Magnetic resonance force microscopy for condensed matter

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Introduction

Nuclear magnetic resonance (NMR) is known for its application as magnetic resonance imaging (MRI). It provides the spatial mapping of ^{1}H nuclei in biological tissues and is therefore used in hospitals around the world. The resolution of MRI is limited to the micrometer scale[1], which makes it impossible to obtain information of structures on the nanometer scale, a holy grail in the fields of medicine, chemistry and physics.

[1] Glover and Mansfield 2002

In the early nineties, Sidles (1991) came with a solution to combine the force microscopy techniques sensitive to atoms with that of magnetic resonance techniques: Magnetic Resonance Force Microscopy (MRFM) was born. The technique was promising, big steps were taken, and the holy grail of atomic resolution imaging of biological tissues seemed within an arm's reach.

Unfortunately, the last steps are the most difficult. The technique is experimentally challenging and so far, the images of biological structures are no better than those obtained by other conventional techniques. In order to be an attractive technique, MRFM needs to be scientifically relevant while the technique is further improved towards the holy grail of imaging biological structures on the nanometer scale.

In this thesis, we show how MRFM can usefully contribute to the field of condensed-matter. In this chapter, we give a short history of why NMR has been, and still is, an important technique in the understanding of condensed-matter systems. Secondly, a short history of

MRFM and its basics are given. Finally, we discuss the outline of this thesis.

1.1 Nuclear Magnetic Resonance in condensed-matter

1.1.1 Prehistory 1922-1946

The concepts of a spin and the associated magnetic moment was established first for the electron in the early nineteen-twenties. Especially important was the Stern-Gerlach experiment[2] where beams of silver atoms were deflected in an inhomogeneous magnetic field according to the orientation of their magnetic moment. Three years later, two young students of Ehrenfest, Goudsmit and Uhlenbeck, introduced the concept of the electron spin[3].

In 1933, more detailed Stern-Gerlach experiments[4] made it clear that the nucleus also needs to exhibit a degree of freedom, and thereby also a magnetic moment similar as that of the electron. In 1943, Otto Stern received the Nobel Prize for his important work[5].

The Dutch physisists Cornelus Jacobus Gorter tried, after his measurements on paramagnetic relaxation, to measure the nuclear magnetic moment by measuring the power absorption due to an oscillating magnetic field in the salts LiF and AlK[6]. Unfortunately, his choice for the sample was unlucky. The slow energy transfer from the nuclear spin system to the lattice caused a negative result of his experiments. A different choice of sample could have made him succeed[7].

But some good came of his work, when he visited the laboratory of Isaac Rabi in 1937, a pioneer in experiments with beams of molecules. Gorter suggested the use of an oscillating radio-frequency field besides the static fields. This led to the successful detection of the nuclear magnetic moment in 1938. In their publication[8] they acknowledge Gorter for his contribution to their experiment. Rabi received the Nobel Prize[9] for his important work in 1944.

In 1946, two physisists both were the first to detect nuclear magnetic resonance in solid states. Purcell used the same technique as Gorter used. He measured the absorption of rf energy in a paraffin sample[10]. Bloch and

[2] Gerlach and Stern 1922

[3] Uhlenbeck and Goudsmit 1925, 1926

[4] Frisch and Stern 1933

[5] **The Nobel Prize in 1943**
To Otto Stern: *"For his contribution to the development of the molecular ray method and his discovery of the magnetic moment of the proton."*

[6] Gorter 1936

[7] Grant and Harris 1996

[8] Rabi et al. 1938

[9] **The Nobel Prize in Physics 1944**
Isidor Isaac Rabi: *"For his resonance method for recording the magnetic properties of atomic nuclei."*

[10] Purcell et al. 1946

coworkers did a different kind of measurement. They used the precession of the nuclear spin around the static field after it is perturbed by an oscillating field. The precession of this magnetic moment gives induction in a pickup coil that is part of an electrical circuit, whose resonance frequency matches the precession frequency of the nuclear magnetic moment[11]. For their important work, Purcell and Bloch both received the Nobel Prize in 1952[12].

[11] Bloch 1946

[12] **The Nobel Prize in Physics 1952** Felix Bloch and Edward Mills Purcell: *"For their development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith."*

1.1.2 *Milestones in condensed-matter physics*

The radio-frequency techniques developed during the second world war together with the commercial availability of homogeneous magnets made the progress in NMR rapid and exciting. Shortly after the early work of Bloembergen et al. (1948), describing the relaxation effects in nuclear magnetic resonance experiments, Knight[13] found deviations from the so-called resonance condition:

[13] Knight 1949

$$\omega_L = \gamma B_0 \tag{1.1}$$

Here ω_L is the Larmor frequency, at which the magnetic resonance occur and B_0 is the external magnetic field. The gyromagnetic ratio γ was believed to be a constant for a given nucleus, but Knight found out that for nuclei in metals there is a shift in the resonance frequency compared to that of the same nuclei in other materials. The ratio between shift of frequency and the Larmor frequency (for a reference sample) is called the Knight shift K.

Inspired by earlier work in 1936 on magnetic cooling of Heitler and Teller[14], Korringa[15] proposed a quantitative relation between the relaxation time of nuclear spins and the Knight shift K:

$$\frac{1}{T_1 T} = \frac{4\pi k_B K^2}{\hbar} \frac{\gamma^2}{\gamma_e^2} \tag{1.2}$$

With γ_e the electron gyromagnetic ratio, $\hbar$ the reduced Planck's constant, T the temperature, T_1 the nuclear spin-lattice relaxation time and k_B the Boltzmann constant[16].

Korringa emphasized the importance of his work by suggesting that measuring $(T_1 T)^{-1}$ is useful to obtain information about the electron-electron correlations at the

[14] Heitler and Teller 1936

[15] **Jan Korringa** Jan Korringa, born on 31 March 1915, was affiliated to Leiden University from 1946 to 1952, after which he became professor at the Ohio State University. He died at the age of one hundred on 9 October 2015, just a few months after we measured in our laboratory his famous Korringa relation for the first time in an MRFM experiment (Ch. 5).

[16] **Korringa relation** In the original paper by Korringa (1950), the Korringa relation (Eq. 1.2) is expressed with the g-factor of the nucleus expressed in "Bohr units". Comparing the original equation with the equation in Slichter (1990), we conclude that both equations are equivalent when $g \equiv 2\frac{\gamma_n}{\gamma_e}$.

surface of the Fermi-sphere. The Knight shift K, which, for a pure metal, is independent of temperature, is proportional to the paramagnetic susceptibility of the conduction electrons[17].

Moriya (1956) showed that for metals which are on the edge of becoming ferromagnetic or antiferromagnetic, large deviations from the Korringa relation arise. For example, this is the case in palladium metal[18]. Yosida (1958) showed that in the case of a superconducting electronic state, the paramagnetic susceptibility vanishes at $T = 0$, and therefore leads to a vanishing Knight shift (see Fig. 1.1). In fact, one can use the Korringa relation to characterize the nature of the superconducting electronic state[19].

For a superconducting simple metal, just below the critical temperature T_c, electronic states are piled up. The increase in the electronic spin susceptibility gives the so-called Hebel-Slichter peak[20]. Both the measurements of the decrease in spin susceptibility far below T_c and the occurance of the Hebel-Slichter peak just below T_c gave one of the early evidences for the applicability of the microscopic theory of superconductivity[21] by Bardeen, Cooper and Schrieffer[22]. The absence of a decrease in spin susceptibility in a superconducting phase can imply triplet superconductivity[23], where the absence of only the Hebel-Slichter coherence peak agrees with a d-wave superconductor or other physical superconducting systems were BCS-theory does not apply[24].

NMR is called a local technique, since one measures only the effect of the electronic states on specific crystal lattice positions of nuclei. However, the signals of nuclei are considered extremely weak, which makes it necessary to probe a large number of nuclei. Sample sizes exceed several cubic micrometers[25] making the NMR not a *nanoscopic* probe. In order to use the powerful NMR technique also to measure variations of the nuclear spin-lattice time at the nanoscale, to study properties of inhomogeneous electron systems which are at the forefront of modern condensed-matter physics, we introduce Magnetic Resonance Force Microscopy.

[17] Korringa 1950

[18] van der Klink and Brom 2000

[19] MacLaughlin 1976

[20] Hebel and Slichter 1959

[21] **The Nobel Prize in Physics 1972** John Bardeen, Leon Neil Cooper and John Robert Schrieffer: *"For their jointly developed theory of superconductivity, usually called the BCS-theory."*

[22] Bardeen et al. 1957; Alloul 2014

[23] Ishida et al. 1998

[24] Hammel et al. 1989

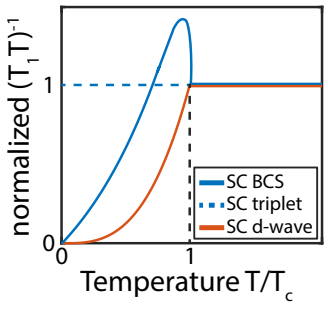

Figure 1.1: Sketch of $(T_1T)^{-1}$ versus temperature for three different kinds of superconductors (SC). For triplet superconductivity, the same behavior as for a simple metal does apply. Superconductors that are described by BCS theory have a characteristic Hebel-Slichter coherence peak just below the critical temperature T_c. D-wave superconductors do not have this coherence peak, and have also a different temperature dependence of $(T_1T)^{-1}$ below T_c (Alloul, 2015).

[25] Glover and Mansfield 2002

1.2 Introduction in Magnetic Resonance Force Microscopy

1.2.1 History of MRFM as imaging technique

In 1981, after the scanning tunneling microscope (STM) was invented[26], different kinds of scanning probe microscopy were proposed and developed.

[26] Binnig et al. 1982

The Nobel Prize in Physics 1986
One half awarded to Gerd Binnig and Heinrich Rohrer: *"For their design of the scanning tunneling microscope."*

While STM can only be used for conductive samples, the later invented atomic force microscope[27] (AFM) can also be used for atomic resolution on insulating surfaces. Both techniques are limited in a way that they cannot be used to resolve the three dimensional structure of large molecules, such as proteins, since they are limited to surface measurements. To overcome these limitations, Sidles proposed to combine nuclear magnetic resonance techniques with that of scanning probes[28].

[27] Binnig et al. 1986

[28] Sidles 1991, 1992; Sidles et al. 1992

Shortly after his proposal, electron spin resonance (ESR) was performed with a scanning probe, obtaining a resolution of 19 μm in one dimension[29]. The first MRFM image using ESR was obtained one year later[30] with μm resolution.

[29] Rugar et al. 1992

[30] Züger and Rugar 1993

The signal strength of nuclear spins is three orders of magnitude smaller than that of electron spins. Despite this large decrease in signal strength. Rugar et al. (1994) were able one year later, in a great technical achievement, to image nuclei with MRFM with μm-resolution.

The technical achievements in MRFM were promising, and in this exciting field, the founding father of MRFM believed in 1995 that the detection of a single electron moment would become practical in only a few years[31]. However, improving the resolution of a new technique goes easier the first orders of magnitude than the subsequent one. But after improving the cantilever design[32] and achieving much lower force noise[33], Rugar et al. (2004) managed to successfully detect a single electron spin with a spatial resolution of 25 nm in one dimension.

[31] Sidles et al. 1995

[32] Stowe et al. 1997

[33] Mamin and Rugar 2001

The three dimensional imaging of tobacco mosaic virus particles[34] in 2009 comes closest to the holy grail of MRFM to obtain the atomic structure of biological samples. Degen et al. (2009) imaged the virus with < 10 nm resolu-

[34] Degen et al. 2009

tion, a result that has not been improved upon.

1.2.2 *The basics of MRFM*

MRFM consists of four basic ingredients (Fig. 1.2). The first is the force sensor, which is a very soft cantilever. The second is a detector to read out the deflection of the force sensor, conventionally this is a laser interferometer[35]. In our case it is a superconducting quantum interference device based read-out scheme consisting a pickup coil. The third is a generator for radio-frequency (rf) signals to manipulate the electron or nuclear spins. The force sensor couples with the spins by means of a high magnetic field gradient, the fourth ingredient.

[35] Züger and Rugar 1993; Hammel et al. 1995; Garner et al. 2004; Degen et al. 2009; Poggio and Degen 2010

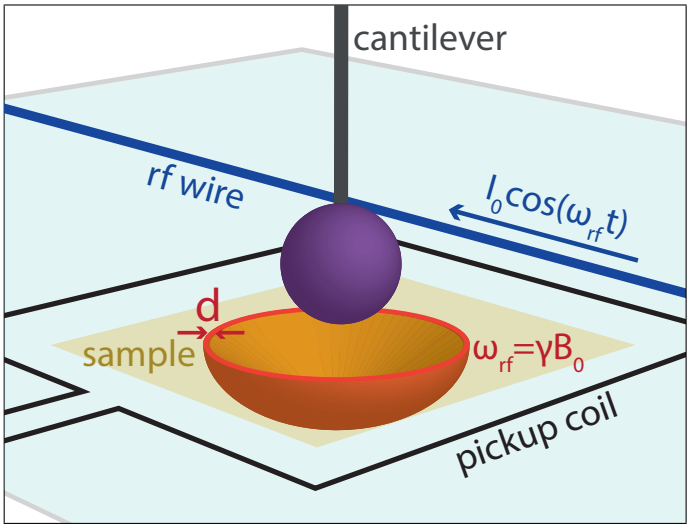

Figure 1.2: Sketch of the four basic ingredients of an MRFM setup. The force sensor couples to spins in the sample (yellow square). When a radio-frequency source perturbs the spins that meet the resonance condition $\omega_{rf} = \gamma B_0$, the force sensor is affected by means of a deflection or a different resonance frequency. The perturbed ensemble of spins forms the resonant slice (orange), with an effective thickness d. The deflection or oscillation of the force sensor is detected by using a superconducting quantum interference device to detect the flux changes in the pickup coil.

One way to obtain the coupling between sample and force sensor is to position the sample under study on the force sensor, and to position the source for the magnetic field gradient externally[36]. A second way, is to position the field gradient source, a magnetic particle, on the cantilever, and the sample externally. This is the scheme used here. Typical field gradients in our MRFM setup are in the order of 10^5 T/m, which is a million-fold larger than the gradients in commercial MRI systems[37].

The magnetic particle on the cantilever polarizes the

[36] Degen et al. 2009

[37] Brown et al. 2014

spins in the sample. An rf pulse can manipulate the orientation of the spin. Because of the large field gradient, only those spins that experience the magnetic field that meets the resonance condition (Eq. 1.1) are perturbed. This ensemble of spins defines a resonant slice[38]. Since the spins are coupled to the force sensor, any perturbation of the spin orientation will affect the motion of the cantilever.

[38] **Resonant slice**
The ensemble of spins that meet the resonance condition in an MRFM experiment. The field of the magnetic particle determines the exact geometry.

Changing the frequency of the rf signals, one can obtain information of resonant slices located at different distances from the magnetic particle on the cantilever. For example, it is possible to obtain information about the density of certain nuclei or electrons, or information about relaxation times. By collecting this information while scanning the sample with the force sensor, one obtains a three dimensional image.

1.3 *Outline of this work*

The main characteristics of the experimental setup we use for the experiments presented in this work are previously discussed by Wijts (2013) and Den Haan (2016), therefore in Ch. 2 we discuss only briefly the key ingredients of our MRFM system. This includes a short discussion of the low-vibration cryogen-free dilution refrigerator, the superconducting quantum interference device based readout scheme for the cantilever, the cantilever itself with the glued magnetic particle and how we position the cantilever with respect to the sample. Finally, we give an analysis of the phase locked loop feedback scheme that we use to detect the resonance frequency of the cantilever, important for the measurements described in this work.

In Ch. 3, we show that previous assumptions about the coupling of a semiclassical spin with a mechanical resonator are not complete. Our analysis[39] between the coupling of a single spin with a mechanical resonator gives a quantitative description of the dissipation caused by the coupling of the resonator with electron or nuclear spins. These results will be used in Ch. 7 to explain the magnetic dissipation effects and to quantitatively determine

[39] Published as De Voogd et al. (2017).

electron spin densities and electron spin relaxation times. Furthermore, the analysis is used in Chs. 5 and 6.

Chapter 4 is about the theory of nuclear magnetic resonance in our experiments, where large magnetic field gradients are present. We use saturation pulses to remove the polarization of nuclear spins within a certain resonant slice. This causes a shift in resonance frequency of the cantilever. Figure 1.2 presents the resonant slice as a two dimensional surface, with a homogeneous thickness d. In fact, also spins that do not meet the resonance condition will be perturbed, when the detuning of the rf frequency is small. In Ch. 4, we use the Bloch equations to give the time dependent mean polarization of (nuclear) spins during a saturation rf pulse, for all possible detunings, allowing us to determine the resonant slice width[40].

[40] Manuscript in preparation (De Wit et al., 2017).

With the experimental setup and the theory discussed, Ch. 5 shows our first nuclear MRFM experiment[41]. We measure the Korringa relation (Eq. 1.2) of a copper sample down to 42 mK, by measuring the nuclear spin-lattice relaxation time as a function of temperature. Furthermore, this chapter uses the results of Ch. 3 to analyze the observed signals. A noise analysis is given together with the obtained sensitivity of our measurements.

[41] Published as Wagenaar et al. (2016)

The measurements on the copper show an interesting feature at specific rf frequencies of the pulses. A detailed analysis in Ch. 6 reveals that the cantilever can itself be used as an rf source. This discovery results in a more easy way for performing saturation experiments in MRFM[42] with ultralow dissipation[43].

[42] **Patent:**
A. M. J. den Haan, J. J. T. Wagenaar, and T. H. Oosterkamp, A Magnetic Resonance Force Detection Apparatus and Associated Methods, United Kingdom Patent No. GB 1603539.6 (1 Mar 2016), patent pending

[43] Published as Wagenaar et al. (2017)

Chapter 7 shows that even without magnetic resonance, information about the electronic states can be obtained with our setup. We are able to extract the electron spin-lattice relaxation time and spin density of dangling bonds present at the Si/SiO interface of our detection chips[44]. The only experimental data we use for this, is the resonance frequency and quality factor of our resonator as a function of the height above our sample and temperature. Our experiment is in agreement with the theoretical analysis of De Voogd et al. (2017) for the coupling between spins and a mechanical resonator, thereby provid-

[44] Published as Den Haan et al. (2015)

ing strong evidence in favor of this theory. Furthermore, the result that magnetic dissipation is a source of non-contact friction is important for the applicability of MRFM with cantilevers exhibiting ultrahigh quality factors.

Finally, we propose some future experiments in Ch. 8. We discuss how we can improve an experiment we performed on a topological insulator, since so far we obtained an inconclusive result. Furthermore, we discuss how MRFM can give an insight in the superconducting mechanism of the two dimensional superconducting electron gas between the interface of lanthanum aluminate ($LaAlO_3$) and strontium titanate ($SrTiO_3$). Thirdly, we argue that the measurements on copper of Ch. 5 can be extended towards showing triplet superconductivity in a triplet spin valve[45]. The sensitive measurements on the dangling bonds of Ch. 7 shows possibilities in detecting the diamagnetic response of iridates, a new family of high-Tc superconductors[46].

While in Ch. 6 we show MRFM is possible without an on-chip rf source, we propose an alternative way to detect the force sensor that removes the need for an on-chip detection scheme on top of the sample to be studied. These two steps will be important towards the development of monolithic MRFM at millikelvin temperatures which can be used for the experiments proposed above.

[45] Singh et al. 2015

[46] Battisti et al. 2017