Springer Theses

Recognizing Outstanding Ph.D. Research

Stefan Thiele

Read-Out and Coherent Manipulation of an Isolated Nuclear Spin

Using a Single-Molecule Magnet Spin-Transistor

Springer

Springer Theses

Recognizing Outstanding Ph.D. Research

Aims and Scope

The series “Springer Theses” brings together a selection of the very best Ph.D. theses from around the world and across the physical sciences. Nominated and endorsed by two recognized specialists, each published volume has been selected for its scientific excellence and the high impact of its contents for the pertinent field of research. For greater accessibility to non-specialists, the published versions include an extended introduction, as well as a foreword by the student’s supervisor explaining the special relevance of the work for the field. As a whole, the series will provide a valuable resource both for newcomers to the research fields described, and for other scientists seeking detailed background information on special questions. Finally, it provides an accredited documentation of the valuable contributions made by today’s younger generation of scientists.

Theses are accepted into the series by invited nomination only and must fulfill all of the following criteria

- They must be written in good English.
- The topic should fall within the confines of Chemistry, Physics, Earth Sciences, Engineering and related interdisciplinary fields such as Materials, Nanoscience, Chemical Engineering, Complex Systems and Biophysics.
- The work reported in the thesis must represent a significant scientific advance.
- If the thesis includes previously published material, permission to reproduce this must be gained from the respective copyright holder.
- They must have been examined and passed during the 12 months prior to nomination.
- Each thesis should include a foreword by the supervisor outlining the significance of its content.
- The theses should have a clearly defined structure including an introduction accessible to scientists not expert in that particular field.

More information about this series athttp://www.springer.com/series/8790

Stefan Thiele

Read-Out and Coherent Manipulation of an Isolated Nuclear Spin

Using a Single-Molecule Magnet Spin-Transistor

Doctoral Thesis accepted by
the University of Grenoble, France

Springer

Author
Dr. Stefan Thiele
Sensirion AG
Staefa
Switzerland

Supervisor
Dr. Wolfgang Wernsdorfer
Nano, Institut Neel
Grenoble
France

ISSN 2190-5053 ISSN 2190-5061 (electronic)
Springer Theses
ISBN 978-3-319-24056-5 ISBN 978-3-319-24058-9 (eBook)
DOI 10.1007/978-3-319-24058-9

Library of Congress Control Number: 2015953250

Springer Cham Heidelberg New York Dordrecht London

Printed on acid-free paper

Springer International Publishing AG Switzerland is part of Springer Science+Business Media (www.springer.com)

Supervisor's Foreword

It is with great pleasure and the highest enthusiasm that I write this foreword to Stefan Thiele's thesis, which reports his most exciting results. Its endeavor is driven by one of the most ambitious, technological goals of today's scientists: the realization of an operational quantum computer. In this regard, the basic building block is generally composed of a two-level quantum system, namely a quantum bit (or qubit). Such a quantum system must be fully controllable and measurable, which requires a connection to the macroscopic world. In this context, solid-state devices, which establish electrical interconnections to the qubit, are of high interest, mainly due to the variety of methods available for fabrication of complex and scalable architectures. Moreover, outstanding improvements in the control of the qubit dynamics have been achieved in the last years. Among the different solid-state concepts, spin-based devices are very attractive because they already exhibit relatively long coherence times. For this reason, electrons possessing a spin 1/2 are conventionally thought as the natural carriers of quantum information. However, the strong coupling to the environment makes it extremely difficult to maintain a stable entanglement. Alternative concepts propose the use of nuclear spins as building blocks for quantum computing, as they benefit from longer coherence times compared to electronic spins, because of a better isolation from the environment. But weak coupling comes at a price: the detection and manipulation of individual nuclear spins remain difficult tasks. In this context, the main objective of the Ph.D. of Stefan Thiele was to lay the foundation of a new field called molecular quantum spintronics, which combines the disciplines of spintronics, molecular electronics, and quantum information processing. In particular, the objective was to fabricate, characterize, and study molecular devices (molecular spin-transistor, molecular spin-valve and spin filter, molecular double-dot devices, carbon nanotube, nano-SQUIDs, etc.) in order to read and manipulate the spin states of the molecule and to perform basic quantum operations. The visionary concept of the project is underpinned by worldwide research on molecular magnetism and supramolecular chemistry, and in particular within the European Institute of Molecular Magnetism (http://www.eimm.eu/), and collaboration with outstanding scientists in the close environment. For the project, we found the following funding: the main contributions came from the French Research Agency (ANR), the Contrat Plan Etat Région (CPER), the European Research Council (ERC), the Réseau Thématique de Recherche Avancé (RTRA), and the support from our institute. The Ph.D. of Stefan Thiele was funded by an ERC advanced grant. Among the most important results before Stefan Thiele's Ph.D., we showed the possibility of magnetic molecules to act as building blocks for the design of quantum spintronic devices and demonstrated the first important results in this new research area. For example, we have built a novel spin-valve device in which a nonmagnetic molecular quantum dot, consisting of a single-wall carbon nanotube contacted with nonmagnetic electrodes, is laterally coupled via supramolecular interactions to a $TbPc_2$ molecular magnet [Ph.D. of Matias Urdampilleta (2012)]. The localized magnetic moment of the SMM led to a magnetic field-dependent modulation of the conductance in the nanotube with magnetoresistance ratios of up to 300 % at low temperatures. We also provided the first experimental evidence for a strong spin–phonon coupling between a single-molecule spin and a carbon nanotube resonator [Ph.D. of Marc Ganzhorn (2013)]. Using a molecular spin-transistor, we achieved the electronic read-out of the nuclear spin of an individual metal atom embedded in a single-molecule magnet (SMM) [Ph.D. of Romain Vincent (2012)]. We could show very long spin lifetimes (several tens of seconds). Here, the Ph.D. of Stefan Thiele started with a completely new breakthrough. He proposed and demonstrated the possibility to perform quantum manipulation of a single nuclear spin by using an electrical field only. This has the advantage of reduced interferences with the device and less Joule heating of the sample. As an electric field is not able to interact with the spin directly, he used an intermediate quantum mechanical process, the so-called hyperfine Stark effect, to transform the electric field into an effective magnetic field. His project was designed to play a role of pathfinder in this—still largely unexplored—field. The main target concerned fundamental science, but applications in quantum electronics are expected in the long run.

Grenoble Dr. Wolfgang Wernsdorfer
April 2015 Research Director

Abstract

The realization of a functional quantum computer is one of the most ambitious, technological goals of today's scientists. Its basic building block is composed of a two-level quantum system, namely a quantum bit (or qubit). Among the other existing concepts, spin-based devices are very attractive because they benefit from the steady progress in nanofabrication and allow for the electrical read-out of the qubit state. In this context, nuclear spin-based devices exhibit additional gain of coherence time with respect to electron spin-based devices due to their better isolation from the environment. But weak coupling comes at a price: the detection and manipulation of individual nuclear spins remain challenging tasks.

Very good experimental conditions were important for the success of this project. Besides innovative radio frequency filter systems and very low noise amplifiers, I developed new chip carriers and compact vector magnets with the support of the engineering departments at the institute. Each part was optimized in order to improve the overall performance of the setup and evaluated in a quantitative manner.

The device itself, a nuclear spin qubit transistor, consisted of a $TbPc_2$ single-molecule magnet coupled to source, drain, and gate electrodes and enabled us to read out electrically the state of a single nuclear spin. Moreover, the process of measuring the spin did not alter or demolish its quantum state. Therefore, by sampling the spin states faster than the characteristic relaxation time, we could record the quantum trajectory of an isolated nuclear qubit. This experiment shed light on the relaxation time T_1 of the nuclear spin and its dominating relaxation mechanism.

The coherent manipulation of the nuclear spin was performed by means of external electric fields instead of a magnetic field. This original idea has several advantages. Besides a tremendous reduction of Joule heating, electric fields allow for fast switching and spatially confined spin control. However, to couple the spin to an electric field, an intermediate quantum mechanical process is required. Such a process is the hyperfine interaction, which, if modified by an electric field, is also referred to as the hyperfine Stark effect. Using the effect, we performed coherent rotations of the nuclear spin and determined the dephasing time T_2^*. Moreover, exploiting the static hyperfine Stark effect we were able to tune the nuclear qubit in and out of resonance by means of the gate voltage. This could be used to establish the control of entanglement between different nuclear qubits.

In summary, we demonstrated the first single-molecule magnet based quantum bit and thus extended the potential of molecular spintronics beyond classical data storage. The great versatility of magnetic molecules holds a lot of promises for a variety of future applications and, maybe one day, culminates in a molecular quantum computer.

Acknowledgements

First of all, I want to say thank you to all the people I encountered during my Ph.D. and that helped me to make a lot of very enjoyable memories and the time in Grenoble a very special part of my life. In particular, I want to thank my supervisor Wolfgang Wernsdorfer, who guided me through the stormy waters of the Ph.D. Thank you for all your support and for being available any time I needed your advice. I am very grateful that you let me join your team and most of all that you encouraged and taught me to pursue many ideas which went beyond my project. This aspect was broadening my horizon unlike anything else and made this thesis one of the most enriching experiences in my life. Last but not least, I want to thank you for taking care of my experiment every time I was in need. Moreover, I want to thank Franck Balestro. Thank you for letting me measure on your setup, providing me with samples, and all the He transfers you did for me. But, most of all, thank you for always finding the words to encourage me, both in my work and personal life and of course for helping me finding the sample of my Ph.D. I am also very grateful to you for reading this manuscript and reshaping it into its almost perfect state;-).

I also want to thank Markus Holzmann, who helped me understanding and performing quantum Monte Carlo simulations. I appreciate very much your enthusiasm and the cheerful working atmosphere. I want to thank Rafik Ballou, who did not give up until he found a theory to properly describe the hyperfine Stark effect. It was always a pleasure to discuss with you. I am also very thankful to my referees Jakob Reichel and Wulf Wulfhekel as well as to my thesis comitee members Vincent Jacques, Patrice Bertet, and Mairbek Chshiev for the sincere work and fruitful comments on my thesis. Moreover, I want to thank all the researchers at the Néel institut I was interacting with, especially Tristan Meunier, Olivier Buisson, and Nicolas Roch for their help and advice.

Furthermore, I want to thank all the present and former members of the NanoSpin group. Thank you Jean-Pierre, Vitto, and Oksana for being very enjoyable office mates and never being tired to discuss personal and work affairs. Many thanks to Edgar and Christophe, who helped me solving a lot of informatics problems. Thank you Jarno, Viet, Antoine, Raoul, and Matias for all the fruitful discussions and coffee breaks. Thank you Romain for letting me measure on your sample and introducing me to the glorious world of Python. Thank you Marc for all your help and support especially during the hard time after the worldcup. Thank you Clément, I am very glad you joined our group and it was always a pleasure to talk to you.

Merci à Eric Eyraud, qui m'a aidé énormément avec mon cryostat et tout ce qui vient avec. Sans toi rien n'était possible. Merci égalment pour m'avoir montré comment on peux faire le "produit". Je voudrais remercier aussi Daniel Lepoittevin qui m'avait beaucoup aidé avec tout ce qui concerne l'électronique de mesure et pour m'avoir expliqué tout son fonctionnement. Un grand merci également á Christophe Hoarau pour m'avoir aidé avec les mesures et simulations á haute fréquence. Merci beaucoup aussi á Yves Deschanels qui m'avait aidé avec la construction des bobines supra et qui a passé une semaine dans la cave avec moi. Un grand merci aussi à Didier Dufeu, Richard Haettel, David Barral et Laurent Del-Rey pour toute leur aide.

I want to thank also all my friends who I have not mentioned yet. Thank you Carina for convincing me to come to Grenoble and for all your help and support. Thank you Angela for sharing the burden of writing this thesis, and of course the secret tiramisu recipe. Thank you Liza for motivating us all to go out for beers and for lending me your appartment to celebrate my birthday. Thank you Peter for your honesty and very funny way to see things. Thank you Claudio and Elena for unbreakable good mood, even if Beatrice stole you the last bit of sleep. Thank you Sven for all parties we had at your place especially in the evening of my defense. Thank you Cornelia and Roman for nice skiing trips. Thank you Ovidiu, Martin, and Marc for the nice evenings at D'Enfert. Thank you Simone and Francesca for the enjoyable evenings with the Scarpe Mobile. Thank you Clément, Dipankar, Angelo, Christoph, Hanno, Farida, and Tobias for all the nice moments in and outside the lab. Merci également à Gosia, Julian, Marine, Juan Pablo, Elenore, Aude et Clément pour m'avoir reçu très chaleureusement dans votre groupe. Je voudrais remercier mon équipe de volley avec qui j'ai passé beaucoup des bonnes moments, en particulier Malo et Olivier pour la meilleur saison de volley de toute ma vie. Vielen Dank auch an meine Freunde aus der Heimat Lars, Christian, Stefan, Daniel, Toni, Anja, Micha, Stefan, Rico für die schönen Momente mit euch.

Je voudrais remercier ma copine Sophie, qui m'a beaucoup soutenu et encouragé pendant ces deux dernières années. Ta constante bonne humeur était toujours une grande motivation pour moi. Un grand merci également à toute ta famille et en particulier à Vincent, Claudine et Céline. Zum Schluss möchte ich ganz besonders meiner Familie danken, die mich die ganze Zeit nach Kräften unterstützt haben und ohne die all dies nicht möglich gewesen wäre. Ein ganz besonderer Dank gilt vor allem meinen Eltern Andreas und Ines, meiner Schwester Sabrina, und meinen Großeltern Hans und Inge, weil ihr immer für mich da gewesen seid, wenn ich euch brauchte.

Stefan Thiele

Contents

1 Introduction . . . 1
1.1 Molecular Spintronics . . . 1
1.2 Quantum Information Processing . . . 4
1.3 Thesis Outline . . . 9
References . . . 10

2 Single Electron Transistor . . . 13
2.1 Equivalent Circuit . . . 13
2.2 Coulomb Blockade . . . 15
2.3 Cotunneling Effect . . . 16
2.4 Kondo Effect . . . 17
References . . . 20

3 Magnetic Properties of $TbPc_2$ . . . 23
3.1 Structure of $TbPc_2$ . . . 23
3.2 Electronic Configuration of Tb^{3+} . . . 23
3.3 Zeeman Effect . . . 25
3.4 Electron-Electron Interaction . . . 25
3.5 Spin-Orbit Interaction . . . 26
3.6 Ligand-Field Interaction . . . 29
3.7 Hyperfine Interaction . . . 32
3.8 Magnetization Reversal . . . 34
3.8.1 Quantum Tunneling of Magnetization . . . 34
3.8.2 Direct Transtions . . . 36
References . . . 37

4 Experimental Details . . . 39
4.1 Overview Setup . . . 39
4.2 Dilution Refrigerator . . . 42
4.3 3D Vector Magnet . . . 45
4.4 Current Leads . . . 49
4.5 Sample Holder . . . 52

4.6 Filter . . . 53
4.6.1 Low Frequency Filters . . . 54
4.6.2 High Frequency Filters . . . 54
4.7 Signal Transducer . . . 56
4.8 Real-Time Data Acquisition . . . 61
4.9 Sample Fabrication . . . 62
4.9.1 Nanowire Fabrication . . . 63
4.9.2 Electromigration . . . 64
4.9.3 Fabrication of a Molecular Spin Transistor . . . 66
References . . . 67

5 Single-Molecule Magnet Spin-Transistor . . . 69
5.1 Mode of Operation . . . 69
5.2 Read-Out Quantum Dot . . . 71
5.3 Magneto-Conductance and Anisotropy . . . 72
5.4 Exchange Coupling . . . 74
5.5 2D Magneto-Conductance of the Read-Out Dot . . . 76
5.6 Electronic Spin Relaxation . . . 78
5.7 Quantum Tunneling of Magnetization . . . 80
5.8 Summary . . . 85
References . . . 86

6 Nuclear Spin Dynamics—T_1 . . . 87
6.1 Signal Analysis . . . 87
6.2 Relaxation Time T_1 and Read-Out Fidelity F . . . 89
6.3 Quantum Monte Carlo Simulations . . . 93
6.3.1 Algorithm . . . 93
6.3.2 Including the Experimental Boundaries . . . 96
6.4 Comparison Experiment—Simulation . . . 97
6.4.1 Relaxation Mechanism . . . 97
6.4.2 Dynamical Equilibrium . . . 100
6.4.3 Selection Rules . . . 101
6.5 Summary . . . 102
References . . . 102

7 Nuclear Spin Dynamics—T_2^* . . . 105
7.1 Introduction . . . 105
7.1.1 Rabi Oscillations . . . 105
7.1.2 Hyperfine Stark Effect . . . 109
7.2 Coherent Nuclear Spin Rotations . . . 112
7.2.1 Frequency Calibration . . . 112
7.2.2 Rabi Oscillations . . . 115
7.3 Experimental Discussion of the Hyperfine Stark Effect . . . 117
7.3.1 DC Gate Voltage Induced Hyperfine Stark Effect . . . 117
7.3.2 AC Induced Hyperfine Stark Effect . . . 118

7.4 Theoretical Discussion of the Hyperfine Stark Effect 120
7.5 Dephasing Time T_2^* 125
7.5.1 Introduction 125
7.5.2 Experimental Results 127
7.5.3 Outlook 129
7.6 Summary 131
References 131

8 Conclusion and Outlook 133
References 136

Appendix A: Spin 137

Appendix B: Stevens Operators 145

Appendix C: Quantum Monte Carlo Code 147

Appendix D: Qutip Code 155

Curriculum Vitae 159

Chapter 1
Introduction

1.1 Molecular Spintronics

The computer industry developed in the course of the last 60 years from its very infancy to one of the biggest global markets. This tremendous evolution was triggered by several historical milestones. In 1947, John Bardeen and Walter Brattain presented the world's first transistor [1] based on Walter Shockley's field-effect theory. Their discovery was soon after rewarded by the Nobel Prize in physics and led to the development of today's semiconductor industry.

Another groundbreaking discovery was made in 1977, when Alan Heeger, Hideki Shirakawa, and Alan MacDiarmid presented the first conducting polymer [2]. Their work opened the way for organic semiconductors, which stand for cheap and flexible electronics like organic LEDs, photovoltaic cells, and field-effect transistors. With still a lot of ongoing fundamental research, some fields already reached maturity. Especially, organic LEDs became an irreplaceable part of modern televisions in the last couple of years. The major impact of organic semiconductors was awarded by Royal Swedish Academy of Sciences with the Nobel Price in chemistry.

On decade later, in 1988, Peter Grünberg and Albert Fert reported an effect, which they called the giant magneto resistance (GMR) [3, 4]. In contrary to conventional electronic devices, which use charges as carriers of information, the GMR exploits the electronic spin degree of freedom. Their discovery led to the development of a completely new branch of research, which is these days referred to as spintronics. With the success of data-storage industry, in the last 25 years, devices using the GMR effect became a part of our everyday live.

The drive for steady innovation led researchers to think about new devices which unify these great ideas and would, therefore, be even more performing. The famous article of Datta and Das in 1990 [5] was the first step towards a new age of spintronic devices. Their proposal described a transistor, which could amplify signals using spins currents only. However, for this transistor to work, efficient spin-polarization, injection, and long relaxation times are necessary. Especially, the relaxation time is usually limited by spin-orbit coupling and the hyperfine interaction.

S. Thiele, *Read-Out and Coherent Manipulation of an Isolated Nuclear Spin*,
Springer Theses, DOI 10.1007/978-3-319-24058-9_1