) becomes [8]

$$\mathcal{E}(2\tau) \simeq \mathcal{E}_0(1 - \cos \theta_2) \left[ 1 - \frac{\tau^2}{2} \sin^2(\theta_2/2) \sum_j' \alpha_{ij}^2 \right], \quad (\text{A.2.2})$$

where the  $\sum_j'$  indicates a sum only over  $^{63}\text{Cu}(2)$  neighbors which are being flipped by the  $\theta_2$  pulse. This means, typically, couplings with the same isotope, and  $m_j$ -values belonging to the resonance transition observed. In high-field NMR for  $I = 3/2$ , this means half of the neighbor spins. For NQR with  $I = 3/2$ , one sums all of the neighbor spins, because they are all part of the observed resonance. The difficulty in applying this is, of course, that often the line is broad and the  $\theta_2$  pulse is not uniform over all of the spins. The factor  $\sin^2(\theta_2/2)$  in such a case is an effective average value.

If we suppose that (A.2.2) gives the first two expansion terms of a Gaussian decay, then we have for the final result for a high-field NMR transition for  $^{63}\text{Cu}(2)$ ,

$$\frac{1}{T_{2g}^2} = \sin^2(\theta_2/2) \frac{c_{63}}{8} \sum_j \alpha_{ij}^2, \quad (\text{A.2.3})$$

where the final sum over all neighbor sites is, of course, independent of  $i$ . In naturally abundant  $^{63}\text{Cu}$   $c_{63} \simeq 0.69$ .

### A.2.1 Indirect Coupling with a Gaussian Susceptibility

The indirect coupling range function used in the text is discussed here for the simple case of a  $\mathbf{q}$ -independent, isotropic HF tensor and a Gaussian susceptibility  $\chi'(\mathbf{q})$ . After deriving the range function from (5.1.7), results for the second moment ( $\sum_{j(\neq i)} a_{ij}^2$ ) obtained in several ways are discussed.

The general result for the indirect coupling coefficient of  $I_{zi}I_{zj}$  is

$$a_\alpha(i, j) = \frac{\hbar}{N_A g_\alpha^2 \mu_B^2} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot (\mathbf{R}_j - \mathbf{R}_i)} \chi'_\alpha(\mathbf{q}) F_{\alpha\alpha}(\mathbf{q})^2, \quad (\text{A.2.4})$$

where the prefactor is suited to a molar susceptibility and an HF tensor in units of  $s^{-1}$ . Here we take  $F_{\alpha\alpha}(\mathbf{q}) = A_0$ , and we use the Gaussian susceptibility form employed by Auler et al. [9], which is

$$\chi'_\alpha(\mathbf{q}) = \chi'_{AF} e^{-(\mathbf{q}-\mathbf{Q})^2 \xi^2/4}. \quad (\text{A.2.5})$$

Since  $\chi'_\alpha(\mathbf{q})$  is symmetric about  $\mathbf{Q}$ , we move the origin to that point with  $\mathbf{q} = \mathbf{p} + (\pi, \pi)$ . The imaginary sine term is then seen to vanish by symmetry. For simplicity we drop the prefactor  $(\hbar \chi'_{AF} A_0^2 / N_A g_\alpha^2 \mu_B^2)$  and restore it at the end. The sums may then be taken as integrals, giving,

$$a(i, j) = \frac{(-1)^{(n_x+n_y)}}{4\pi^2} \int_{-\pi}^{\pi} dp_x \int_{-\pi}^{\pi} dp_y e^{-(p_x^2+p_y^2)\xi^2/4} \cos(n_x p_x + n_y p_y). \quad (\text{A.2.6})$$

The cosine factor can be written  $\cos(n_x p_x) \cos(n_y p_y)$ , since the sine terms vanish. The integrals can now be written  $g(n_x)g(n_y)$ , where

$$g(n) = \frac{(-1)^n}{\pi} \int_0^\pi dp e^{-p^2 \xi^2/4} \cos(np) \simeq \frac{(-1)^n}{\sqrt{\pi} \xi} e^{-n^2/\xi^2}, \quad (\text{A.2.7})$$

where the last step approximates the upper limit of the integral as  $\infty$ . This is a reasonable approximation, since the exponential factor at  $p = \pi$  is  $\simeq 0.015$ . We shall check this approximation below, as well. The final result for our dimensionless range function is

$$a(i, j) = \frac{(-1)^{(n_x+n_y)}}{\pi \xi^2} e^{-(n_x^2+n_y^2)/\xi^2}. \quad (\text{A.2.8})$$

We now evaluate the second moment sum  $\sum_{j(\neq i)} a(i, j)^2$  in three separate ways, in order to test the approximation in (A.2.7). First, we may do this directly with (A.2.8), giving the expression

$$\sum_{j(\neq i)} a(i, j)^2 = \frac{1}{\pi^2 \xi^4} \left[ \sum_{n_x, n_y} e^{-2(n_x^2+n_y^2)/\xi^2} - 1 \right], \quad (\text{A.2.9})$$

where the summation is over all integer values of  $n_x, n_y$  which would give an appreciable contribution. In what may seem a crude approximation for  $\xi \simeq 1.3$  (see text), we evaluate the sums in (A.2.9) as an integral in a continuum approximation. This is straightforwardly shown to yield the value  $\pi \xi^2/2$ , so that we find

$$\sum_{j(\neq i)} a(i, j)^2 = \frac{1}{\pi^2 \xi^4} \left[ \frac{\pi \xi^2}{2} - 1 \right]. \quad (\text{A.2.10})$$

The foregoing result gives the value  $\sum_{j(\neq i)} a(i, j)^2 = 0.0587$  for  $\xi = 1.3$ , which is the minimum value we shall use it for. This sum has also been evaluated by computer for the same value of  $\xi$ , giving 0.0588 for the result. It seems

then that the continuum approximation to the  $(n_x, n_y)$  sums is accurate to a fraction of a percent. However, the range function itself is an approximate result from (A.2.7).

We make a check on the latter result by evaluating the second moment sum using the  $\mathbf{q}$ -space result (6.1.8), which in the present context becomes

$$\sum_{j(\neq i)} a(i, j)^2 = \sum_{\mathbf{q}} \sum_{\mathbf{p}} e^{-(q^2+p^2)\xi^2/4} - \left[ \sum_{\mathbf{q}} e^{-q^2\xi^2/4} \right]. \quad (\text{A.2.11})$$

When the first sum is converted to an integral in polar coordinates, the integrand is proportional to  $\exp(-q^2\xi^2/2)$ , which, at  $q = \pi$  falls to the value  $\sim 2.4 \times 10^{-4}$ . While this could be accounted for in approximate fashion, we neglect errors of this magnitude for simplicity here. This term then becomes  $1/(2\pi\xi^2)$ . The second term in (A.2.11) can be cast into a very similar form as that of (A.2.7), where we neglect a correction term of the order of 1.5%. Since this is squared, neglecting these correction means that the second term in (A.2.11) is small by about 3%. The two terms together give  $\sum_{j(\neq i)} a(i, j)^2 = 1/(2\pi\xi^2) - 1/(\pi^2\xi^4)$ , which is identical to the summing result in (A.2.10). We now see that for  $\xi = 1.3$ , this result probably errs on the high side by an amount of order 1%. For larger values of  $\xi$  the error will diminish rapidly.

Restoring the prefactor and multiplying by the factor  $c_{63}/8$  gives the physically correct second moment (or  $(1/T_{2g})^2$ ), which is

$$\left[ \frac{1}{T_{2g}} \right] = \frac{c_{63}}{8} \sum_{j(\neq i)} a(i, j)^2 = \frac{c_{63}}{8} \frac{\hbar \chi'_{AF} A_0^2}{N_A g_\alpha^2 \mu_B^2} \frac{1}{\pi^2 \xi^4} \left[ \frac{\pi \xi^2}{2} - 1 \right]. \quad (\text{A.2.12})$$

### A.3 Spin Echo Decay via Spin-Lattice Relaxation

Spin-lattice relaxation of a spin echo was first treated to explain the large disparity between conventional  $T_1$  values and the enhanced exponential decay rates  $1/T_{1E}$  of spin echoes for nuclear spins with large  $I$  values [10]. The relaxation rate for the  $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$  transition was shown to be  $1/T_{1E} = 2 W_0(I + \frac{1}{2})^2$ , where  $1/T_1 = 2 W_0$ . This result was modified for the case of an anisotropic  $T_1$  process by Narath [11], finding

$$\frac{1}{T_{1Ez}} = (W_x + W_y)[I(I+1) - 1/4] + W_z, \quad (\text{A.3.1})$$

where  $W_\alpha$  is the contribution of fluctuations along the  $\alpha$  axis to the relaxation rate for a quantization axis perpendicular to that axis. Thus,  $1/T_{1z} = W_x + W_y$ . The latter results have been derived using the “fictitious spin  $\frac{1}{2}$ ” technique. They have been derived using other methods as well [3, 12].

Since the  $W_\alpha$ ’s are not measured directly, it is also useful to express the result (A.3.1) in terms of the anisotropic  $T_1$  values  $T_{1x,y,z}$ :

$$\frac{1}{T_{1Ez}} = \frac{1}{T_{1z}}[I(I+1) - 3/4] + \frac{1}{2T_{1x}} + \frac{1}{2T_{1y}}. \quad (\text{A.3.2})$$

We also treat the case of arbitrary direction for the quantization axis, represented by the Euler angles  $(\theta, \phi)$ . We let that be the  $z'$  axis with corresponding  $x'$  axis in the  $xy$  plane and mutually perpendicular  $y'$  axis. The associated rate parameters for the  $(x', y', z')$  axes are

$$W_{x'} = W_x \sin^2 \phi + W_y \cos^2 \phi \quad (\text{A.3.3a})$$

$$W_{y'} = W_x \cos^2 \theta \cos^2 \phi + W_y \cos^2 \theta \sin^2 \phi + W_z \sin^2 \theta \quad (\text{A.3.3b})$$

$$W_{z'} = W_x \sin^2 \theta \cos^2 \phi + W_y \sin^2 \theta \sin^2 \phi + W_z \cos^2 \theta, \quad (\text{A.3.3c})$$

whereupon  $1/T_{1Ez'}$  is given in terms of the  $W_{\alpha'}$ 's by (A.3.1). This result was used to correct the planar  $^{17}\text{O}$  spin echo decay data in [8] for  $T_1$  effects.

## References

1. E.L. Hahn, Phys. Rev. **80**, 580 (1950) 253
2. R.E. Walstedt, "The two-pulse spin echo revisited", in *Pulsed Magnetic Resonance: NMR, ESR and Optics*, ed. by D.M.S. Bagguley (Clarendon Press, Oxford, 1992), p. 242 253, 256
3. C.H. Pennington, D.J. Durand, C.P. Slichter, Phys. Rev. **B39**, 274 (1989) 253, 260
4. C.H. Pennington, C.P. Slichter, Phys. Rev. Lett. **66**, 381 (1991) 253, 255
5. A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1983) 254
6. D. Kaplan and E.L. Hahn, J. Phys. Radium **19**, 821 (1958) 255
7. R.E. Walstedt and J.H. Wernick, Phys. Rev. Lett. **20**, 856 (1968) 255
8. R.E. Walstedt, S.-W. Cheong, Phys. Rev. **B51**, 3163 (1995) 258, 261
9. T. Auler, M. Horvatic et al., Physica C **313**, 255 (1999) 259
10. R.E. Walstedt, Phys. Rev. Lett. **19**, 146 (1967); **19**, 816 (1967) 260
11. A. Narath, Phys. Rev. **B13**, 3724 (1976) 260
12. T. Imai et al., Phys. Rev. Lett. **71**, 1254 (1993) 260

---

# Index

- AFM enhancement effects below  $T_c$ ,  
109, 111
- AFM fluctuations, 5
- antiferromagnetic correlations, 4, 90,  
102
- ARPES studies of cuprates, 2, 136
- ARPES studies of energy gap effects,  
136
- axial EFG symmetry, 15
- axial shift component for  $^{17}\text{O}(2,3)$  in  
YBCO7, 95
- axial shift powder patterns, 23
  
- BCS energy gap anisotropy from  
coherence peak, 43
- BCS energy gap value from  $T_1$  in Al  
metal, 43
- BCS theory of  $T_1$  for  $T < T_c$ , 41
- BCS theory of  $T_1$  for the d-wave case,  
108
  
- characterization of samples, 4, 5
- chemical shifts in NMR, 21, 118, 120,  
122, 233
- $\chi''(\mathbf{q}, \omega)$ , 5, Sect. 3.5, Chap. 5, 6
- $\chi'(\mathbf{q}, 0)$  values derived from  $T_{2g}$   
measurements, 220
- coherence factor:  $T_1$  for  $T < T_c$ , 40
- coherence peak, gap anisotropy effect,  
43
- core diamagnetic susceptibility for  
YBCO, 83
- core polarization of  $\text{Y}^{3+}$ , 78
- core-polarization  $T_1$  process in d-band  
metals, 51
- core-polarization HF field, 44
- core-polarization HF mechanism, 46
- core-polarization NMR shift, 5, 48, 58
- crossover in phase diagram, 70, 146,  
243, 246
- $^{63,65}\text{Cu}$ , 4
- Cu(1,2) site assignment, 75
- cuprate phase diagram, 3, 70, 146, 243
  
- d-wave pairing, 6
- d-wave confirmation by  $T_{2g}$  for  $T < T_c$ ,  
225
- d-wave model for  $T_1$  at  $T < T_c$ , 104, 206
- detailed balance in spin-lattice  
relaxation, 25
- Dipolar Contribution to  $^{89}\text{Y}$  HF  
Coupling, 125, 183
- dipolar HF interaction, 33
- dipolar NMR shift, 5
- discovery of high- $T_c$ , 1
- dynamic susceptibility, Sect 3.5, Chap.  
5, 6
- dynamical structure factor, 101
- dynamical susceptibilities for LSCO:x  
from INS data, 230
- dynamical susceptibility, a simplified  
model, 127
- dynamical susceptibility, exact solution  
for Heisenberg AFM, 248
- dynamical susceptibility, Gaussian  
model, 180

- dynamical susceptibility, RPA model, 173
- EFG Tensor, 14
- exchange enhancement from  $\mathcal{K}(\alpha)$ -table, 37
- Exchange enhancement of  $1/T_1$  – Moriya theory, 36
- Fermi surface in cuprates, 2, 136
- Ferrell–Anderson theory of spin–orbit scattering below  $T_c$ , 39
- field-dependent  $T_1$  effects in type-II superconductors, 61, 111, 200
- first-order quadrupolar broadening, 15, 94
- fluctuation dissipation theorem, 101
- fluctuation-dissipation theorem, 5
- g-factors for YBCO7, 86
- gamma, nuclear gyromagnetic ratio, 21
- Ginzburg-Landau parameter  $\kappa$ , 54
- Ginzburg-Landau theory, 54
- gyromagnetic ratio, nuclear moment, 21
- Hamiltonian for NMR/NQR spectra, 14
- HF coefficients for YBCO6.63 from scaling of shifts, 123
- HF constants for LSCO:0.15 from NMR shift data, 232
- HF couplings, 4, 82
- HF Hamiltonian–general, 33
- HF tensor for  $^{89}\text{Y}$  in YBCO7, 96
- HF tensor for  $^{17}\text{O}(2,3)$  in YBCO7, 96
- HF tensor, general, for cuprates, 82
- HF tensors for YBCO7, 84
- hole doping, 3
- hole doping in cuprates, 71
- Hubbard model calculation of NMR shift below  $T_c$ , 205
- Hubbard model for  $T_1$  at  $T < T_c$ , 199
- Hubbard model, large  $U$ , of spin dynamics, 192
- Hubbard model, negative  $U$ , 127
- Hubbard model, small  $U$ , for spin dynamics, 187
- indirect spin–spin coupling, 6, 19, 214
- indirect spin–spin coupling in LSCO:0.15 from INS data, 239
- INS data for  $\chi''(\mathbf{q}, \omega)$ , case of pseudogap, 128
- INS data for  $\chi''(\mathbf{q}, \omega)$  in LSCO:x, 227
- INS studies of cuprates, 2, 128, Chap. 6
- K- $\chi$  analysis, 47
- K- $\chi$  plot for Pt metal, 48
- Knight shift, 32
- Knight shift for  $T < T_c$ : BCS (Yosida) theory, 38, 108, 206
- Korringa calculation of  $T_1$  in metals, 34
- Korringa product table for metals, 35
- Korringa relation, 35, 37
- Korringa relation, modified for multiple HF sources, 127
- Korringa relaxation, 33
- Kramers–Kronig evaluation of  $\chi'(\mathbf{q}, 0)$  for LSCO:0.15, 240
- LSCO phase diagram, 2, 46, 70
- LSCO structure, 68
- LSCO,  $^{63,65}\text{Cu}$   $T_1$  data, 153, 245
- LSCO:x, 2
- LSCO:x dynamical susceptibility from INS, 227
- LSCO:x,  $^{17}\text{O}$   $T_1$  and shift data, 153, 241
- LSCO:x, NMR shifts, 152
- LSCO:x, NQR spectra, 153
- LSCO:x, pseudogap effects, 148, 241
- LSCO:x, scaling of susceptibility, 149
- Mila–Rice HF tensor, 81
- Mott insulator, 1, 69
- NMR in d-band metals, 44
- NMR probe, 4
- NMR shift defined, 22
- NMR shift below  $T_c$ , Hubbard model calculation, 205
- NMR shift correction for superconducting diamagnetism, 105
- NMR shift for cuprates at  $T < T_c$ , 105
- NMR shift in the mixed state of 3d superconductor, 57
- NMR shift tensor, 14, 21
- NMR shift tensor, scalar approximation, 22
- NMR shift tensors for Cu(1) in YBCO7, 84

- NMR shift tensors for Cu(2) in YBCO7, 84
- NMR shift, anisotropic, powder pattern, 23
- NMR shift, powder pattern, 23
- NMR spectra, 5
- NMR spectrum, quadrupolar satellites, 15
- NMR studies in the mixed state of type-II superconductors, 55
- NQR determination of  $\eta$ , 17
- NQR spectrum in zero field, 17
- $^{17}\text{O}(2,3)$ , 5
- $^{17}\text{O}$  doping, 4
- $^{17}\text{O}$  EFG tensors for YBCO7, 95
- $^{17}\text{O}$  NMR data for YBCO7, 93, 162
- $^{17}\text{O}$  relaxation in YBCO7, 92
- $^{17}\text{O}$  shift tensors for YBCO7, 75, 95, 164
- orbital  $T_1$  process in d-band metals, 51
- orbital  $T_1$  theory by Varma, 195
- orbital (Van Vleck) shift and susceptibility – general, 46
- orbital HF interaction, 33
- orbital NMR shift, 5
- orbital shift and  $T_1$  process, 44
- orbital susceptibilities for YBCO, 83
- orbital susceptibility tensors in YBCO7, 85, 86
- oriented powder samples for cuprate NMR, 80
- orthorhombic phase of LSCO:x, 3, 69
- oxygen hole band in YBCO7, 98
- oxygen hole bands, 72, 81
- Pennington Slichter theory of indirect spin–spin coupling, 214
- phase diagram for scaling theory of AFM fluctuations, 242
- phase diagram of cuprate superconductor, 2, 146, 243
- phenomenology of high- $T_c$ , 1
- pseudogap effects for YBCO6+x vs. x, 117
- pseudogap effects on  $T_1$  in underdoped YBCO, 116
- pseudogap energy derived from Arrhenius plot, 122, 143
- pseudogap isotope effect, Y248, 143
- pseudogap NMR shift scaling in YBCO6.63, 120
- pseudogap temperature, 3
- pseudogap, theory by Varma, 146
- pseudogaps in cuprates, 115
- quadrupolar effects, 4
- quadrupolar perturbation, high-field limit, 15
- quadrupolar powder pattern, 16, 23
- quadrupolar powder pattern, second order, 16, 23
- quadrupolar tensor, sign of, 15
- quantum chemistry of YBCO7, 87
- resonant field shifts, relation to K, 22
- review of bulk properties, 4
- RPA calculation of dynamical susceptibility, Monien and Pines, 108
- s-contact (Knight) shift, 33, 47
- s-contact HF interaction, 33
- s-contact NMR shift, 5, 33, 47
- saturating comb to measure  $T_1$ , 31
- scaling theory of  $\chi(\mathbf{q}, \omega)$  in quantum critical region, 242
- shift vs. susceptibility analysis, 47
- simulations of spin-echo decay for LSCO:0.15, 236
- specific heat, pseudogap effects, 134
- spin echo spectroscopy, frequency resolution, 19
- spin echo, observation of, 20
- spin echo, two-pulse, 18, 251
- spin Hamiltonian parameters for  $^{63}\text{Cu}(2)$  in YBCO7, 86
- spin HF tensor for Cu(2) in YBCO, 89
- spin susceptibilities for YBCO, 83
- spin susceptibility anisotropy for YBCO7, 86
- spin-echo decay, 6, 20, 251, 255
- spin-echo decay analysis for LSCO:0.15 from INS data, 236
- spin-echo decay by indirect spin–spin coupling, 218, 255
- spin-echo decay via  $T_1$ , 20, 258
- spin-lattice relaxation, definition, 23

- spin-orbit NMR shift, 5, 89
- spin-orbit scattering effect on
  - susceptibility for  $T < T_c$ , 39
- spin-spin correlations below  $T_c$ , ab plane, 207
- spin-spin correlations below  $T_c$ , c axis, 208
- spin-spin correlations in terms of  $\chi''(\mathbf{q}, \omega)$ , 102
- Spin-spin below  $T_c$ , Uldry-Meier analysis, 207
- spin-spin correlations in YBCO7, 91, 161, 165
- Stoner enhancement of susceptibility, 189
- structures of compounds with  $\text{CuO}_2$ , 2, 69
- superconducting diamagnetism, 5, 55
- susceptibility – uniform, 5, 33, 38, 45
- susceptibility analyses for  $\text{V}_3\text{X}$  compounds, 49
- susceptibility anisotropy in YBCO7, 87
- symmetry factors in d-band  $T_1$  processes, 51
- $T_1$  at  $T < T_c$ , Hubbard model, 199
- $T_1$  eigenmodes, 25, 27
- $T_1$  fit for  $T < T_c$  by Monien and Pines, 110
- $T_1$  fitting parameters for  $T < T_c$ , Monien and Pines, 110
- $T_1$  for  $^{17}\text{O}$  in YBCO7, 97
- $T_1$  for d-band metals, 50
- $T_1$  formulated in terms of  $\chi''(\mathbf{q}, \omega)$ , 99
- $T_1$  in mixed state via spin diffusion to normal cores, 62
- $T_1$  measurement techniques, 27
- $T_1$  measurements for  $T < T_c$ : simple metals, 41
- $T_1$  model for YBCO using INS data, 179
- $T_1$  model for cuprates by Millis, Monien, and Pines, 172
- $T_1$  models for cuprates, 159
- $T_1$  parameterization by Uldry and Meier, 160
- $T_1$  ratios in YBCO7, Mila–Rice interpretation, 90
- $T_1$  recovery for  $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$  transition, 28
- $T_1$  recovery for NQR, 28
- $T_1$  recovery with inversion, 28
- $T_1$  recovery with saturation, 28
- $T_1$  recovery with spectral diffusion, 29
- $T_1$  studies in type-II superconductors, 58
- $T_1$  with  $\mathbf{q}$ -dependent structure factors, 101
- $T_1$  with Gaussian model compared with UM analysis, 184
- $T_1$ , definition, 23
- $T_1$ , magnetic dipolar processes, 23
- $T_1$ , quadrupolar processes, 23
- $T_1$ : Quadrupolar vs. magnetic dipole, 24
- $T_1$ 's for LSCO:0.15 calculated from INS data, 230
- $T_2$  decay for  $^{17}\text{O}$  in LSCO:0.15, 240
- $T_2$  for spin echoes, 19, 251, 255
- $T_2$ , definition, 19
- $T_{2g}$ , 6, 255
- $T_{2g}$  dependence on correlation length, 222
- $T_{2g}$  used to calibrate dynamical susceptibility, 182
- $T_{2g}$  values from various systems, 220
- $T_{2g}$  variation below  $T_c$ , Hubbard model, 224
- $T_{2g}$  variation with temperature, 223
- $T_{2g}$ , Gaussian model for, 217
- t-J model of quasiparticle behavior, 71
- tetragonal phase of LSCO:x, 3
- transferred HF coupling in cuprates, 81
- Type-II superconductivity in d-band metals, 54
- Type-II superconductor NMR studies, 53
- Wannier wavefunction for Cu(2) – Mila Rice model, 88
- $^{89}\text{Y}$ , 4, 5
- $^{89}\text{Y}$  HF coupling from dipolar interaction, 183
- $^{89}\text{Y}$  chemical shift by extrapolation, 122
- $^{89}\text{Y}$  relaxation in YBCO7, 92
- Y248, 2, 74, 92, 118, 160, 175, 181
- Y248 analysis by Uldry and Meier, 169
- Y248 dynamical crossover  $T_1 T / T_{2g}$  study, 245

- Y248, NMR shift and  $T_1$ , 139
- Y248, pseudogap behavior, 138
- Y248, pseudogap energy, 141
- YBCO structure, 70
- YBCO, evaluation of HF coefficients, 83
- YBCO, introduction of the Spin Hamiltonian model for  $^{63}\text{Cu}(2)$ , 79
- YBCO6+x, chemical shift of  $^{89}\text{Y}$ , 77
- YBCO6+x, variation of  $^{89}\text{Y}$  shift with  $x$ , 76
- YBCO6.63 analysis by Uldry and Meier, 167
- YBCO6.63 discussion by Millis, Monien, and Pines, 178
- YBCO6.63 pseudogap NMR data, 117
- YBCO6.63,  $^{89}\text{Y}$   $T_1$  behavior, 132
- YBCO6.63,  $T_1$  data, 130
- YBCO7, 4
- YBCO7  $T_1$  modeling by Millis, Monien, and Pines, 175
- YBCO7 - early results on  $^{63,65}\text{Cu}$  NMR studies, 73
- YBCO7 -  $^{63,65}\text{Cu}$   $T_1$  data, 74
- YBCO7 -  $^{63}\text{Cu}(2)$  powder pattern, 76
- YBCO7 - early NMR results, 72
- YBCO7 - NQR studies, 74, 111
- YBCO7 analysis by Uldry and Meier, 163
- YBCO7,  $^{63}\text{Cu}(2)$   $T_1$  anisotropy, 79
- YBCO7,  $^{63}\text{Cu}(2)$  relaxation models, 79, 159
- YBCO7, early results on  $^{89}\text{Y}$  NMR, 73
- YBCO7-x, 2
- Yosida function calculation for cuprates, 108
- Yosida function measurement in Al metal, 40
- Zhang-Rice singlet, 70