
Muon-spin relaxation and density functional
techniques in the study of novel magnetic systems



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The main focus of this thesis is the experimental muon-spin relaxation technique (μ^+ SR) and its application to study novel and unconventional magnetic behaviour. I present a range of experimental measurements which I supplement with theoretical calculations to remove the two main limitations inherent to μ^+ SR and thereby improve the understanding of the experimentally observed behaviour. Additionally, I investigate the potential effects of demagnetising fields on high field μ^+ SR measurements.

μ^+ SR employs positively charged muons as sensitive local magnetic probes but has the essential drawback that there is normally a lack of knowledge about where the muons implant in a given sample and the extent of subsequent local distortions. In some cases this nescience makes interpretation of μ^+ SR data very challenging and severely limits the conclusions that can be drawn. Two research projects presented in this thesis are centred around utilising *ab initio* structural calculations based on density functional theory in order to remove these two inherent limitations of μ^+ SR and gain insights into the stopping sites of the muons and their local environments.

In the case of the Pr based pyrochlores $\text{Pr}_2\text{B}_2\text{O}_7$ (B=Sn, Hf, Zr, Ir) I combine such *ab initio* computations of the muon sites with calculations of the crystal field levels of the Pr^{3+} ions. I demonstrate that the non-Kramers doublet ground state of the Pr ions is split due to the presence of the muons and that this consequently results in a hyperfine enhancement of the Pr nuclear moments. By showing the theoretically calculated values of the ground state splittings to be in fair agreement with those obtained from fits to the experimental data, I demonstrate that the μ^+ SR measurements of $\text{Pr}_2\text{B}_2\text{O}_7$ reflect muon induced effects rather than intrinsic behaviour. I subsequently investigate the conceptually very similar spin ices $\text{A}_2\text{Ti}_2\text{O}_7$ (A= Dy, Ho) using the same methodology and confirm that in this case the muons act as passive probes.

A second project presented in this thesis concerns the compound $\alpha\text{-RuCl}_3$, in which Ru ions form nearly perfect two-dimensional honeycomb layers. The experimental μ^+ SR data reveal two magnetic phase transitions, the origins of which I study by combining calculations of the potential muon sites with computations of the dipolar fields experienced by the muons at these sites for different magnetic structures. I show that the experimental observations are only fully explained through a temperature regime between the two measured transitions in which the Ru spins share significant correlations within the honeycomb layers but not between the separate layers.

A final research aspect I present is a study of the potential effects of demagnetising fields in high field μ^+ SR measurements. I derive an analytical solution for the demagnetising tensor of a uniformly magnetised finite cylinder and use it to show that edge regions of a sample suffer the most from demagnetising effects. I subsequently discuss the resulting experimental signatures and methods to identify and reduce them.

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Chapter 1

Introduction

The main aim of this thesis is to develop and present a set of theoretical and computational tools that can be employed to supplement the experimental muon spin rotation technique (μ^+ SR) in order to gain a better understanding of experimental observations. The first three chapters of this thesis are introductory and aim to give an overview of the essential background information on the concepts and experimental and theoretical techniques relevant to this thesis. These are subsequently drawn upon in the following three chapters, each of which presents a self-contained, in-depth research project in which I investigate either a particular aspect of the μ^+ SR technique or an unconventional magnetic behaviour observed in μ^+ SR measurements (or both).

1.1 Thesis outline

Chapter 2, Magnetism: In this chapter I give an overview of the magnetic phenomena relevant to this thesis.

Chapter 3, Muon spin rotation and relaxation: Introduction of the experimental μ^+ SR technique.

Chapter 4, Density functional theory: Outline of density functional theory and its application to μ^+ SR.

Chapter 5, Magnetism: Theoretical study of the effects of demagnetising fields in cylindrically shaped μ^+ SR samples.

Chapter 6, Pyrochlores: Investigation that combines μ^+ SR measurements of Pr and Ti based pyrochlore magnets with theoretical calculations to determine the impact of muon induced effects and to demonstrate their dominance in the Pr pyrochlores.

Chapter 7, α -RuCl₃: Study of the unconventional magnetism observed in α -RuCl₃ via a combination of μ^+ SR experiments and electronic structure and dipolar field calculations.

1.2 Glossary

μ^+ SR: Muon spin rotation/relaxation/resonance (with positive muons)

NMR: Nuclear magnetic resonance

MRI: Magnetic resonance imaging

DFT: Density functional theory

DFT+ μ : Density functional theory applied to μ^+ SR related scenarios

LDA: Local density approximation

GGA: Generalised gradient approximation

FM: Ferromagnet, ferromagnetic

AFM: Antiferromagnet, antiferromagnetic

TF: Transverse field

LF: Longitudinal field

KT: Kubo-Toyabe

FT[$f(x)$]: Fourier transform of function $f(x)$

Tr[**M**]: Trace of matrix **M**

$E[n(\mathbf{r})]$: Functional of function $n(\mathbf{r})$

a.u.: Hartree atomic units ($m = \hbar = 4\pi/\epsilon_0 = e = 1$); note that distances in

a.u. are in terms of the Bohr radius

u.c.: unit cell

WP: Wyckoff position

SS: Site symmetry

Chapter 2

Magnetism

2.1 History and significance

Dwarfs love iron. And that's what the stones contained. The love of iron. A love so strong that it drew all iron things to itself. [...], on worlds designed with less imagination, the (compass) needle turns because of the love of iron.

— Terry Pratchett: *Lords and Ladies* (Discworld novel 14)

This passage by novelist Terry Pratchett rather poetically puts into words the great puzzle that the phenomenon of magnetism posed to humans for thousands of years. First accounts of a strange attractive behaviour of an iron ore called lodestone date back to Greek scholars nearly three thousand years ago. The name magnetism derives from the Greek region of Magnesia where in those times lodestones could be found that mysteriously attracted or repelled each other and that were drawn to iron based materials, hence provoking Pratchett's phrase "love of iron". For our ancestors magnets became of practical use once it was realised that the earth itself resembles a giant magnet that will attract the tip of a compass needle towards a well defined, fixed point ("fixed" on human time scales at least). The invention of the compass opened up new possibilities of navigation and first documented attempts at explaining its function date back to around 1600 [1]. It

was not until the relatively recent discoveries of special relativity and quantum mechanics that we started to truly understand the reasons why (and how) certain materials exhibit this magnetic behaviour. One crucial realisation was that magnetism and electricity are inseparable and that either phenomenon can be described in terms of the other through a change of the frame of reference of the observer. In other words, the magnetism of free charges, isolated atoms and electromagnetic radiation is purely a relativistic effect due to the relative motion of the observer. However, the interest of modern research on magnetism has changed to macroscopic (condensed matter) systems in which collective behaviours of the atoms and molecules can result in magnetic properties that are fundamentally different to those of their constituents. The inventions that have emerged from this research are at the heart of many of the technological advances of the past century and devices based on magnetic phenomena are now pervading our every day lives, be it through computers, smart phones, electric motors or medical visualisation techniques such as magnetic resonance imaging (MRI).

In this chapter I will give a brief introduction to a range of concepts and models within condensed matter magnetism that are pertinent to the research presented in this thesis. The following sections are intended to give an overview and summary of the most important aspects of the described phenomena, but they are not meant as a general introduction to condensed matter magnetism. I can recommend Ref. [1] as an excellent primer for those interested in a more complete introduction.

2.2 Order and frustration

The main reason why condensed matter systems can exhibit any long range order of their constituent magnetic moments is because of interactions between the moments. While the classical dipole-dipole interaction can result in an aligning of neighbouring moments, it generally is far too weak to account for the occurrence of magnetism above mK temperatures. Instead, a collective phenomenon rooted

in quantum mechanical behaviour lies at the heart of most of condensed matter magnetism: exchange interactions between electron spins. When we consider a system of two monovalent atoms that are joined to form a diatomic molecule, a fundamental quantum mechanical requirement is that the total electronic wave function of the joint system, which is a product of a spatial and a spin part, has to be antisymmetric upon exchange of the two electrons. Consequently, the spin part of the wave function can either describe a symmetric or antisymmetric alignment of the two electron spins depending on the spatial part of the wave function. The energy difference between the two spin states (in fact half this difference) is defined as the exchange constant or exchange integral J and its sign determines which alignment of the spins is energetically favourable. The effective Hamiltonian describing this scenario is

$$H = -2J\mathbf{S}_1 \cdot \mathbf{S}_2, \quad (2.1)$$

where the two spins $\mathbf{S}_i$ align either parallel if $J>0$, or antiparallel if $J<0$. While the above scenario only describes the scenario of two electrons, it turns out that for many-body systems this interaction is still applicable but in general can occur between all spins. In practice however nearest neighbour exchanges tend to dominate and are often sufficient to describe experimentally observed properties. The associated Hamiltonian of these spin exchanges is called the Heisenberg Hamiltonian:

$$H = - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (2.2)$$

The above Hamiltonian applied to a lattice of electron spins can model a range of magnetic phenomena, the most common of which are ferro- and antiferromagnetism, which occur when $J_{ij}=J>0$ or $J<0$, respectively (and nearest neighbour J only). However, for the case of antiferromagnetic coupling there is an additional complexity: the type of lattice itself. As illustrated in Figure 2.1 spins arranged on a square (or rectangular) lattice with $J<0$ can adopt a configuration in which all

nearest neighbour interactions minimise the exchange energy, whereas spins on a triangular lattice can never satisfy all neighbouring antiferromagnetic alignments simultaneously. This is an example of what is known as geometric frustration. Frustrated spin behaviour can lead to a plethora of interesting and complex phenomena and occurs mainly on lattices that contain triangular elements. An example of such a magnetically frustrated structure is given in the following section, and materials exhibiting that structure are examined experimentally in chapter 6.

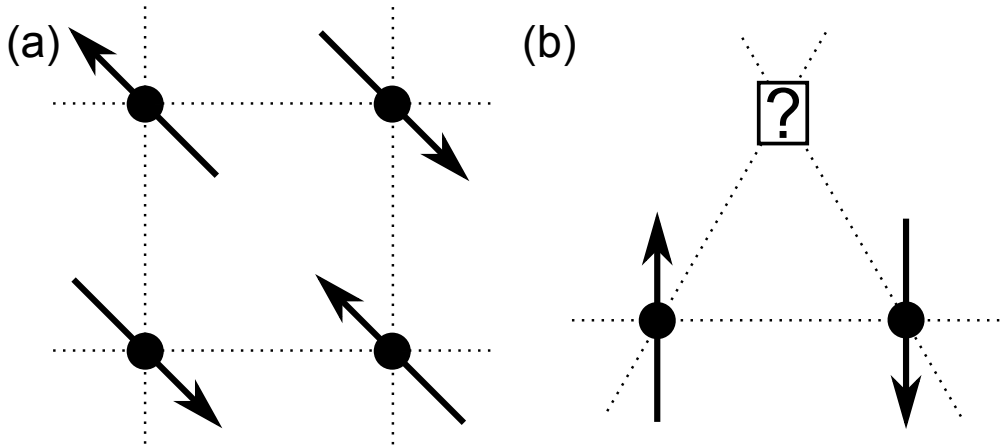


Figure 2.1: Illustration of geometric frustration in the case of antiferromagnetic nearest neighbour interactions. Panels (a) and (b) represent a square and triangular lattice of spins, respectively. The question mark in panel (b) signifies the impossibility to satisfy the antiferromagnetic alignment with both nearest neighbour spins at the same time.

2.2.1 Pyrochlores and magnetic monopoles

The pyrochlore lattice (space group $Fd\bar{3}m$) describes a lattice of corner sharing tetrahedra, as illustrated in panel (a) of Figure 2.2. If spins are placed on the vertices of each tetrahedron one obtains a scenario in which the spins are geometrically frustrated. Materials that comprise such a structure include $\text{Ho}_2\text{Ti}_2\text{O}_7$, $\text{Dy}_2\text{Ti}_2\text{O}_7$ [2] or the Pr based pyrochlores $\text{Pr}_2\text{B}_2\text{O}_7$, all of which are subject of chapter 6. The aforementioned titanate pyrochlores are experimentally observed to adopt a magnetic ground state that does not exhibit long range order even at low temperatures despite the presence of ferromagnetic interactions [2, 3]. Instead it is found that at low temperatures the spins associated with each tetrahedron

are constrained to point along their local $(1, 1, 1)$ axis, such that they behave like Ising spins with respect to this axis. Additionally, the spins have to arrange such that two of them point into and two point out of each tetrahedron [3]. This state is illustrated in panel (b) of Figure 2.2 and is known as a spin ice ground state in analogy to the proton coordination in traditional water ice, which is depicted in panel (c) of Figure 2.2. The minimal theoretical Hamiltonian that is required to model the spin ice ground state is a sum of the Heisenberg Hamiltonian for nearest neighbour interactions and the magnetic dipolar interaction [4, 5]:

$$H = -J \sum_{\langle ij \rangle} S_i S_j \hat{\mathbf{z}}_i \cdot \hat{\mathbf{z}}_j + \frac{\mu_0 \mu^2}{4\pi} \sum_{\langle ij \rangle} \left[\frac{S_i S_j \hat{\mathbf{z}}_i \cdot \hat{\mathbf{z}}_j}{|\mathbf{r}_{ij}|^3} - \frac{3S_i S_j (\hat{\mathbf{z}}_i \cdot \mathbf{r}_{ij})(\hat{\mathbf{z}}_j \cdot \mathbf{r}_{ij})}{|\mathbf{r}_{ij}|^5} \right], \quad (2.3)$$

where μ is the size of the ion's magnetic moment, $\mathbf{r}_{ij}$ is the vector connecting moments i and j , and $S_i = \pm 1$. Additionally, the $\hat{\mathbf{z}}_i$ denote the local $(1, 1, 1)$ axis of moment i , along which it behaves like an Ising spin.

The spin ice ground state is a highly degenerate one due to a vast number of spin configurations having the same energy. This is reflected in the large residual entropy at low temperatures, which can be measured to be in good agreement with the Pauling entropy for water ice, $S \approx (1/2) \log(3/2)$ per spin [6].

The main reason why spin ice materials have attracted a great amount of research interest is because of the form their thermal excitations take. When one of the spins is given the energy to flip, both tetrahedra the spin is associated with locally violate the ice rule and become mathematically equivalent to magnetic monopoles. Importantly these monopoles are deconfined and can propagate independently from each other as there are always spins at the vertices of their associated tetrahedra that can be flipped at no additional energy cost. This process of monopole creation and propagation is illustrated in Figure 2.3 and has indeed been experimentally confirmed [3, 7–9]. Nevertheless, it should be noted that these “monopoles” really only represent a collective quantum mechanical behaviour whose mathematical description is equivalent to magnetic monopoles.

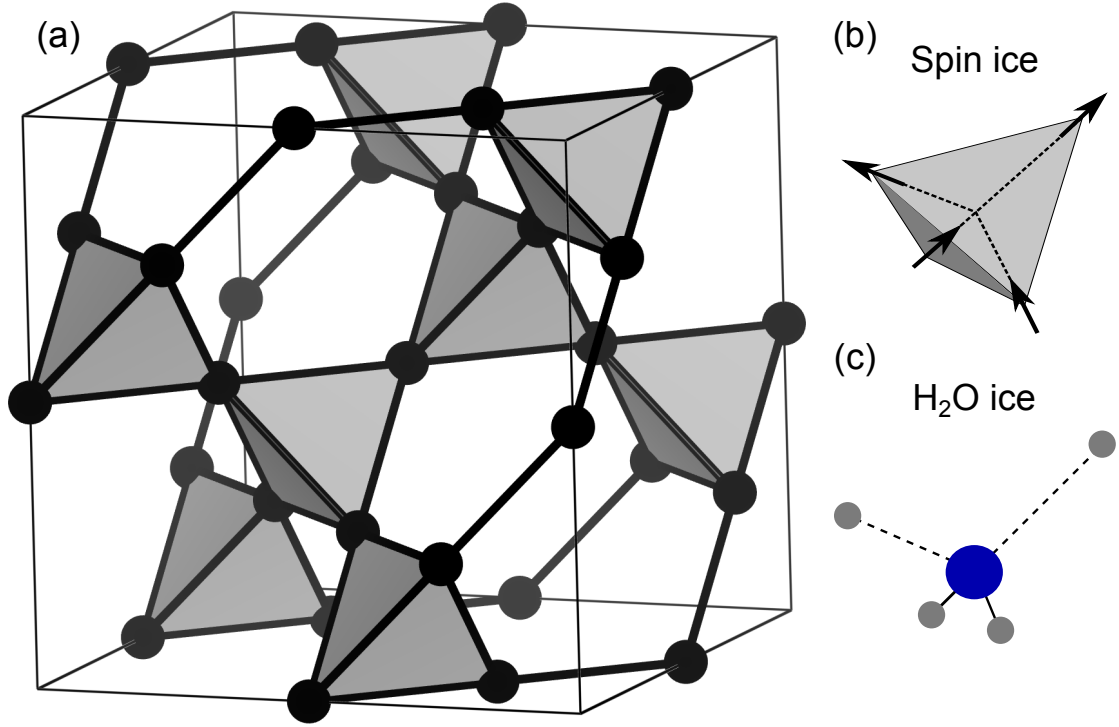


Figure 2.2: (a) Pyrochlore lattice of corner sharing tetrahedra (space group 227: $Fd\bar{3}m$) with black spheres denoting positions of the spins in spin ice materials. (b) Example of spin configuration that obeys the “2in-2out” ice rule. (c) Illustration of the proton coordination in water ice obeying the ice rule.

2.2.2 Honeycomb lattice and Kitaev model

Another structure that contains triangular elements and that is relevant to the research in this thesis is the honeycomb lattice, which is depicted in Figure 2.4 for a two-dimensional scenario, although three-dimensional equivalents called hyper-honeycombs exist. The arrangement of spins on the vertices of the honeycomb hexagons became the focus of intense research interests about 10 years ago when it was first shown that a model containing bond directional interactions can result in a quantum spin liquid ground state in this case [11] with no long range order even at very low temperatures. Furthermore, the model proposed by Alexei Kitaev [11] is exactly solvable and the spin liquid state is robust to small Heisenberg like perturbations [12, 13]. Even more significant is the nature of the thermal excitations of this spin liquid state: they are expected to behave like Majorana fermions, i.e. (quasi-) particles that are their own antiparticles [11–14].

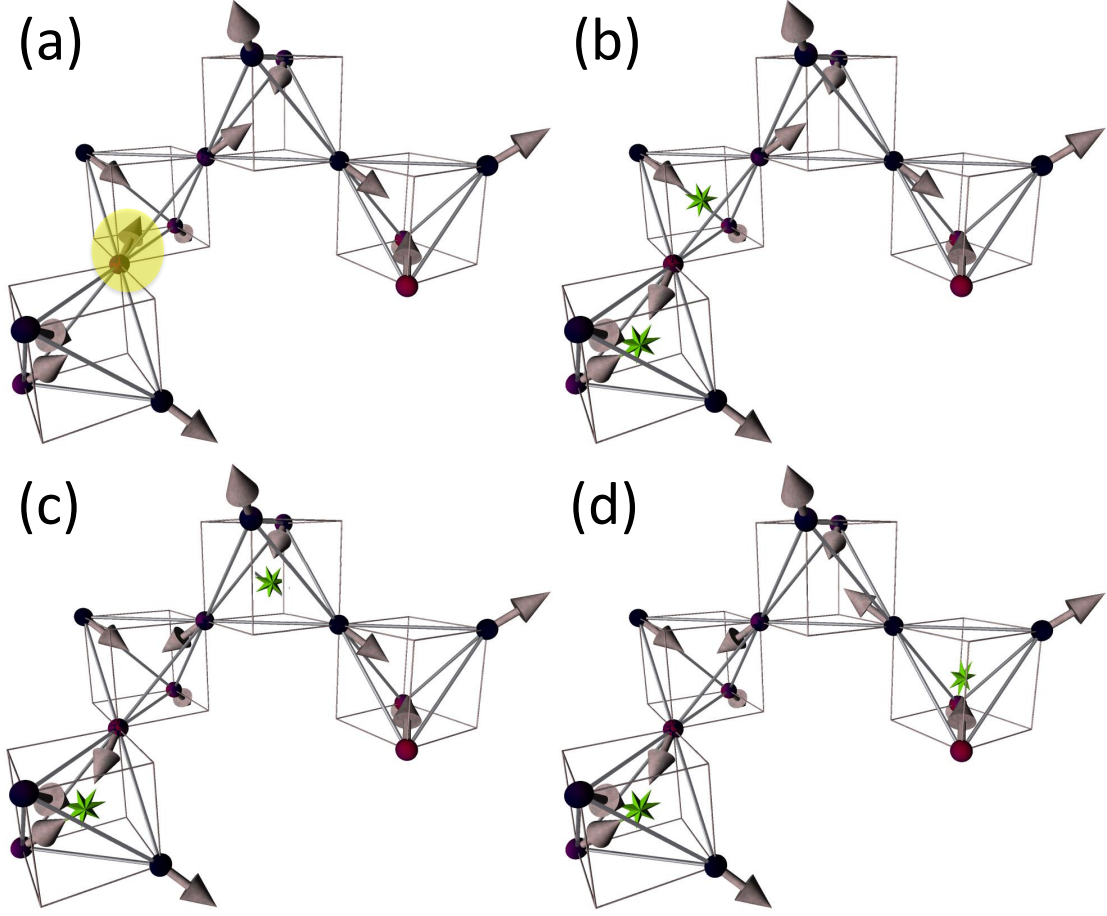


Figure 2.3: Schematic of spin ice configuration and magnetic monopole excitation. Panel (a) represents one possible spin configuration obeying the 2in-2out ice rule; note that not all tetrahedra are drawn for visibility. In panel (b) the spin highlighted by the yellow in circle in (a) has been flipped and the resulting effective monopoles are indicated by the green stars. Panels (c) and (d) illustrate how the monopoles can move independently and at no extra energy cost through successive flips of spins in adjacent tetrahedra. Images courtesy of S.J. Blundell [10].

A typical Hamiltonian describing a model that contains both Heisenberg and Kitaev like interactions can be written as [11, 14, 15]

$$H_{\text{Kitaev}} = -J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{\gamma=x,y,z} \sum_{\substack{\langle ij \rangle, \\ \gamma \text{ bonds}}} K_{\gamma} S_i^{\gamma} S_j^{\gamma}, \quad (2.4)$$

where $\langle ij \rangle$ signifies a sum over neighbouring spins, J and K_{γ} are the exchange constants and γ denotes the different directions of the bonds and the spin components along them. Both nearest neighbour and further neighbour interactions can be included, as depicted in Figure 2.4. The Hamiltonian in equation (2.4) applied

to a honeycomb lattice of spins can lead to quantum spin liquid behaviour and also a whole range of magnetically ordered ground states (see Figure 2 in Ref. [15] for example) depending on the complex interplay of the exchange constants. While experimental observations have revealed compounds that require a Kitaev model to accurately describe their physical behaviour [16–21], the search for a material exhibiting the coveted quantum spin liquid ground state is still on-going. However, there have now been reports of unconventional excitations in the honeycomb magnet α - RuCl_3 that have been proposed as evidence that this compound is close to the Kitaev quantum spin liquid state [22–24]. A μ^+ SR study of this material is the focus of chapter 7.

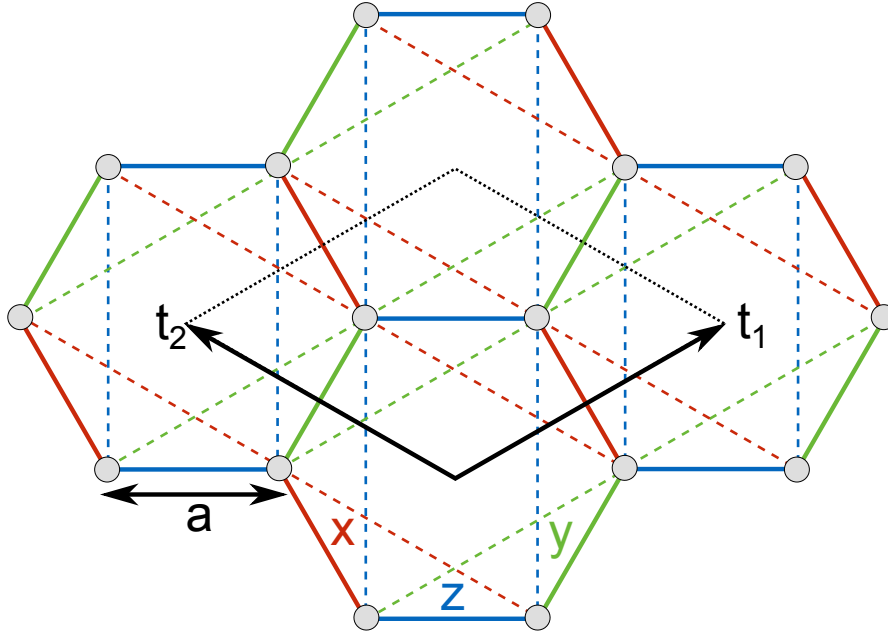


Figure 2.4: Honeycomb lattice and bond directional interactions of the Kitaev model. The grey spheres represent spins that form a honeycomb lattice with side length a , a suitable set of primitive lattice vectors $\{t_1, t_2\} = a/2(\pm 3\hat{x} + \sqrt{3}\hat{y})$ and a unit cell as indicated by the black dotted line. The solid (dashed) coloured lines illustrate the bond directional interactions between (next) nearest neighbour spins, labelled by x , y and z .

2.3 Demagnetisation

When investigating magnetisable materials it is important to be cautious when drawing conclusions about the internal fields of the sample at hand. This is because

the externally applied fields, call them $\mathbf{B}_a$ and $\mathbf{H}_a$, can differ significantly from the ones inside the sample due to the fields produced by the magnetic moments inside the solid. These moments will lead to a magnetisation $\mathbf{M}$, which at the surface of the sample has to vanish discontinuously. Therefore, there is a divergence of $\mathbf{M}$ at the boundary and an equal and opposite divergence of $\mathbf{H}$ described by (recall that $\nabla \cdot \mathbf{B} = 0$):

$$\nabla \cdot \mathbf{H} = -\nabla \cdot \mathbf{M}. \quad (2.5)$$

This is mathematically equivalent to “magnetic charges”, i.e. magnetic monopoles, populating the sample’s boundary and acting as a source of what is referred to as the demagnetising field $\mathbf{H}_d$.

It is important to note that the demagnetising field represents an important energy associated with the divergence of the magnetisation $\mathbf{M}$. It can be shown that this energy takes the form [1]

$$-\frac{\mu_0}{2} \int_V d\tau \mathbf{M} \cdot \mathbf{H}_d, \quad (2.6)$$

where the integration is performed over the volume V of the sample. This energy cost also incorporates contributions due to other sources of divergence of the magnetisation such as domain walls, which act as to decrease the demagnetising energy at the expense of the energy cost involved in realigning the magnetic moments locally to create the domain walls in the first place.

The demagnetising field in general is very complex and depends on both the shape of the ferromagnetic object and the position inside it; unless the shape is ellipsoidal, in which case $\mathbf{H}_d$ takes the simple form:

$$\mathbf{H}_d = -N\mathbf{M} \quad (2.7)$$

$$= N_x M_x \hat{\mathbf{x}} + N_y M_y \hat{\mathbf{y}} + N_z M_z \hat{\mathbf{z}}, \quad (2.8)$$

where M_i denotes the components of $\mathbf{M}$ along the principal axes $\hat{\mathbf{i}}$ of the ellipse and the N_i are position independent constants. In virtually all other scenarios the demagnetising tensor $\mathbf{N}$ appearing in equation (2.7) cannot be diagonalised and additionally is a function of position inside and shape of the ferromagnet. Consequently, the total field

$$\mathbf{H} = \mathbf{H}_a - \mathbf{N}\mathbf{M} \quad (2.9)$$

can be very challenging to evaluate. Demagnetising field effects are of particular relevance to experiments employing high magnetic fields or strongly ferromagnetic samples in which an exact knowledge of the internal fields is required. An example of this is the experimental technique called μ^+ SR, which is an integral aspect of this thesis and introduced in chapter 3. With the recent development of high magnetic field spectrometers for μ^+ SR research it has become increasingly important to understand, identify and quantify demagnetising effects. Chapter 5 presents a detailed investigation of the demagnetising fields of cylindrically shaped samples by employing a recently reported Fourier transform method for evaluating the demagnetising tensor $\mathbf{N}$.

Chapter 3

Muon spin rotation and relaxation

The terms muon-spin rotation/relaxation/resonance (μ^+ SR) refer to an experimental technique in which an ensemble of spin-polarised muons is implanted into a sample and the time evolution of the muon spins is measured through observing the angular distribution of the muon decay products. Analysis of the Larmor precession of the muon spins and the evolution of the spin polarisation gives important insights into the magnetic properties of the sample. In general, both positive (μ^+) and negative muons (μ^-) can be used, although in practice predominantly the positive muon is employed due to its propensity to stop near regions of large electron density, where its spin interacts with the local magnetic field. Therefore, the μ^+ acts as a local magnetic probe. Any work presented in this report is restricted to μ^+ SR scenarios.

This chapter is intended as an overview of the fundamentals of the μ^+ SR technique. First I briefly cover the historic background of the relevant muon science, before presenting the various steps involved in carrying out a μ^+ SR experiment, such as production, implantation and decay of the muons. I furthermore discuss the significance of the various local field contributions that can influence the muon Larmor precession inside a sample. Subsequently, I give an overview of the differ-

ent types of muon sources and experimental geometries available, and summarise the theoretical models for the experimental scenarios pertinent to this thesis. Finally, I highlight the inherent limitations of μ^+ SR and their possible resolution through complementary experimental and theoretical techniques. For a more in-depth introduction to μ^+ SR I recommend the reviews in Refs. [25–28].

3.1 History

The first experimental evidence for the existence of the muon was gathered while studying cosmic rays in 1936 [29], where they left a trace in the cloud chamber that necessitated a previously unknown particle with mass between those of the electron and the proton. The muon was confirmed to exist about a year later [30, 31], and it was initially thought to correspond to a particle previously predicted by Yukawa [32] to be a mediator of the nuclear force. When it was eventually recognised, to many researchers’ surprise, that the muon was instead a heavy version of the electron, Nobel laureate I.I. Rabi is said to have quipped “Who ordered that?”. The actual “order” of Yukawa’s particle(s), the pions, was not delivered until about 10 years later [33, 34], earning Yukawa his Nobel Prize in 1949. The positive pion plays an indispensable role in μ^+ SR as I will discuss in the next section.

The door to the development of modern day μ^+ SR experiments was opened in the mid 1950s when two simultaneously published experiments confirmed the proposal by Lee and Yang [35] that the weak interaction involved in nuclear decays violates parity. The first, by Wu *et al.* [36], observed an asymmetric spatial distribution of the electrons emitted in the beta decay of polarised Co^{60} nuclei. Whereas the second experiment, due to Garwin, Lederman and Weinrich [37], discovered that the positron emitted in the decay of a muon also exhibited an asymmetric spatial distribution with respect to the muon polarisation and that it was in fact preferentially emitted along the muon’s magnetic moment. This

observation eventually sparked the development of the modern μ^+ SR technique, and the experiment of Garwin *et al.* can rightfully be described as the first ever μ^+ SR experiment (with the sample an eight inch thick piece of carbon).

3.2 Muon production

The first step in generating positive muons is to produce positive pions through the collisions of protons with a target:

$$p + A \rightarrow A + n + \pi^+,$$

where $A = \{p, n\}$. The total threshold energy for this process is $E_{\text{tot},p} = ((m_n + m_p + m_{\pi^+})^2 - m_p^2 - m_n^2)/2m_n$ assuming the target neutron to be free. This gives a threshold kinetic energy of the protons of $E_{\text{tot},p} - m_p c^2 \approx 290$ MeV, hence requiring a particle accelerator in practice. Both cyclotrons and synchrotrons are currently employed to this end, which produce a beam of high energy protons and guide it into a collision target (typically graphite) in a continuous or pulsed fashion, respectively. Consequently, the emerging pions and ultimately the positive muons are also generated either continuously or in pulsed bursts.

The π^+ decay via the weak interaction with a mean lifetime of 2.6×10^{-8} s and a branching ratio of 99.99 % [38]:

$$\pi^+ \rightarrow \mu^+ + \nu_\mu.$$

Most commonly, the π^+ decaying at rest near the surface of the target are used in μ^+ SR experiments, hence leading to the name “surface muons”. In this case the kinetic energy and momentum of the muons in the laboratory frame are equivalent to those in the rest frame of the pion:

$$E_{\mu,\text{kin}} = \frac{(m_{\pi^+} - m_\mu)^2 c^2}{2m_{\pi^+}} = 4.1 \text{ MeV}, \quad (3.1)$$

$$p_\mu = \frac{(m_{\pi^+}^2 - m_\mu^2)c}{2m_{\pi^+}} = 29.8 \text{ MeV}, \quad (3.2)$$

where c denotes the speed of light and m_{π^+} and m_μ represent the masses of the positive pions and muons. The pion has zero spin and the muon-neutrino (spin 1/2) has a negative helicity (its spin and linear momentum are antiparallel). Thus, conservation of (linear and angular) momentum dictates that if the pion decays at rest the resulting muon must necessarily also be spin-1/2 and in a negative helicity state. Hence, the direction of the spin of the surface muons can be uniquely determined from their momentum direction. Table 3.1 summarises some of the fundamental properties of the aforementioned particles.

q	m (m_e)	S ($\hbar$)	μ (μ_B)	$\gamma/2\pi$ (MHz T $^{-1}$)	τ
$e^\pm$ $\pm e$	1	1/2	± 1.001	28024	$> 4.6 \times 10^{26}$ yr
$\mu^\pm$ $\pm e$	207	1/2	$\pm 4.88 \times 10^{-3}$	135.5	2.197 μ s
n 0	1840	1/2	-1.04×10^{-3}	29.16	880.1 s
p e	1836	1/2	1.521×10^{-3}	42.58	$> 2.1 \times 10^{29}$ yr
$\pi^\pm$ $\pm e$	273	0	0	0	26.03 ns

Table 3.1: Fundamental properties of particles relevant to μ^+ SR. The columns denote (from left to right) the charge, mass, spin, magnetic moment, gyromagnetic ratio and mean life time. Data are taken from Refs. [39, 40].

In some experimental situations muons with different kinetic energies are required to alter their interaction cross section with matter and thus their stopping range. Both muons with higher kinetic energy, obtained from in-flight decay of pions, and lower energy, through slowing down in a moderator before re-accelerating the muons, are available. Applications of these muons include pressure cell experiments, where high energy muons can penetrate the cell wall, and thin film investigations, in which the sample thickness necessitates slow muons. Neither of these more specialised techniques are subject of this thesis.

3.3 Implantation

The spin-polarised muons are guided to the sample by dipole (steering) and quadrupole (focussing) magnets. The spin-polarisation is maintained in the guiding

process since the muon's g -factor is 2 (excluding a small anomalous correction [41]) and therefore both its spin and linear momentum are affected equally by the guiding magnets. Furthermore, the steering magnets automatically filter the muon beam and select particles with a fixed ratio of momentum p to charge q since the trajectory of a charged particle in an orthogonal magnetic field B has the radius $r = p/(qB)$. To remove any remaining contaminating particles, particularly positrons, an additional Wien filter is employed. By applying both an electric (E) and a magnetic field (B), mutually orthogonal and also perpendicular to the particle beam, this filter results in curved trajectories except for particles with velocity E/B . Thus, by judicious choice of E/B the Wien filter can be calibrated to select particles with the desired mass of a muon only (after the steering dipoles selected the desired momentum). Figure 3.1 contains a schematic of the various components involved in producing and guiding the positive muons for the specific example of the ISIS muon facility.

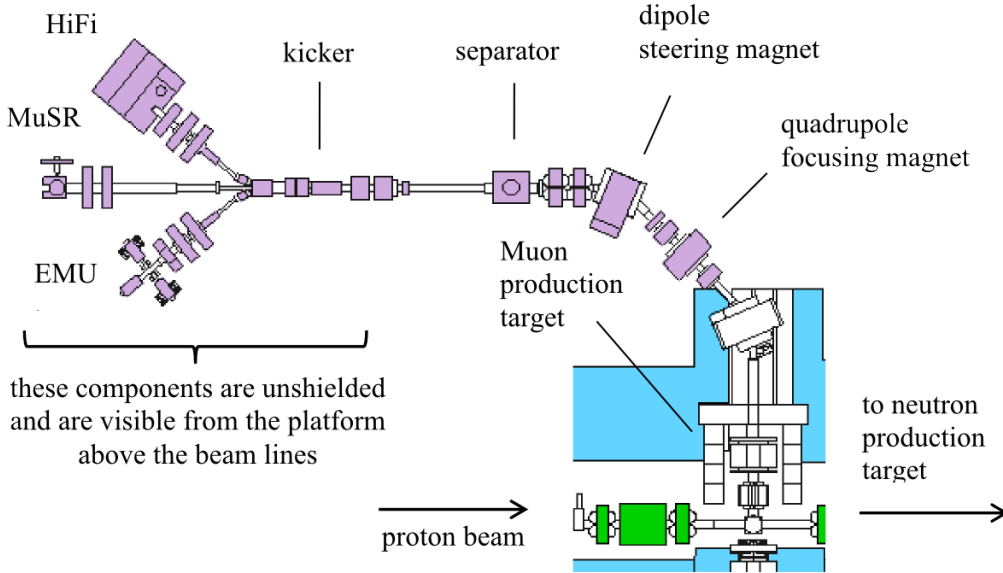


Figure 3.1: Schematics of the ISIS muon facility from the user handbook of the EMU spectrometer [42]. Note that the DEVA spectrometer has since been replaced by the high-field instrument HiFi (see Figure 3.3) and that the separator corresponds to the Wien filter mentioned in the main text. The kicker is a set of capacitor plates that are used to create a strong electric field that splits up the two muon pulses produced by the ISIS proton beam and distributes it into the three separate instruments.

Once the muons have been guided to the sample they lose their 4.1 MeV kinetic

energy through a series of different interactions with the sample [25]. In the first 0.1–1 ns the muons shed their energy through scattering off electrons and ionising atoms in their pathway. After reaching an energy of the order of 10 keV they subsequently undergo a very rapid series of electron capture and loss reactions in which the muon forms a hydrogen like state called muonium (Mu). This reduces the kinetic energy to a few hundred eV in about 1 ps. The final energy can be shed through further electron capture/loss or muonium-atom collisions. Once the muon has thermalised it typically comes to rest at an interstitial site, where it can form either a diamagnetic μ^+ state, taking on the role of a light proton, or the aforementioned (paramagnetic) hydrogen like muonium. Surface muons have a density dependent penetration depth that is typically 110 mg/cm² with a variance of about 20 % [43, 44]. Therefore they can be regarded to probe the bulk of a sample.

Crucially, the interactions through which the muons thermalise are all Coulombic in origin and do not interact with the muon spin. Consequently, the spin-polarisation of the muon ensemble remains almost unchanged [45] in the stopping process. Furthermore, any radiation damage caused by the impinging muons is restricted to the entry region into the sample. This is due to the energy barrier for vacancy production being high enough that muons retain enough energy to propagate a further few μm [45] after dropping below this threshold. Thus leaving the final muon stopping sites far from any vacancies.

It should be noted that in general it is possible for multiple muon stopping sites to exist in any sample, including the formation of both bare μ^+ and muonium. Each of these crystallographically inequivalent sites lends itself to a distinct muon signal in principle. Additionally, a fraction of the muons can also implant into parts of the sample environment, e.g. the sample holder. Typically silver is chosen for those parts of the setup since the corresponding slowly relaxing background signal is well characterised and can readily be subtracted from experimental data.

Thin sheets of silver are sometimes also added in front of the sample to act as a degrader in which the muons lose some fraction of their kinetic energy. This method is typically utilised if the sample is too thin for muons to stop in it.

3.4 Precession

Once a positive muon has come to a halt, its spin Larmor precesses around the local magnetic field $\mathbf{B}_{\text{tot}}$ at an angular frequency $\omega = \gamma_{\mu}|\mathbf{B}_{\text{tot}}|$ where $\gamma_{\mu} = 2\pi \times 135.4 \text{ MHz/T}$ is the muon gyromagnetic ratio (see Table 3.1). In general a variety of magnetic interactions can contribute to this local field, although in practice not all of them might be present or significant [26]:

$$\mathbf{B}_{\text{tot}} = \mathbf{B}_{\text{ext}} + \mathbf{B}_{\text{hf,con}} + \mathbf{B}_{\text{hf,trans}} + \mathbf{B}_{\text{dia}} + \mathbf{B}_{\text{dip}} + \mathbf{B}_{\text{L}} + \mathbf{B}_{\text{demag}}. \quad (3.3)$$

The individual terms in this equation denote the following.

$\mathbf{B}_{\text{ext}}$: Any externally applied field, including stray fields (e.g. the earth's field).

$\mathbf{B}_{\text{hf,con}}$: Hyperfine contact interaction caused by a spin density of polarised conduction electrons at the muon site.

$\mathbf{B}_{\text{hf,trans}}$: Transferred hyperfine field due to conduction electrons mediating a coupling with the local moments via the RKKY interaction [46–48].

$\mathbf{B}_{\text{dia}}$: The diamagnetic field pertinent to superconductors.

In this thesis the hyperfine and diamagnetic fields above are not considered. The remaining three terms in equation (3.3) constitute the dipolar coupling of the muon spin to localised electronic or nuclear magnetic moments. In general, this can be written as a sum over the interactions with all the individual magnetic moments present in the entire sample. However, it is possible to separate it into three individual terms by considering a finite size sphere, called the Lorentz sphere.

The sum over all the moments $\boldsymbol{\mu}_i$, at positions $\mathbf{r}_i$, within the Lorentz sphere is

$$\mathbf{B}_{\text{dip}} = \sum_i \frac{\mu_o}{4\pi|\Delta\mathbf{r}_i|^3} \left[\frac{3(\boldsymbol{\mu}_i \cdot \Delta\mathbf{r}_i)\Delta\mathbf{r}_i}{|\Delta\mathbf{r}_i|^2} - \boldsymbol{\mu}_i \right], \quad (3.4)$$

where the muon is located at position $\mathbf{r}_\mu$ and I defined $\Delta\mathbf{r}_i = \mathbf{r}_i - \mathbf{r}_\mu$. A sufficiently large radius for the sphere has to be chosen to ensure the convergence of this sum. Typically, a Lorentz sphere should contain at least a few hundred spins to guarantee an accuracy of at least a few percent, commensurate with usual experimental measurement accuracies. Assuming the sample to be of sufficient size that the Lorentz sphere is negligibly small in comparison, the sum over all the moments outside the Lorentz sphere to a good approximation can be extended over all space, in which case one obtains the following simple expression for the Lorentz field:

$$\mathbf{B}_L = \mu_0 \mathbf{M}_{\text{sat}}/3, \quad (3.5)$$

where μ_0 is the permeability of free space and $\mathbf{M}_{\text{sat}}$ is the saturation magnetisation of the sample. The final term in equation (3.3) refers to the demagnetising field due to the finite size of the sample and the subsequent divergence of the magnetisation at the sample surface. The demagnetising field has already been discussed in chapter 2.3 above and it takes the form

$$\mathbf{B}_{\text{demag}} = -\mu_0 \mathbf{N} \mathbf{M}_{\text{bulk}}, \quad (3.6)$$

where $\mathbf{N}$ is the demagnetising tensor and $\mathbf{M}_{\text{bulk}}$ the bulk magnetisation. It should be noted that for antiferromagnets, such as $\alpha\text{-RuCl}_3$ discussed in chapter 7, both the Lorentz and demagnetising fields are trivially zero.

3.5 Decay

After a mean life time of $\tau = 2.2 \mu\text{s}$ the muon decays via the weak interaction:

$$\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu.$$

Because this is a three-body decay the e^+ can access a continuous set of momenta. However, the direction of the e^+ emission does not follow a homogeneous distribution. Due to the parity-violating nature of the weak interaction the e^+ is predominantly emitted into the direction of the muon spin at decay. The probability of the decay positron being emitted at an angle θ to the muon spin as a function of its energy ξ is given by:

$$N(\theta) = N_0(1 + a(\xi) \cos \theta). \quad (3.7)$$

In this expression $a(\xi)$ takes the value 1 for the maximum possible positron energy (52.8 MeV) and 1/3 for an average over all available positron energies. The resulting positron distribution is plotted in Figure 3.2, demonstrating the correlation between the muon spin and the positron trajectory. In summary, by measuring the angular distribution of the decay positrons it is possible to infer the time evolution of the muon spins since their initial momentum and thus spin direction is known.

3.5.1 Positron detection

The positrons emitted by the decaying muons are observed in a set of detectors located around the sample. They are specifically placed in front of and behind the direction of the initial muon spin polarisation. Figure 3.3 illustrates this arrangement for the HiFi spectrometer at the ISIS muon facility. The detectors are typically made of scintillators in which an incoming positron yields a small burst of photons upon passing through, which is subsequently enhanced by photomultiplier tubes and turned into an electric signal. Furthermore, a discriminator is

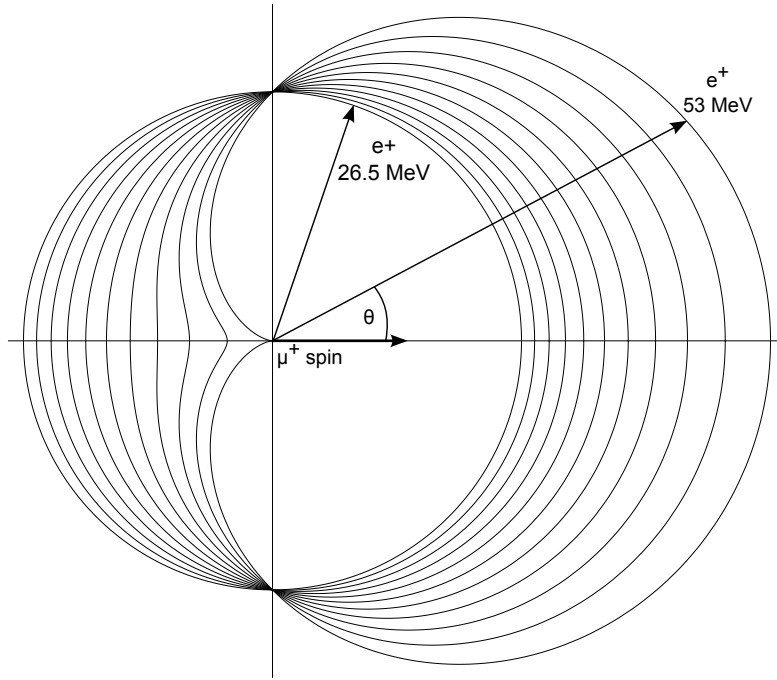


Figure 3.2: Asymmetry in the angular distribution of positron emission, adapted from Ref. [49]. In the muon rest frame the maximum positron energy is 52.8 MeV.

employed that discards all electric signals below a noise threshold. Due to the time limitation of the electronic responses, scintillation detectors can only detect one positron event about every 10 ns. This is known as the dead-time and it is the reason why pulsed muon sources have highly segmented sets of detectors in order to capture as many positron events as possible during the pulse window.

In the simplest possible configuration there are only two detectors surrounding the sample, one in the forward and one in the backward direction of the initial muon polarisation. Routinely such a setup is artificially simulated by grouping multiple detectors on either side of the sample together. The spatial asymmetry of the positron emission, and hence the muon spin direction, can subsequently be extracted by taking the difference between the two detector counts. Since we are also interested in the time evolution of the spin polarisation of the muon ensemble, we additionally normalise the count rate by the total population of detected muon decays (which falls off exponentially). The subsequently obtained quantity is known

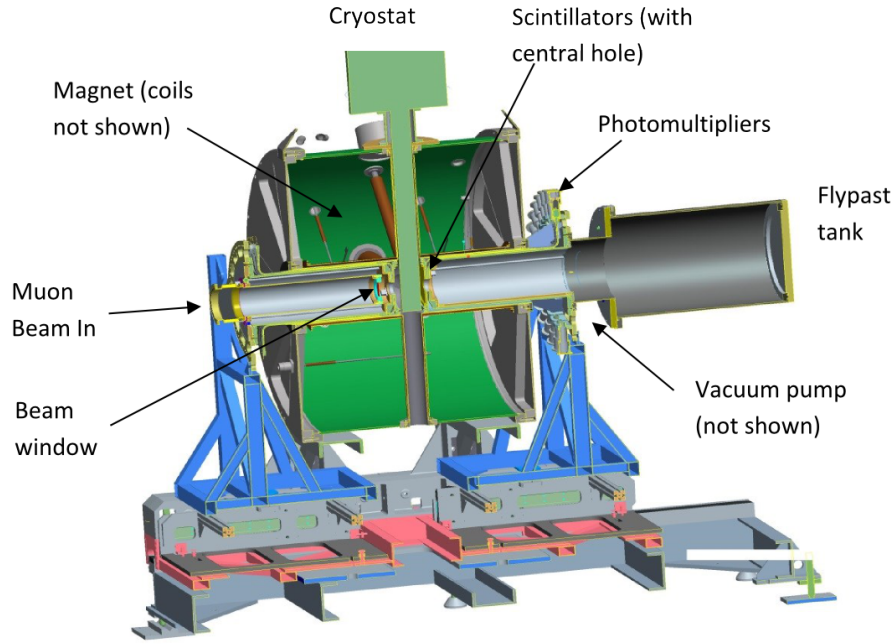


Figure 3.3: Illustration of the HiFi spectrometer at the ISIS muon facility. From the corresponding user manual [50].

as the (positron) asymmetry:

$$A(t) = \frac{N_F(t) - \alpha N_B(t)}{N_F(t) + \alpha N_B(t)}, \quad (3.8)$$

where N_F and N_B are the positron counts registered in the forward and backward detectors, and α is an experimental calibration factor accounting for any asymmetry introduced by the setup of the experiment, such as detector efficiencies or sample placement. Figure 3.4 illustrates how a magnetic field applied transverse to the muon spin polarisation yields an oscillating signal in the asymmetry $A(t)$. Such oscillations also occur in zero (applied) field experiments if the sample exhibits long range magnetic order (see section 3.6 below).

Crucially, the asymmetry $A(t)$ is proportional to the spin-polarisation of the muons and thus by analysing $A(t)$ the magnetic structure of the sample can often be inferred uniquely. In an ideal experimental arrangement all the muon spins would initially point towards the forward detector, in which case the asymmetry at the time of muon implantation would simply be given by the energy integrated value of $a(\xi)$ appearing in equation (3.7). Consequently, one expects $A(t = 0) =$

1/3. However, in reality a variety of factors decrease the initial asymmetry, such as incomplete solid angle coverage of the detectors, positrons stopping in the sample holder and curved positron trajectories in applied magnetic fields. Typically, a value of $A(t = 0) \approx 0.25$ is experimentally observed.

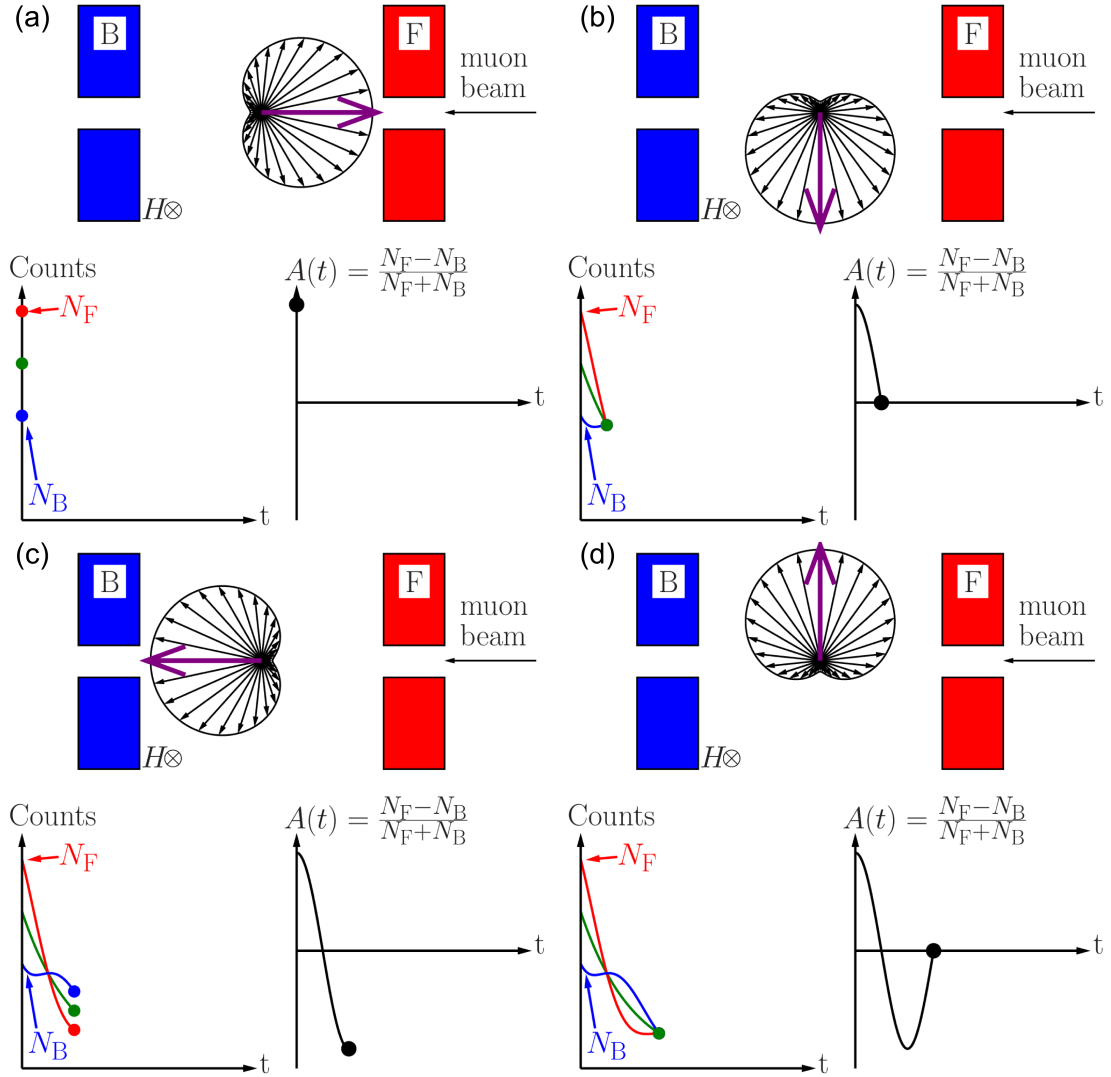


Figure 3.4: Schematic of experimental observation of muon Larmor precession. Each panel represents a particular time screenshot and includes a depiction of the sample environment with backwards and forwards detectors B and F, as well as the muon spin direction and positron emission. Additionally, the two graphs at the bottom of each panel show the muon exponential decay together with the detector counts (N_F and N_B), as well as the extracted asymmetry. Panel (a) corresponds to the time of implantation of the spin polarised muons with subsequent panels (b)–(d) portraying time evolution.

3.6 Polarisation functions

This section is aimed at presenting the different types of applied field geometries that are possible within μ^+ SR and give an overview of the most common polarisation functions that can arise in these different scenarios. While a whole library of polarisation functions has been developed, with each corresponding to a particular experimental setup and sample behaviour, I will focus on situations pertinent to the measurements presented in this thesis. For a very detailed account of polarisation functions I can recommend Ref. [51].

3.6.1 Longitudinal geometry

The most basic situation one can imagine is that of the muons initially polarised along the z -direction, with a single muon stopping site at which the local magnetic field $\mathbf{B}$ is at an angle θ to the z -axis. In the subsequent Larmor precession of the spins, illustrated in Figure 3.5, the projection of the spin along its initial direction evolves as

$$s_z(t) = \cos^2 \theta + \sin^2 \theta \cos \omega t, \quad (3.9)$$

where $\omega = \gamma_\mu |B|$ represents the precession frequency. If the magnetic field is identical at all the muon sites the ensemble of spins oscillate in phase and retain their collective spin-polarisation, thereby allowing s_z in equation (3.9) to be replaced by P_z , the polarisation component along the z -axis. In the case of polycrystalline samples, applicable to the measurements in chapter 6, a powder average of equation (3.9) can be performed. Bearing in mind that there are two crystallite orientations perpendicular to $\mathbf{B}$ and only one parallel, gives the following expression for the polarisation

$$P_z(t) = \frac{1}{3} + \frac{2}{3} \cos \omega t. \quad (3.10)$$

The above case describes a longitudinal field (LF) scenario since the polarisation component along the initial spin direction P_z is investigated. A particular

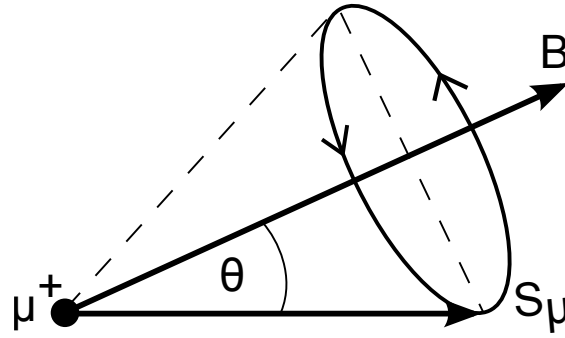


Figure 3.5: Precession of the muon spin in a magnetic field at an angle θ . Adapted from Ref. [25]

subset of LF measurements is that of a zero field (ZF) measurement in which no external field is applied. ZF experiments are most commonly performed to investigate any potential magnetic ordering of the atomic spins. In the case of long range magnetic order the muons experience the same local field and precess coherently, thereby leading to an oscillatory signal of the asymmetry (polarisation).

However, in real materials thermal (and/or quantum) fluctuations will always result in a variability of the local magnetic field $\mathbf{B}$. These variations can have a spatial or temporal nature and both of these result in a dephasing of the muon oscillations. The result of which is a relaxation of the spin polarisation, referred to as static or dynamic relaxation depending on whether it stems from spatial or temporal changes of the local field. It should be noted that temporal in this case means that significant changes occur dynamically on a time scale similar to that of the muon life time ($2.2 \mu\text{s}$). The relaxation of the polarisation is typically well described by a Gaussian $\exp(-\gamma_\mu^2 \langle B^2 \rangle t^2 / 2)$ for a static distribution of fields with mean square width $\langle B^2 \rangle$ (the second moment of the field distribution), whereas for dynamically fluctuating fields the polarisation is better described by an exponential of the form $\exp(-\lambda t)$ [51]. The quantities $\Delta = \sqrt{\gamma_\mu^2 \langle B^2 \rangle}$ and λ are called the static and dynamic relaxation rates, respectively. See section 3.6.2 below for more details and justifications of these statements.

The case of statically distributed fields in the longitudinal geometry was first described theoretically by Kubo and Toyabe [52] and derived by taking a statistical

average of equation (3.9). The resulting formula for the muon polarisation was named in their honour Kubo-Toyabe (KT) relaxation function [25, 53]:

$$P_z(t) = \frac{1}{3} + \frac{2}{3} \exp(-\Delta^2 t^2 / 2) (1 - \Delta^2 t^2), \quad (3.11)$$

which corresponds to the curve plotted in Figure 3.6 in the limit $\omega/\Delta = 0$. The rise of the baseline asymmetry to the “1/3” tail in equation (3.10) at long times is used as another experimental indicator for long range order in powder samples in addition to any oscillatory signals.

If an additional longitudinal field B_L is applied externally, the LF Kubo-Toyabe function is obtained [53]:

$$P_z(t) = 1 - \frac{2\Delta^2}{\omega^2} [1 - \exp(-\Delta^2 t^2 / 2) \cos \omega t] + \frac{2\Delta^4}{\omega^3} \int_0^t d\tau \exp\{-\Delta^2 \tau^2\} \sin \omega \tau, \quad (3.12)$$

where $\omega = \gamma_\mu B_L$ as before and the field width Δ incorporates the applied field. This function is plotted in Figure 3.11 for a range of ratios of ω/Δ , illustrating how the application of an externally applied field can quench the “1/3” tail. Experimentally this allows a useful insight into the strength of the internal fields by measuring how strong a LF is required to decouple the muon spins from the internal fields.

In addition to static field distributions, the muon polarisation can also be relaxed through dynamical (temporal) fluctuations. While analytical solutions modelling such a scenario exist [53], they are rather complex and are omitted here since they are not required to form an understanding of the μ^+ SR measurements presented in this thesis.

3.6.2 Transverse geometry

An alternative to measuring the polarisation along the z -axis (P_z) is to study the components perpendicular to the initial muon spin direction (P_x). This represents

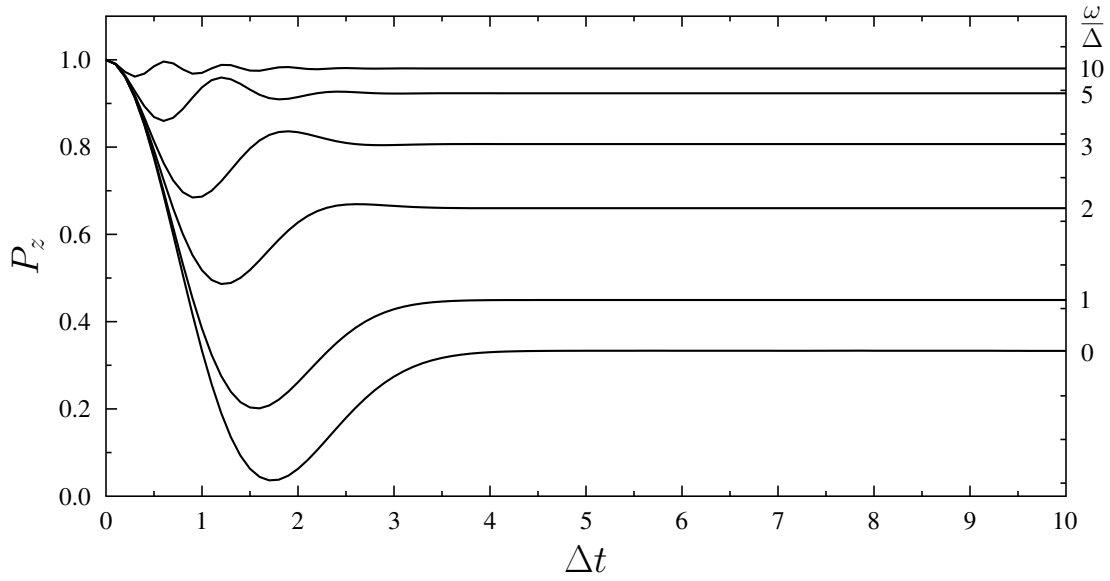


Figure 3.6: Longitudinal-field Kubo-Toyabe function from equation (3.12). Note that in the limit $\omega/\Delta = 0$ the ZF version in equation (3.11) is recovered. Adapted from Ref. [25].

the transverse field scenario, which is illustrated in Figure 3.4 and that has been extensively studied due to its importance in nuclear magnetic resonance (NMR). Taking the external field $\mathbf{B}_{\text{TF}}$ to be applied along the x -axis, perpendicular to the initial polarisation, and allowing for both static field distributions with width Δ and dynamical fluctuations with correlation time τ_c results in the so-called Abragam function [54]:

$$P_x(t) = \exp\left[-\Delta^2\tau_c^2(e^{-t/\tau_c} - 1 + t/\tau_c)\right] \cos \omega t, \quad (3.13)$$

where $\omega = \gamma_\mu|\mathbf{B}_{\text{TF}}|$ as before. In the limit of negligible dynamical fluctuations when $t/\tau_c \rightarrow 0$ this becomes:

$$P_x(t) = \exp\left[-\Delta^2 t^2/2\right] \cos \omega t, \quad (3.14)$$

which represents a Gaussian relaxation of the transverse polarisation. In the limit of fast fluctuations with $t/\tau_c \gg 1$ equation (3.13) simplifies to

$$P_x(t) = \exp\left[-\Delta^2\tau_c t\right] \cos \omega t = \exp[-\lambda t] \cos \omega t. \quad (3.15)$$

Thus, in the case of significant dynamical fluctuations the relaxation is exponential with relaxation rate $\lambda = \Delta^2\tau_c$. Equations (3.14) and (3.15) are the reason why most experimental data can be fitted with either Gaussian or exponential relaxation functions (in addition to any oscillatory signals). Notice also that the dynamical relaxation rate λ actually decreases for faster fluctuations (with shorter correlation times τ_c). This effect is named motional narrowing and also occurs in the LF geometry discussed in the previous section (although no proof of this statement is given here).

3.7 Capabilities and limitations

Positive muons can be employed as extraordinarily sensitive local magnetic probes in both bulk and surface measurements. They are routinely used to detect local fields of the order of 1 Gauss (0.1 mT) and even smaller, making them ideal probes for systems with dilute spins or nuclear magnetic moments. In such systems μ^+ SR often offers the only available method for experimental investigations. Smaller fields are very challenging to detect due to the exponential decay of the muons suppressing long time data rates. On the other hand, the largest detectable fields depend on the type of muon source considered. In a pulsed source the highest resolvable precession frequency is determined by the muon pulse width, since too high a field will cause the muons in the early times of the pulse to dephase before the remainder has implanted. In contrast, the time resolution of a continuous muon source is ultimately set by the precision in timing the muon arrival and detection of its decay product positron, which is in general much better than the time resolution at a pulsed source. The largest currently detectable local fields are of the order of 10 T. However, the increased time resolution of a continuous muon source comes at the expense of a lower data rate, because only one muon can be permitted in the sample at any time to unambiguously identify and link any positron detection with the decayed muon. Whereas pulsed sources have no theoretical upper limit

to the amount of muons that each pulse can contain, practically the dead time of the detectors will limit the maximum detectable amount of muon decays.

μ^+ SR is a very versatile technique since it can be applied to any material phase (solid, liquid, gas) in a large range of possible environments (any temperature, applied fields up to about 10 T, high pressure, irradiation by RF or laser pulses and others). Besides, both single crystal and powder samples can be studied and μ^+ SR is not limited by the presence of particular nuclei (like needed for NMR) or strong absorbers (as in the case of neutrons). In addition, any non-magnetic impurity signals can be straightforwardly identified and subtracted in most situations and volume fractions of different phases can be extracted.

In terms of the time scale of magnetic fluctuations that can be probed, μ^+ SR (10^4 – 10^{12} Hz) is complementary to other techniques such as neutrons (10^8 – 10^{13} Hz) and NMR (10^{-2} – 10^5 Hz) [28].

Although the μ^+ SR technique presents a useful tool in probing local magnetic structures –with great successes in many areas of condensed matter physics and chemistry– it suffers from two inherent limitations. In general, the muon stopping site is not known, thereby limiting the possible conclusions about the magnetic field distribution inside a sample. And more importantly, the effect of the muon on its local environment can normally not be quantified. This raises the crucial question whether the μ^+ acts as an passive probe or whether it can perturb its environment to such a degree that the measurements reflect the local distortions more than the intrinsic behaviour of the sample. This lack of knowledge about the character of the muon environment can be removed by using *ab initio* calculations based on density functional theory, which is introduced in chapter 4. In chapter 6 I employ this theoretical technique to argue that in Pr based pyrochlores the muon indeed alters the local environment in such a way that our experimental observations reflect the local response to the muon rather than any intrinsic properties. Chapter 7 also utilises DFT computations to gain insights about the muon stopping sites.

Chapter 4

Density functional theory

In the early stages of the development of quantum mechanics Paul Dirac is reported to have said “Chemistry has come to an end.” [55]. His exclamation reportedly was a reaction to the successful spectroscopic validation in simple systems, such as He and H₂, of the equation for the electronic wave function put forward by Erwin Schrödinger [56], for which Schrödinger received the Nobel Prize in Physics in 1933 (jointly with Dirac). This equation is one of the founding blocks of quantum mechanical theory and even 90 years after its discovery it is still at the very heart of our modern understanding of atomic level behaviour. While in theory the Schrödinger equation embodies all the information necessary to quantitatively describe a system’s behaviour once the associated Hamiltonian is determined, hence provoking Dirac’s iconic quote, it is in practice impossible to solve for systems with more than a handful of atoms. Or using Dirac’s words again: “Too bad that in almost all cases, this (Schrödinger’s) equation is far too complex to allow solution” [55].

In this chapter I introduce density functional theory (DFT), which in essence is a method of reformulating the many-body Schrödinger equation in such a way that it becomes tractable and numerically solvable on modern computers for system sizes containing of the order of 100 atoms. DFT is most frequently employed to calculate electronic and ionic structures of condensed matter systems or molec-

ular dynamics, and while in theory it only provides approximate solutions to the Schrödinger equation, in practice it often produces surprisingly accurate results.

After giving a brief account of the essential concepts underlying DFT and its capabilities and limitations, I discuss some of the most important aspects of its practical implementation. Subsequently, I give a short introduction to a technique called “DFT+ μ ” which utilises DFT computations to address the inherent limitations of μ^+ SR experiments, outlined in chapter 3.7, and that is employed in chapters 6 and 7 below. This chapter is intended to give the reader an overview of the most essential aspects of DFT necessary to understand the rest of this thesis. For a more comprehensive introduction I can recommend Refs. [57, 58].

4.1 Theoretical foundation

4.1.1 The many-body Schrödinger equation

The time-independent Schrödinger equation for a non-relativistic system with Hamiltonian $\hat{H}$ reads in Dirac’s bra-ket notation:

$$\hat{H} |\Psi\rangle = \epsilon |\Psi\rangle, \quad (4.1)$$

where ϵ is the total energy of the system and $|\Psi\rangle$ is a function of all degrees of freedom pertaining to it. For the case of an ensemble of electrons and nuclei the Hamiltonian takes the form

$$\hat{H} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{i \neq j} \frac{e^2}{2|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I \neq J} \frac{Z_I Z_J e^2}{2|\mathbf{R}_I - \mathbf{R}_J|}, \quad (4.2)$$

where the lower (upper) case subscripts denote electrons (nuclei) with positions $\mathbf{r}_i$ ($\mathbf{R}_I$), charge e ($Z_I e$) and mass m_e (M_I). This expression for $\hat{H}$ can be simplified upon applying the Born-Oppenheimer approximation, which assures us that the kinetic energy term for the nuclei can be treated as negligibly small to first order

due to the large nuclei mass M_I suppressing it. In this approximation, which is an excellent one for most practical purposes, the electronic and nuclear degrees of freedom decouple, thereby resulting in a Schrödinger equation for the total electronic wave function in which the nuclear coordinates are fixed parameters:

$$\left[-\sum_i \frac{\nabla_i^2}{2} + V_{n-n} + \sum_i V_n(\mathbf{r}_i) + \sum_{i \neq j} \frac{1}{2|\mathbf{r}_i - \mathbf{r}_j|} - E \right] \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots) = 0, \quad (4.3)$$

where Hartree atomic units ($m = \hbar = 4\pi/\epsilon_0 = e = 1$) have been applied in addition to the following definitions for the nuclear potentials:

$$V_{n-n} = -\sum_{I \neq J} \frac{Z_I Z_J}{2|\mathbf{R}_I - \mathbf{R}_J|}, \quad V_n(\mathbf{r}) = -\sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|}. \quad (4.4)$$

It should be noted that the many-particle wave function Ψ in general also depends on the electron spins, which are omitted here for readability, and that it furthermore has to obey the usual exchange principle of swapping signs upon an odd permutation of its space and spin coordinates.

Equation (4.3) is the foundation of electronic structure theories and for suitably simple systems, such as He and H₂, it can be solved via variational methods [57, 58]. However, as the system size is increased the electron-electron interaction term leads to an exponentiation of the variational parameters required, thereby creating an “exponential wall” [55] and rendering variational methods infeasible for systems containing more than roughly 10 electrons. Larger system sizes only became solvable with the advent of an alternative approach based on DFT, which the rest of this chapter is devoted to.

4.1.2 Hohenberg-Kohn-Sham

The foundations for DFT were laid out in two seminal papers by Hohenberg, Kohn and Sham, which in a review in 2003 were found to be the most cited articles in the *Physical Review* family of journals [59] at the time. Although they have

both gathered about 20 to 25 thousand (!) citations at the time of writing this sentence, they have since lost the title of most cited papers to another one (with 44 thousand citations) [60] that opened up the possibility of practical implementation of the theories developed by Hohenberg, Kohn and Sham.

The first paper, by Hohenberg and Kohn [61], gives a disarmingly simple proof that in the Born-Oppenheimer approximation *any* property of an interacting many-body system can be expressed as a functional of the ground state density $n_0(\mathbf{r})$. The proof proceeds by assuming that there are two different densities which both lead to the same ground state energy, and establishing that these two assumptions contradict each other. The milestone corollary of Hohenberg and Kohn's theorem is that the Schrödinger equation can be solved through suitable functionals of the density only, which reduces the degrees of freedom involved from $3N$ for N electrons to just three. However, the Hohenberg-Kohn theorem only ascertains the existence of such functionals, but it does not provide any guidance on how to construct them.

The next important insight, by Kohn and Sham [62], was to replace the many-body problem with an *auxiliary* independent-particle problem. This ansatz assumes that there exists a non-interacting system which results in the same ground state density as that of the original interacting system. This assumption culminates in a set of independent-particle equations in which all difficult many-body interactions are incorporated into what is called the exchange-correlation functional $E_{xc}[n(\mathbf{r})]$. Although the existence of a suitable auxiliary system has been proven for the homogeneous electron gas and small deviations from it [62], no general proof exists. Nevertheless, numerical calculations based on this assumption have been remarkably successful even in inhomogeneous systems.

The governing equations of DFT are in Hartree atomic units ($m = \hbar = 4\pi/\epsilon_0 =$

$e = 1$) [57]:

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'^3 + V_{xc}(\mathbf{r}) - \epsilon_i\right)\psi_i = 0, \quad (4.5)$$

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}, \quad (4.6)$$

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2. \quad (4.7)$$

Here, V_{ext} represents the external potential (including the nuclear Coulomb potentials), E_{xc} incorporates all the complex many-body interactions, ψ_i are the auxiliary single-particle wave functions with energies ϵ_i , and $n(\mathbf{r})$ is the electron density. This set of equations has to be solved self-consistently and iteratively with an initial estimate for the density $n(\mathbf{r})$. The ground state energy is then evaluated via

$$E_0 = \sum_i \epsilon_i + E_{xc}[n_0(\mathbf{r})] - \int V_{xc} n_0(\mathbf{r}) d^3\mathbf{r} - \frac{1}{2} \int \frac{n_0(\mathbf{r}) n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}'. \quad (4.8)$$

4.1.3 Exchange-correlation

In spite of the stroke of genius by Kohn and Sham to group all the exchange-correlation interactions that make the many-body Schrödinger equation intractable into a single functional $E_{xc}[n]$, no exact expressions are known for $E_{xc}[n]$. However, a number of approximate forms exist that have successfully yielded results in agreement with experimental measurements. These functionals typically either employ the local density approximation (LDA), where the functional is calculated assuming an exchange-correlation energy equal to that of the homogeneous electron gas, or the generalised gradient approximation (GGA), which improves the LDA by including local variations of the density:

$$E_{xc}^{\text{GGA}}[n] = \int d^3\mathbf{r} n(\mathbf{r}) \epsilon_{xc}^{\text{GGA}}(n, \nabla n). \quad (4.9)$$

There are a variety of available approximations for $\epsilon_{xc}^{\text{GGA}}(n, \nabla n)$. One of the most popular and widely used ones is due to Perdew, Burke and Ernzerhof [60], which is also the one employed in all DFT calculations performed as part of this thesis.

4.1.4 Capabilities and limitations

Modern implementations of numerical algorithms that solve the Kohn-Sham equations (4.5)–(4.7), while capable of calculating small systems on personal computers, are typically designed for use on large parallelised computer clusters. Depending on the crystal symmetries, the types of electron orbitals modelled and other complexities, the largest systems that are currently solvable contain multiple hundreds of atoms per unit cell.

Despite the great successes of DFT in *ab initio* modelling of condensed matter systems, it fundamentally is only an approximate theory for the electronic ground state properties and as such has limitations. Properties DFT is known to reliably predict with good accuracy comprise equilibrium crystal structures, vibrational properties and phonon spectra, electrostatic and ionisation potentials, binding energies of molecules and solids, as well as band structures for systems with no or small band gaps. In contrast, DFT struggles to produce accurate predictions for band gaps in semiconductors and insulators (in fact it consistently underestimates them), systems with atoms containing *d* or *f* electronic orbitals (due to the more complex nature of the associated spherical harmonics), and sparse matter such as proteins. Furthermore, metallic systems can pose difficulties because of the discontinuous change of orbital occupancies across the Brillouin zone.

Notwithstanding its limitations, DFT based on the Kohn-Sham equations is often utilised as an initial starting point for more complex and specialised theories. By now a wide range of techniques have been developed that improve and extend the capabilities of materials modelling in the DFT framework e.g. dynamical mean-field theory [63] for investigating Mott-Hubbard insulators.

4.2 Practical computation

4.2.1 General considerations

As mentioned before, implementations of DFT typically comprise numerical algorithms for solving the Kohn-Sham equations (4.5)–(4.7) self-consistently that are optimised for parallelised computer clusters. Approaches common to DFT codes are that the electronic wave functions and density are expanded in a truncated Fourier series of plane waves and any integration over the Brillouin zone is performed on a discrete set of $\mathbf{k}$ states in the smallest fraction of the Brillouin zone needed to reconstruct it (the irreducible Brillouin zone). In the DFT simulations presented in this work the method of Monkhorst and Pack [64] is employed to determine k -space grids for efficient integration. Suitable values for the energy cut-offs in the Fourier series and the density of the k -space grid in general have to be determined in a convergence test, for example by investigating the agreement between calculated and experimentally observed crystal or band structures. In addition, DFT implementations assume periodic boundary conditions and for systems with a charged unit cell a jellium background is added to neutralise the charge as otherwise the energy of the system would diverge.

4.2.2 Crystal structures

In chapter 3 I have already expanded upon the two primary limitations of the μ^+ SR technique, which are a lack of knowledge about where the muons implant in the unit cell and how they perturb their local environment. Fortunately, it is possible within DFT to perform structural optimisations of the atomic coordinates and the unit cell dimensions, making it an ideal tool for quantitatively simulating the effect of muons implanting into a sample. The structural optimisations employ the Hellmann-Feynman force [65, 66] and stress [67] theorems, which enable the computation of the atomic forces from the ground state electron density. Since

cut-offs in the plane wave expansions and thus reduces the computational time required greatly. Figure 4.2 demonstrates this for the radial wave functions of the valence electron shells in a Ti nucleus.

Generating pseudopotentials is an art of itself. While they can greatly reduce computational requirements, this comes at the expense of knowledge about the nuclear core regions and transferability. Generally a delicate balance has to be struck when choosing the pseudisation (or core) radius between computational time gains (which would favour a larger radius) and accuracy (which improves for a smaller radius). Furthermore, careful testing of the pseudopotentials is generally required to ensure that they do not produce spurious electron states (known as “ghosts”) and that they lead to a reasonable agreement of the energies of different electron configurations with those obtained from an all-electron calculation.

In addition, pseudopotentials come in two flavours called norm-conserving [68] and ultrasoft [69]. For norm-conserving ones the total charge density inside the core regions exactly matches the all-electron one, and the charge density cut-off in the plane wave expansion is exactly four times the wave function cut-off. On the other hand, ultrasoft pseudopotentials require an augmented charge density inside the core region and a ratio significantly larger than four (typically about 10) for the charge density and wave function cut-offs. While norm-conserving pseudopotentials are more readily available and more reliable and robust, ultrasoft pseudopotentials can reduce the required computational resources greatly.

4.3 Application in “DFT+ μ ”

In recent years DFT was realised to be a powerful tool to investigate the effect of implanting muons into a sample and try to remove the two main limitations of μ^+ SR as mentioned in section 3. A good review of some successful applications of DFT to muon site calculations can be found in Ref. [70]. The general procedure to determine the muon stopping sites and evaluate the distortion of the ionic structure

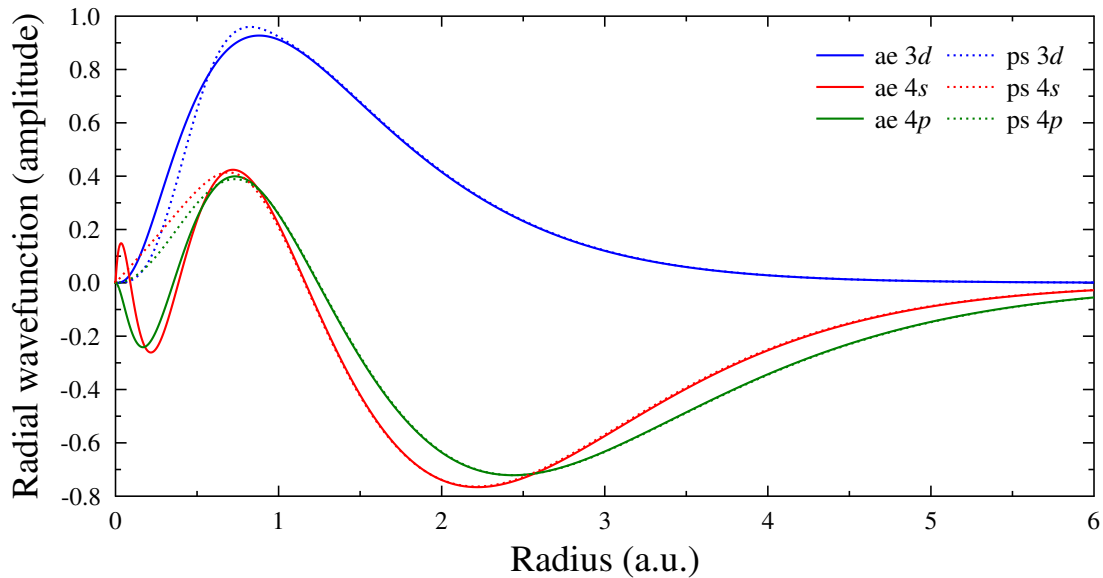


Figure 4.2: Radial wave functions for the outer orbitals in a Ti atom as calculated by DFT. Solid and dotted lines represent the results from all-electron and pseudopotential computations, respectively. The pseudisation radii were chosen to be 1.3 a.u. for the 3d and 2.9 a.u. for the 4s and 4p states. Note that the full electron wave functions are obtained by combining the radial wave functions plotted here with the typical spherical harmonics.

due to the presence of the muon typically involves the following steps.

1. Select a suitable exchange-correlation functional and set of pseudopotentials for the compound of interest.
2. Conduct a test to determine the energy cut-offs for the wave functions and density and the number of k -grid points required for convergence.
3. Verifying that the ionic structure, lattice parameter and band gap (if applicable) of the undisturbed bulk (without muon) obtained by DFT is in sufficient agreement with existing experimental measurements.
4. Introduce a single muon, modelled via a hydrogen pseudopotential, into a supercell containing as many conventional unit cells as computational time allows (to reduce effects due to the periodicity). The initial muon positions should be chosen on a regular grid of low-symmetry points.
5. For each initial muon position perform a structural relaxation calculation in which all ions (including the muon) are allowed to move until the forces are

below a convergence threshold.

6. From the relaxed structures determine the potential muon site candidates and their relative energies, and extract the distorted ionic structures in each case.

This generic procedure can be supplemented with further calculations –if not too computationally demanding– to characterise the system’s behaviour in more detail. Examples include the computations of charge- and spin-density, hyperfine couplings, vibrational modes and crystal fields. Furthermore, there is currently an active interest in developing an automated routine to evaluate the shape of the muon wave function around the stopping sites and the probability for the muon to tunnel between them.

4.4 Summary of computational details

In parts of this thesis the implantation sites of a muon and the subsequent perturbation of its local environment are calculated within the DFT framework. The reported DFT simulations employ both pseudopotential (chapter 6) and all-electron (chapter 7) codes. The DFT simulations I performed myself, presented in chapter 6, utilised the pseudopotential based QUANTUM ESPRESSO [71] plane-wave software suit. Furthermore, I employed the GGA functional due to Perdew, Burke and Ernzerhof [60] and the muon was modelled with a norm-conserving hydrogen potential, since the plane wave cut-offs are dominated by the larger atoms in the systems I considered.

Chapter 5

Demagnetisation

In this chapter I investigate the effect of demagnetising fields on high transverse field μ^+ SR experiments. I focus in detail on cylindrically shaped objects, such as samples grown in mirror furnaces, but I also consider more general polyhedral shapes. Much of this work has been previously published in two papers, one in the Journal of Magnetism and Magnetic Materials [72], and one in the conference proceedings of the 2014 International Muon Conference (μ SR2014) [73].

First I introduce a recently developed Fourier space approach that elegantly describes the demagnetising tensor for uniformly magnetised objects of arbitrary shape. Subsequently, I employ this formalism to comprehensively derive the analytical solution for the demagnetisation tensor of a cylinder of finite size and uniform magnetisation. For this I use a previously published solution as guidance, which I show via simple arguments has to necessarily be incomplete. Furthermore, I expand my solution to objects of general cylindrical symmetry and derive an expression for the corresponding demagnetisation tensor that involves a single remaining integral over a finite domain, thereby enabling the use of conventional numerical tools for efficient calculations. Afterwards, I quantitatively investigate the effects of demagnetising fields in a cylindrical sample and how they change as a function of the cylinder dimensions. I describe the potential signatures of demagnetising effects in μ^+ SR measurements, as well as possible ways of reducing

their impact. Finally, I show how the Fourier space approach can be used in practice for more complex shapes by giving two explicit examples of previous μ^+ SR samples, polyhedral in shape, for which I computed the demagnetising fields using a superposition of simpler shapes.

All of the work presented in this chapter has been carried out by myself, with guiding inputs by my supervisor S. Blundell. The EuS and $\text{Sr}_3\text{Ru}_2\text{O}_7$ samples presented were kindly grown for us by D. Prabhakaran.

5.1 Introduction

As already elucidated in chapter 2.3 demagnetisation effects can be of great importance in magnetism both because the demagnetising field is associated with an important energy contribution and also because the stray field from a magnetic material has the potential to affect its surroundings. While the development of new high transverse field muon spectrometers such as Hifi, HiTime, GPD or HAL-9500 has opened up new possibilities for experimental investigations of samples with exotic magnetic phases, the applied high magnetic fields involved may magnetise the sample and subsequently induce a demagnetising field. Since muons are very sensitive local magnetic probes it is therefore of paramount importance to understand to what extent the measured variations in the internal magnetic field distribution might be caused by variations of the demagnetising field rather than by intrinsic effects.

However, demagnetising fields inside magnetised objects are difficult to calculate unless the sample is ellipsoidal in shape, since only then the demagnetising field is uniform [74]. This simple scenario includes the sphere, the flat plate, and the infinitely long cylinder as subsets. In other geometries an analytical solution is not so forthcoming. Though a rather unwieldy method for analytical solutions was outlined some time ago [75], a recently developed Fourier space approach [76] has extended the range of analytically solvable geometries in a much more gen-

eral and elegant fashion (for examples see Ref. [77–82]). This ingenious approach has been used to calculate the demagnetisation tensor of a uniformly magnetised cylinder [83], but I found the published solution to contain vital errors and room for a significant extension.

The following sections first present a comprehensive rederivation and extension of the demagnetisation tensor for a cylinder that closely follows the original argument while accounting for the necessary corrections. The result is then applied to μ^+ SR measurements of cylindrical objects, such as one grown using a mirror furnace, and I demonstrate that the demagnetising field leads to a subsequent broadening of the field distribution, as experienced by the muons implanted in the sample. The characteristic shape includes a low field tail and a sharp high-field cut-off. By studying this field broadening as a function of the aspect ratio of the cylinder I find that it is significant and largest for aspect ratios corresponding to typical samples sizes. I identify viable strategies to minimise this broadening, which include adding a degrader so that muons implant closer to the surface of the sample, and using a circular mask or decreasing the muon beam spot to stop muons from implanting near the radial edge. Finally, I give explicit examples of demagnetising field calculations for actual μ^+ SR samples of more complex shapes.

5.2 Fourier transform method

Assuming a uniform magnetisation of an arbitrarily shaped object, Beleggia and De Graef [76] showed that the position dependent demagnetisation tensor $N_{ij}(\mathbf{r})$ of the object can be elegantly expressed as an inverse Fourier transform of an expression involving the Fourier transform of a single function $D(\mathbf{r})$. This is called the shape function and it encodes the shape of the object, taking the value 1 if $\mathbf{r}$ is inside the object and 0 if $\mathbf{r}$ is outside. The demagnetisation tensor is then given by

$$N_{ij}(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d^3\mathbf{k} \frac{D(\mathbf{k})}{k^2} k_i k_j e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (5.1)$$

where $D(\mathbf{k})$ is the Fourier transform of $D(\mathbf{r})$. Note that equation (5.1) implies that the demagnetisation tensor is symmetric ($N_{ij} = N_{ji}$). Additionally, it can be shown that the trace of the tensor has to satisfy

$$\text{Tr}[N_{ij}(\mathbf{r})] = D(\mathbf{r}), \quad (5.2)$$

which presents a straightforward method for verifying the correct computation of the tensor.

A very important observation that follows immediately from equation (5.1) is that the demagnetising tensor for an object of any shape can be described as a combination of tensors for simpler shapes. This is because any shape function $D(\mathbf{r})$ can be decomposed into simpler shape functions, e.g. $D(\mathbf{r}) = D^\alpha(\mathbf{r}) + D^\beta(\mathbf{r})$. Because the Fourier transform is linear, i.e. $\text{FT}(D^\alpha + D^\beta) = \text{FT}(D^\alpha) + \text{FT}(D^\beta)$, it follows that $N_{ij} = N_{ij}^\alpha + N_{ij}^\beta$. An example of this is shown for the case of a cylindrical object in equation (5.5) and the associated Figure 5.1, and in section 5.4.2 I apply this method to polyhedral samples.

5.3 Theoretical derivation for cylindrical samples

Samples grown in mirror furnaces are roughly cylindrical rods and experiments are typically performed on cylindrical discs cut from them. Therefore, this sample shape is of importance and in this section I derive the demagnetising tensor for this geometry using equation (5.1) as a starting point and Ref. [83] as guidance.

I will present a set of integrals and their solutions with comparisons to known standard integrals whenever necessary, which are reproduced in appendix A for completeness.

Furthermore, I employ the following conversion between Cartesian and cylin-

drical coordinates for coordinates in real space ($\mathbf{r}$) and reciprocal space ($\mathbf{k}$).

$$\begin{aligned}\mathbf{r} &= (x, y, z) = (r \cos \theta, r \sin \theta, z), & d^3\mathbf{r} &= r dr d\theta dz \\ \mathbf{k} &= (k_x, k_y, k_z) = (k_\perp \cos \phi, k_\perp \sin \phi, k_z), & d^3\mathbf{k} &= k_\perp dk_\perp d\phi dk_z\end{aligned}\quad (5.3)$$

5.3.1 Shape amplitude in cylindrical symmetry

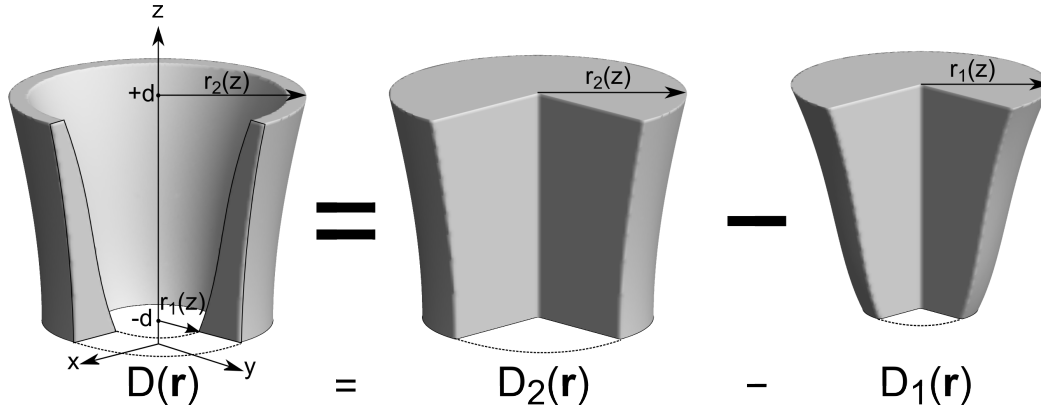


Figure 5.1: Schematic of a cylindrically symmetric object and the decomposition into simpler shape functions.

An object of general cylindrical symmetry is shown in Figure 5.1. Defining the multidimensional Heaviside Theta function

$$H_\theta(x_1, x_2, \dots) = \begin{cases} 0, & \text{if any of the } x_i < 0, \\ 1, & \text{otherwise} \end{cases}, \quad (5.4)$$

the shape amplitude $D(\mathbf{k})$ of the object can be evaluated as follows

$$\begin{aligned}D(\mathbf{k}) &= \int d^3\mathbf{r} H_\theta(r - r_1(z), r_2(z) - r, d - |z|) e^{-i\mathbf{k} \cdot \mathbf{r}} \\ &= \int_{-d}^d dz e^{-izk_z} \int_{r_1(z)}^{r_2(z)} dr r \int_0^{2\pi} d\theta e^{-ir k_\perp \cos(\theta - \phi)} = \int_{-d}^d dz e^{-izk_z} \int_{r_1(z)}^{r_2(z)} dr r 2\pi J_0(r k_\perp) \\ &= \int_{-d}^d dz e^{-izk_z} \frac{2\pi}{k_\perp} [f_2(k_\perp, z) - f_1(k_\perp, z)],\end{aligned}\quad (5.5)$$

where $f_i(k_\perp, z) = r_i(z) J_1(r_i(z) k_\perp)$. The functions J_i are the Bessel functions of the first kind and I made use of the definition of J_0 and equation (5.52.1) in Ref. [84]. Note that because $r \geq 0$ and $k_\perp \geq 0$ the magnitude signs in the Bessel functions'

arguments can be removed. For a finite cylinder applying $r_1 \rightarrow 0$ and $r_2 \rightarrow R$ yields

$$D(\mathbf{k}) \rightarrow \frac{4\pi R \sin(dk_z) J_1(Rk_\perp)}{k_\perp k_z}, \quad (5.6)$$

in agreement with equation (57) in Ref. [83]. However, it turns out to be easier to work with equation (5.5) to compute the inverse Fourier transforms contained in the expression for $N_{ij}(\mathbf{r})$.

The functional form of equation (5.5) shows that the object of general cylindrical symmetry can equivalently be described using the shape functions of two simply connected (no holes) cylindrical objects. This is depicted in Figure 5.1 and represents an example of decomposing the shape function of an object into a combination of simpler shape functions and thereby “build” the object of interest. In this case, the two emerging terms in equation (5.5) are functionally identical and therefore in the following discussion I restrict myself to one term of this form, where I will denote the function $f_i(k_\perp, z)$ simply by $f(k_\perp, z) \equiv R(z)J_1(R(z)k_\perp)$.

5.3.2 Demagnetisation tensor

Combining equations (5.1) and (5.5) yields

$$N_{ij}(\mathbf{r}') = \frac{1}{4\pi^2} \int_{-d}^d dz \int_0^\infty dk_\perp f(k_\perp, z) \int_0^{2\pi} d\phi e^{ik_\perp r' \cos(\phi - \theta')} \int_{-\infty}^\infty dk_z \frac{k_i k_j}{k_\perp^2 + k_z^2} e^{ik_z(z' - z)}. \quad (5.7)$$

Inserting the Cartesian components for k_i and k_j the six unique Cartesian tensor elements become

$$\begin{pmatrix} N_{xx} \\ N_{yy} \\ N_{zz} \\ N_{xy} \\ N_{xz} \\ N_{yz} \end{pmatrix} = \frac{1}{4\pi^2} \int_{-d}^d dz \int_0^\infty dk_\perp f(k_\perp, z) \int_0^{2\pi} d\phi e^{ik_\perp r' \cos(\phi - \theta')} \int_{-\infty}^\infty dk_z \frac{e^{ik_z(z' - z)}}{k_\perp^2 + k_z^2} \begin{pmatrix} \cos^2 \phi \\ \sin^2 \phi \\ 1 \\ \cos \phi \sin \phi \\ \cos \phi \\ \sin \phi \end{pmatrix} \begin{pmatrix} k_\perp^2 \\ k_\perp^2 \\ k_z^2 \\ k_\perp^2 \\ k_\perp k_z \\ k_\perp k_z \end{pmatrix}. \quad (5.8)$$

I now consider the integrals over ϕ and k_z in turn.

5.3.3 Integrals over ϕ

The integrals over ϕ can be solved by employing trigonometric addition formulae and using the standard integral with equation number (3.915.2) in Ref. [84]. In addition, I utilise the fact that we are free to choose the limits of the integral range, as long as the lower and upper integral limits differ by 2π . Without loss of generality I can thus define the limits to be ψ and $\psi + 2\pi$, where I choose the constant ψ to have the value $\psi = \theta' - \pi$ in order to symmetrise the limits of the final integrals. Defining the variable $\varphi = \phi - \theta'$ the integrals can all be solved by the same procedure as follows

$$xy : \int_{\psi}^{\psi+2\pi} d\phi e^{ik_{\perp} r' \cos(\phi-\theta')} \frac{\sin 2\phi}{2} = \int_{-\pi}^{\pi} d\varphi e^{ik_{\perp} r' \cos \varphi} \frac{\sin 2(\varphi + \theta')}{2} = -\pi \sin 2\theta' J_2(k_{\perp} r') \quad (5.9)$$

$$xx : \frac{1}{2} \int_{-\pi}^{\pi} d\varphi e^{ik_{\perp} r' \cos \varphi} (1 + \cos(2\varphi + 2\theta')) = \pi (J_0(r' k_{\perp}) - \cos 2\theta' J_2(r' k_{\perp})) \quad (5.10)$$

$$yy : \frac{1}{2} \int_{-\pi}^{\pi} d\varphi e^{ik_{\perp} r' \cos \varphi} (1 - \cos(2\varphi + 2\theta')) = \pi (J_0(r' k_{\perp}) + \cos 2\theta' J_2(r' k_{\perp})) \quad (5.11)$$

$$zz : \int_{-\pi}^{\pi} d\varphi e^{ik_{\perp} r' \cos \varphi} = 2\pi J_0(r' k_{\perp}) \quad (5.12)$$

$$xz : \int_{-\pi}^{\pi} d\varphi e^{ik_{\perp} r' \cos \varphi} \cos(\varphi + \theta') = i2\pi \cos \theta' J_1(r' k_{\perp}) \quad (5.13)$$

$$yz : \int_{-\pi}^{\pi} d\varphi e^{ik_{\perp} r' \cos \varphi} \sin(\varphi + \theta') = i2\pi \sin \theta' J_1(r' k_{\perp}). \quad (5.14)$$

This leads to equation (5.8) becoming:

$$\begin{pmatrix} N_{xx} \\ N_{yy} \\ N_{zz} \\ N_{xy} \\ N_{xz} \\ N_{yz} \end{pmatrix} = \frac{1}{4\pi} \int_{-d}^d dz \int_0^{\infty} dk_{\perp} f(k_{\perp}, z) \begin{pmatrix} k_{\perp}^2 (J_0(r' k_{\perp}) - \cos 2\theta' J_2(r' k_{\perp})) \\ k_{\perp}^2 (J_0(r' k_{\perp}) + \cos 2\theta' J_2(r' k_{\perp})) \\ 2J_0(k_{\perp} r') \\ -k_{\perp}^2 \sin 2\theta' J_2(r' k_{\perp}) \\ i2k_{\perp} \cos \theta' J_1(r' k_{\perp}) \\ i2k_{\perp} \sin \theta' J_1(r' k_{\perp}) \end{pmatrix} \int_{-\infty}^{\infty} dk_z \frac{e^{ik_z(z'-z)}}{k_{\perp}^2 + k_z^2} \begin{pmatrix} 1 \\ 1 \\ k_z^2 \\ 1 \\ k_z \\ k_z \end{pmatrix}. \quad (5.15)$$

It should be noted that in all the above formulae $|r'k_{\perp}| = r'k_{\perp}$ holds since $k_{\perp} \geq 0$ and $r' \geq 0$.

5.3.4 Integrals over k_z

For the k_z integrals the authors of Ref. [83] report the use of the standard integrals in equations (3.723.2), (3.723.3) and (3.738.2) in Ref. [84] to arrive at their solution. Unfortunately, the convergence criteria of these standard integrals, as given in Ref. [84], are not always fulfilled in this problem. It turns out that for the integrals containing 1 and k_z in the numerator it does not make a difference, whereas for the integral containing k_z^2 an extra term appears, i.e. the authors of Ref. [83] used (3.738.2) in the case $m = 2n + 1$ (with $n = 1$, $m = 3$) which is outside the domain of applicability of this standard integral. I will now solve these integrals, while taking particular care with their convergence.

The first integral with $k_{\perp}^0 = 1$ in the numerator is readily solved by using the standard integral (3.723.2) in Ref. [84], in the case that $\text{Re}(k_{\perp}) > 0$ and $(z' - z) \geq 0$. The latter restriction can be resolved by writing $(z' - z) = -|z' - z|$ for the case that $(z' - z) < 0$. For $k_{\perp} > 0$ the integral evaluates to

$$k_z^0 : G_0 \equiv \int_{-\infty}^{\infty} dk_z \frac{e^{ik_z(z'-z)}}{k_{\perp}^2 + k_z^2} = \frac{\pi}{k_{\perp}} e^{-|z'-z|k_{\perp}} = \frac{\pi}{k_{\perp}} \begin{cases} e^{-(z'-z)k_{\perp}}, & z' - z \geq 0 \\ e^{+(z'-z)k_{\perp}}, & z' - z < 0 \end{cases}. \quad (5.16)$$

However, the restriction of $k_{\perp} > 0$ requires attention now, because in the limit of $k_{\perp} \rightarrow 0$, which is covered by the range of the integral over $k_{\perp}$ as shown in equation (5.15), this result clearly diverges. To resolve this we have to go back to equation (5.15) and include all the functions that contain factors of $k_{\perp}$. The expansions of the Bessel functions for small arguments are:

$$\lim_{x \rightarrow 0} J_{\nu}(x) = c_{\nu} x^{\nu} + \dots, \quad (5.17)$$

from equation (9.1.10) in Ref. [85], where c_{ν} are simple constants. Thus, the limit

for the terms including $k_\perp$ is

$$\lim_{k_\perp \rightarrow 0} \frac{e^{ik_z(z'-z)}}{k_\perp^2 + k_z^2} J_1(Rk_\perp) k_\perp^2 (c_{ij} J_0(r'k_\perp) + d_{ij} J_2(r'k_\perp)) = \lim_{k_\perp \rightarrow 0} \frac{e^{ik_z(z'-z)}}{k_\perp^2 + k_z^2} (Ck_\perp^3 + O(k_\perp^5)) = 0, \quad (5.18)$$

where c_{ij} , d_{ij} and C are constants. Therefore, I conclude that in this case we can safely use the integral (5.16), as the case of $k_\perp = 0$ is assured to give no contribution.

The next integral with k_z in the numerator can be solved in two ways. The first, and slightly longer route, is to use the standard integral in Ref. [84] with number (3.723.3) and combine it with standard integral (3.721.1) for the special case $k_\perp = 0$. A second approach is to apply Leibniz's Theorem for the differentiation of an integral, $\frac{d}{dc} \int_{a(c)}^{b(c)} f(x, c) dx = \int_{a(c)}^{b(c)} \frac{\partial}{\partial c} f(x, c) dx + f(b, c) \frac{db}{dc} - f(a, c) \frac{da}{dc}$, e.g. from equation (3.3.7) in Ref. [85], to differentiate the earlier integral (5.16) with respect to $(z' - z)$ as follows

$$k_z^1 : G_1 \equiv \int_{-\infty}^{\infty} dk_z \frac{k_z e^{ik_z(z'-z)}}{k_\perp^2 + k_z^2} = \frac{dG_0}{id(z' - z)} = i\pi (e^{-(z'-z)k_\perp} H_\theta(z' - z) - e^{(z'-z)k_\perp} H_\theta(z - z')), \quad (5.19)$$

Note that the result vanishes for $z' - z = 0$, which is easily verified due to the odd symmetry of the integral in that case.

The final integral with k_z^2 in the numerator is obtained by differentiating equation (5.19) again.

$$\begin{aligned} k_z^2 : G_2 &\equiv \int_{-\infty}^{\infty} dk_z \frac{k_z^2 e^{ik_z(z'-z)}}{k_\perp^2 + k_z^2} = \frac{dG_1}{id(z' - z)} \\ &= \pi [e^{-(z'-z)k_\perp} (-k_\perp H_\theta(z' - z) + \frac{dH_\theta(z'-z)}{d(z'-z)}) - e^{(z'-z)k_\perp} (k_\perp H_\theta(z - z') - \frac{dH_\theta(z-z')}{d(z-z')})] \\ &= -\pi k_\perp (e^{-(z'-z)k_\perp} H_\theta(z' - z) + e^{(z'-z)k_\perp} H_\theta(z - z')) + 2\pi \delta(z' - z) e^{-|z'-z|k_\perp}. \end{aligned} \quad (5.20)$$

In the last step I used $dH_\theta(x)/dx = \delta(x)$, see for example chapter 5 in Ref. [86]. The crucial difference between the results above and those reported in Ref. [83] is the extra delta-function term that appears in equation (5.20), which is essential in

satisfying the condition on the trace (see equation (5.2) above) of the demagnetisation tensor. With these integrals the expression for N_{ij} becomes

$$\begin{pmatrix} N_{xx} \\ N_{yy} \\ N_{zz} \\ N_{xy} \\ N_{xz} \\ N_{yz} \end{pmatrix} = \frac{1}{4} \int_{-d}^d dz \int_0^\infty dk_\perp f(k_\perp, z) k_\perp e^{-|z'-z|k_\perp} \begin{pmatrix} J_0(r'k_\perp) - \cos 2\theta' J_2(r'k_\perp) \\ J_0(r'k_\perp) + \cos 2\theta' J_2(r'k_\perp) \\ -2J_0(r'k_\perp)(1 - 2\delta(z' - z)/k_\perp) \\ -\sin 2\theta' J_2(r'k_\perp) \\ -2\cos \theta' J_1(r'k_\perp) \text{sgn}(z' - z) \\ -2\sin \theta' J_1(r'k_\perp) \text{sgn}(z' - z) \end{pmatrix} \quad (5.21)$$

$$= \int_0^\infty dk_\perp \int_{-d}^d dz f(k_\perp, z) e^{-|z'-z|k_\perp} [k_\perp \bar{S}_{ij}(k_\perp, r', \theta') \xi_{ij}^{\text{sgn}(z-z')} + \delta_{i3}\delta_{j3} J_0(r'k_\perp) \delta(z' - z)]. \quad (5.22)$$

(Note the Einstein summation convention is *not* employed.) The following symbols have been defined

$$\bar{S}_{ij}(k_\perp, r', \theta') \equiv \sum_{\mu=0}^2 \bar{\alpha}_{ij}^\mu(\theta') J_\mu(r'k'_\perp), \quad (5.23)$$

$$\begin{aligned} \bar{\alpha}_{ij}^0(\theta') &\equiv \frac{1}{4} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, & \bar{\alpha}_{ij}^1(\theta') &\equiv \frac{1}{2} \begin{pmatrix} 0 & 0 & \cos \theta' \\ 0 & 0 & \sin \theta' \\ \cos \theta' & \sin \theta' & 0 \end{pmatrix}, \\ \xi_{ij}^\pm &\equiv \begin{pmatrix} 1 & -1 & \pm 1 \\ -1 & 1 & \pm 1 \\ \pm 1 & \pm 1 & -1 \end{pmatrix}, & \bar{\alpha}_{ij}^2(\theta') &\equiv \frac{1}{4} \begin{pmatrix} -\cos 2\theta' & \sin 2\theta' & 0 \\ \sin 2\theta' & \cos 2\theta' & 0 \\ 0 & 0 & 0 \end{pmatrix}. \end{aligned} \quad (5.24)$$

5.3.5 Trace condition

Substituting the expression for $f(k_\perp, z) = R(z)J_1(R(z)k_\perp)$ into equation (5.22) enables the evaluation of the two remaining integrals over z and $k_\perp$. However, it is first instructive to show that equation (5.22) satisfies the trace condition (5.2). Applying $\text{Tr}[a\mathbf{M} + b\mathbf{N}] = a\text{Tr}[\mathbf{M}] + b\text{Tr}[\mathbf{N}]$ for scalars a, b and matrices $\mathbf{M}, \mathbf{N}$ yields

$$\begin{aligned} \text{Tr}[N_{ij}(\mathbf{r}')] &= \sum_{\mu=0}^2 g^{\mu}(r', z') \text{Tr}[\bar{\alpha}_{ij}^{\mu}(\theta') \xi_{ij}^{\text{sgn}(z-z')}] \\ &+ \int_{-d}^d dz \delta(z' - z) \int_0^{\infty} dk_{\perp} R(z) J_1(R(z)k_{\perp}) J_0(k_{\perp}r') \end{aligned} \quad (5.25)$$

$$= H_{\theta}(R(z) - r', d - |z'|) = D(\mathbf{r}'). \quad (5.26)$$

The scalar functions $g^{\mu}(r', z')$ represent the integrals involving the $\bar{S}_{ij}$ term in equation (5.22). The first term of equation (5.25) is trivially zero by the structure of the matrices defined in equation (5.24), whereas for the second term the standard integral (6.512.3⁸) from Ref. [84] has been utilised.

5.3.6 Finite cylinder case - remaining integrals

The integral over $k_{\perp}$ in equation (5.22) can be solved in full generality, as done in section 5.3.12 below. However, for the case of a finite cylinder, for which $R(z) = R$, it turns out to be easier to first integrate over z . Substituting $f(k_{\perp}) = RJ_1(Rk_{\perp})$ into equation (5.22) and using the result from combining equations (5.25) and (5.26) leads to

$$\bar{N}_{ij}(\mathbf{r}') = N_{ij}(\mathbf{r}') - \delta_{i3}\delta_{j3}D(\mathbf{r}') = \int_0^{\infty} dk_{\perp} \int_{-d}^d dz Rk_{\perp} J_1(Rk_{\perp}) \bar{S}_{ij}(k_{\perp}, r', \theta') \xi_{ij}^{\text{sgn}(z-z')} e^{-|z'-z|k_{\perp}}. \quad (5.27)$$

The remaining z -integral can now be evaluated in the different regions:

$$z' < -d : \int_{-d}^d dz \xi_{ij}^{+} e^{(z'-z)k_{\perp}} = 2\xi_{ij}^{+} e^{z'k_{\perp}} \frac{\sinh(dk_{\perp})}{k_{\perp}}, \quad (5.28)$$

$$z' > d : \int_{-d}^d dz \xi_{ij}^{-} e^{-(z'-z)k_{\perp}} = 2\xi_{ij}^{-} e^{-z'k_{\perp}} \frac{\sinh(dk_{\perp})}{k_{\perp}}, \quad (5.29)$$

$$\begin{aligned} -d < z' < d : & \int_{-d}^{z'} dz \xi_{ij}^{-} e^{-(z'-z)k_{\perp}} + \int_{z'}^d dz \xi_{ij}^{+} e^{(z'-z)k_{\perp}} \\ &= \frac{\xi_{ij}^{-}}{k_{\perp}} (1 - e^{-(d+z')k_{\perp}}) + \frac{\xi_{ij}^{+}}{k_{\perp}} (1 - e^{-(d-z')k_{\perp}}). \end{aligned} \quad (5.30)$$

Therefore, I find that

$$\bar{N}_{ij} = \sum_{\mu=0}^2 \bar{\alpha}_{ij}^{\mu}(\theta') \int_0^{\infty} dK J_1(K) J_{\mu}(\rho K) \begin{cases} \xi_{ij}^{-}[e^{-(\zeta-\tau)K} - e^{-(\zeta+\tau)K}], & \zeta > \tau \\ \xi_{ij}^{-}(1 - e^{-(\tau+\zeta)K}) + \xi_{ij}^{+}(1 - e^{-(\tau-\zeta)K}), & |\zeta| < \tau \\ \xi_{ij}^{+}[e^{(\zeta+\tau)K} - e^{(\zeta-\tau)K}], & \zeta < -\tau \end{cases} \quad (5.31)$$

where I introduced a new set of coordinates scaled by the radius R of the cylinder:

$$\rho \equiv \frac{r'}{R}, \quad \zeta \equiv \frac{z'}{R}, \quad K \equiv Rk_{\perp}, \quad \rho K = r'k_{\perp}, \quad \tau = \frac{d}{R} = \text{aspect ratio of cylinder.} \quad (5.32)$$

The remaining integrals (which are of Lipschitz-Hankel type) can be written as

$$I_{\mu}(\rho, \alpha) \equiv \int_0^{\infty} dK J_1(K) J_{\mu}(K\rho) e^{-\alpha K}. \quad (5.33)$$

Defining the quantities α_{-} and α_{+} by (recall that $\tau = d/R > 0$)

$$\alpha_{-} \equiv |\zeta - \tau| = \begin{cases} \zeta - \tau, & \zeta > \tau \\ \tau - \zeta, & \zeta < \tau \end{cases}, \quad \alpha_{+} \equiv |\zeta + \tau| = \begin{cases} \zeta + \tau, & \zeta > -\tau \\ -(\zeta + \tau), & \zeta < -\tau \end{cases}, \quad (5.34)$$

enables one to rewrite the demagnetisation tensor in the following way:

$$\bar{N}_{ij} = \sum_{\mu=0}^2 \bar{\alpha}_{ij}^{\mu}(\theta') \begin{cases} \xi_{ij}^{-}(I_{\mu}(\rho, \alpha_{-}) - I_{\mu}(\rho, \alpha_{+})), & \zeta > \tau \\ \xi_{ij}^{-}(I_{\mu}(\rho, 0) - I_{\mu}(\rho, \alpha_{+})) + \xi_{ij}^{+}(I_{\mu}(\rho, 0) - I_{\mu}(\rho, \alpha_{-})), & |\zeta| < \tau \\ \xi_{ij}^{+}(I_{\mu}(\rho, \alpha_{+}) - I_{\mu}(\rho, \alpha_{-})), & \zeta < -\tau \end{cases} \quad (5.35)$$

Note again that I am *not* employing the Einstein summation convention here.

5.3.7 Solutions to Lipschitz-Hankel Integrals I_{μ}

The integrals in equation (5.33) have known analytical solutions, which can be either taken from Ref. [87] or [88] (see section (2.12.38.1) in Ref. [88]). It should

be noted that because we are interested in the case of $\mu = \{0, 1, 2\}$, we are in the regime where the integrals always converge except at the boundary points where $\rho = 1$ and $\alpha_{\pm} = 0$ (see the introduction section in Ref. [87]), which correspond to the rims of the flat cylinder surfaces.

Let me first introduce the notation used in Ref. [87] for the integrals at hand.

$$I(\mu, \nu; \lambda) = \int_0^{\infty} J_{\mu}(at) J_{\nu}(bt) e^{-ct} t^{\lambda} dt \quad (5.36)$$

5.3.8 Integral I_0

For this integral we identify $a = 1$, $b = \rho$, $c = \alpha_{\pm}$ and combine equations (4.7) and (3.4) in Ref. [87] to obtain

$$I_0(\rho, \alpha_{\pm}) = I(1, 0; 0) = \begin{cases} -\frac{k_{\pm}\alpha_{\pm}}{2\pi\sqrt{\rho}} K(m_{\pm}) - \frac{1}{2}\Lambda_0(\beta_{\pm}, \kappa_{\pm}) + 1, & \rho < 1 \\ -\frac{k_{\pm}\alpha_{\pm}}{2\pi\sqrt{\rho}} K(m_{\pm}) + \frac{1}{2}, & \rho = 1 \\ -\frac{k_{\pm}\alpha_{\pm}}{2\pi\sqrt{\rho}} K(m_{\pm}) + \frac{1}{2}\Lambda_0(\beta_{\pm}, \kappa_{\pm}), & \rho > 1 \end{cases} \quad (5.37)$$

where the following functions have been defined

$$m_{\pm} = k_{\pm}^2 = \sin^2(\kappa_{\pm}) = \frac{4\rho}{(\rho + 1)^2 + \alpha_{\pm}^2}, \quad (5.38)$$

$$\beta_{\pm} = \sin^{-1} \left(\frac{\alpha_{\pm}}{\sqrt{(\rho - 1)^2 + \alpha_{\pm}^2}} \right), \quad (5.39)$$

$$\Lambda_0(\beta, \kappa) = \frac{2}{\pi} [K(m)E(\beta, \pi/2 - \kappa) - (K(m) - E(m))F(\beta, \pi/2 - \kappa)]. \quad (5.40)$$

The functions $K(m)$ and $E(m)$ are the complete elliptic integrals of the first and second kind, respectively. The (incomplete) elliptic integrals $F(\beta, \gamma)$ and $E(\beta, \gamma)$, of the first and second kind respectively, are used to define Heuman's Lambda Function $\Lambda_0(\beta, \kappa)$ (see section 17.4.39 in Ref. [85]).

5.3.9 Integral I_1

After making the identification $a = 1$, $b = \rho$, $c = \alpha_{\pm}$ one can combine equations (4.2) and (3.4) from Ref. [87] to arrive at

$$I_1(\rho, \alpha_{\pm}) = I(1, 1; 0) = \frac{1}{\pi k_{\pm} \sqrt{\rho}} ((2 - m_{\pm})K(m_{\pm}) - 2E(m_{\pm})). \quad (5.41)$$

5.3.10 Integral I_2

For this integral I make use of some of the recurrence relations reported in Ref. [87]. In this case the wanted integral is $I(2, 1; 0)$ with the identification $a = \rho$, $b = 1$, $c = \alpha_{\pm}$. Using equations (8.1) and (9.5) from Ref. [87] I obtain

$$I_2(\rho, \alpha_{\pm}) = I(2, 1; 0) = \frac{b}{a} I(1, 0; 0) - \frac{c}{a} I(1, 1; 0). \quad (5.42)$$

Substituting from equations (4.2), (4.7) and (3.4) in Ref. [87] and rearranging yields

$$I_2(\rho, \alpha_{\pm}) = \begin{cases} \frac{2\alpha_{\pm}}{\pi k_{\pm} \rho^{3/2}} E(m_{\pm}) - \frac{\alpha_{\pm} k_{\pm} (\alpha_{\pm}^2 + \rho^2 + 2)}{2\pi \rho^{5/2}} K(m_{\pm}) - \frac{1}{2\rho^2} \Lambda_0(\beta_{\pm}, \kappa_{\pm}) + \frac{1}{\rho^2}, & \rho > 1 \\ \frac{2\alpha_{\pm}}{\pi k_{\pm} \rho^{3/2}} E(m_{\pm}) - \frac{\alpha_{\pm} k_{\pm} (\alpha_{\pm}^2 + \rho^2 + 2)}{2\pi \rho^{5/2}} K(m_{\pm}) - \frac{1}{2\rho^2}, & \rho = 1 \\ \frac{2\alpha_{\pm}}{\pi k_{\pm} \rho^{3/2}} E(m_{\pm}) - \frac{\alpha_{\pm} k_{\pm} (\alpha_{\pm}^2 + \rho^2 + 2)}{2\pi \rho^{5/2}} K(m_{\pm}) + \frac{1}{2\rho^2} \Lambda_0(\beta_{\pm}, \kappa_{\pm}), & \rho < 1 \end{cases} \quad (5.43)$$

5.3.11 Transformation to cylindrical coordinate system

So far I have expressed the demagnetisation tensor in a Cartesian coordinate system, as in equations (5.22) and (5.35). The transformation matrix $\mathbf{M}$ between a Cartesian and a cylindrical coordinate system is

$$\begin{pmatrix} \hat{r} \\ \hat{\theta} \\ \hat{z} \end{pmatrix} = \begin{pmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \hat{x} \\ \hat{y} \\ \hat{z} \end{pmatrix} \equiv \mathbf{M} \begin{pmatrix} \hat{x} \\ \hat{y} \\ \hat{z} \end{pmatrix}. \quad (5.44)$$

The demagnetisation tensor in the cylindrical coordinate system is then

$$\mathbf{N}_{cyl} = \begin{pmatrix} N_{rr} & N_{r\theta} & N_{rz} \\ N_{r\theta} & N_{\theta\theta} & N_{\theta z} \\ N_{rz} & N_{\theta z} & N_{zz} \end{pmatrix} = \mathbf{M} \mathbf{N}_{cart} \mathbf{M}^T = \mathbf{M} \begin{pmatrix} N_{xx} & N_{xy} & N_{xz} \\ N_{xy} & N_{yy} & N_{yz} \\ N_{xz} & N_{yz} & N_{zz} \end{pmatrix} \mathbf{M}^T, \quad (5.45)$$

where I used the symmetry requirement $N_{ij} = N_{ji}$. Substituting the Cartesian components from equation (5.22) and simplifying the resulting expression yields the simple and intuitive relation

$$\mathbf{N}_{cyl} = \mathbf{N}_{cyl}(r, z) = \mathbf{N}_{cart}|_{\theta=0} = \begin{pmatrix} N_{xx} & 0 & N_{xz} \\ 0 & N_{yy} & 0 \\ N_{xz} & 0 & N_{zz} \end{pmatrix} \Big|_{\theta=0}. \quad (5.46)$$

This holds for the case of an object of general cylindrical symmetry. In the specific scenario of a finite cylinder, the non-zero components of the tensor in the reduced cylindrical coordinate system are

$$N_{rr} = \frac{1}{4} [2(I_0(\rho, 0) - I_2(\rho, 0))H_\theta(\tau - |\zeta|) + (I_0(\rho, \alpha_-) - I_2(\rho, \alpha_-))(H_\theta(\zeta - \tau) - H_\theta(\tau - \zeta)) + (I_0(\rho, \alpha_+) - I_2(\rho, \alpha_+))(H_\theta(-\tau - \zeta) - H_\theta(\tau + \zeta))] \quad (5.47)$$

$$N_{\theta\theta} = \frac{1}{4} [2(I_0(\rho, 0) + I_2(\rho, 0))H_\theta(\tau - |\zeta|) + (I_0(\rho, \alpha_-) + I_2(\rho, \alpha_-))(H_\theta(\zeta - \tau) - H_\theta(\tau - \zeta)) + (I_0(\rho, \alpha_+) + I_2(\rho, \alpha_+))(H_\theta(-\tau - \zeta) - H_\theta(\tau + \zeta))] \quad (5.48)$$

$$N_{zz} = D(\rho, \zeta) - \frac{1}{2} [2I_0(\rho, 0)H_\theta(\tau - |\zeta|) + I_0(\rho, \alpha_-)(H_\theta(\zeta - \tau) - H_\theta(\tau - \zeta)) + I_0(\rho, \alpha_+)(H_\theta(-\tau - \zeta) - H_\theta(\tau + \zeta))] \quad (5.49)$$

$$N_{rz} = \frac{1}{2}(I_1(\rho, \alpha_+) - I_1(\rho, \alpha_-)), \quad (5.50)$$

where expressions for $I_0(\rho, 0)$ and $I_2(\rho, 0)$ can be most easily obtained by employing equation (6.512.3⁸) in Ref. [84]. The above results can be shown to agree with previously published components [75, 89] upon a simple translation of the coordinate system: $\zeta \rightarrow \zeta + \tau$ (equivalent to $z \rightarrow z + d$). As before, the trace condition (equation (5.2)) is satisfied with $\text{Tr}[\mathbf{N}_{cyl}(\rho, \zeta)] = D(\rho, \zeta)$.

For an excellent discussion concerning the eigenvalues and eigenvectors of the demagnetisation tensor I can recommend section 4.2 in Ref. [83].

5.3.12 General cylindrical case - remaining integrals

It is possible to simplify the expression for the demagnetisation tensor in general cylindrical symmetry given in equation (5.22) even further. Remembering from section 5.3.1 that N_{ij} can always be written in terms of contributions due to simply connected objects of cylindrical symmetry we only need to focus on one such simply connected object. Defining the outer radius of such an object as $R(z)$ and focussing on the non-trivial part of $N_{ij}(\mathbf{r}') = \delta_{i3}\delta_{j3}D(\mathbf{r}') + \bar{N}_{ij}(\mathbf{r}')$ I find that in the notation of equation (5.36)

$$\bar{N}_{ij} = \sum_{\mu=0}^2 \bar{\alpha}_{ij}^{\mu}(\theta') \int_{-d}^d dz R(z) \xi_{ij}^{\text{sgn}(z-z')} \int_0^{\infty} dk_{\perp} k_{\perp} J_1(R(z)k_{\perp}) J_{\mu}(r'k_{\perp}) e^{-|z'-z|k_{\perp}} \quad (5.51)$$

$$= \sum_{\mu=0}^2 \bar{\alpha}_{ij}^{\mu}(\theta') \int_{-d}^d dz R(z) \xi_{ij}^{\text{sgn}(z-z')} I(1, \mu; 1). \quad (5.52)$$

Note that setting $\theta' \rightarrow 0$ yields the tensor in a cylindrical coordinate system, as demonstrated in section 5.3.11 above. In the cases of $\mu = 0$ and $\mu = 1$ the solutions for $I(1, \mu; 1)$ can be taken from equations (4.8) and (4.4) in Ref. [87], respectively, whereas for $\mu = 2$ I first exploit the recurrence relation (8.2) in Ref. [87]. Defining $k^2 = 4ab/((a+b)^2 + c_{\pm}^2)$ with the identification $a = R(z)$, $b = r'$ and $c_{\pm} = \pm(z - z')$

results in

$$I(1, 0; 1) = \frac{k^3(a^2 - b^2 - c_{\pm}^2)}{8\pi a(1 - k^2)(ab)^{3/2}}E(k) + \frac{k}{2\pi a\sqrt{ab}}K(k), \quad (5.53)$$

$$I(1, 1; 1) = \frac{c_{\pm}k}{4\pi(ab)^{3/2}}\left(\frac{(2 - k^2)}{1 - k^2}E(k) - 2K(k)\right), \quad (5.54)$$

$$I(1, 2; 1) = \frac{2}{b}I(1, 1; 0) - I(1, 0; 1), \quad (5.55)$$

$$= \frac{8a - k^2(4a + b)}{2\pi k(ab)^{3/2}}K(k) - \frac{32a^2(1 - k^2) + k^4(a^2 - b^2 - c^2)}{8\pi(1 - k^2)ka(ab)^{3/2}}E(k). \quad (5.56)$$

The $I(1, \mu; 1)$ integrals converge if $c_{\pm} > 0$ (see the introduction section in Ref. [87]). This is true in our case, with the $c_{\pm} = 0$ contribution already included in the $\delta_{i3}\delta_{j3}D(\mathbf{r}')$ term. More formally writing $\xi_{ij}^{\text{sgn}(z-z')} = \xi_{ij}^+ H_{\theta}(z - z') + \xi_{ij}^- H_{\theta}(z' - z)$ in equation (5.52) would emphasise this. Furthermore, the $I(1, \mu; 1)$ are finite if $k \neq 1$, which is satisfied as long as $c \neq 0$ and $a \neq b$, i.e. not on the boundary of the object.

Expression (5.52) is as far as the demagnetisation tensor for a simply connected object of general cylindrical symmetry can be simplified without knowing its radius $R(z)$ as a function of position along the symmetry axis. The major advantage of this result is that the only remaining integral is over a finite domain, which makes it accessible to conventional numerical techniques and thereby greatly reduces computational costs and enhancing its utility in practical applications.

5.4 Effects on μ^+ SR experiments

With the advent of high field muon spectrometers it has become increasingly important to identify and quantify the impact of demagnetising fields on μ^+ SR measurements in order to separate them from any intrinsic sample behaviour. As described in chapter 3 and summarised in equation (3.3) the total magnetic field experienced by an implanted muon is a sum of external, hyperfine, dipolar, Lorentz and demagnetising fields. In this section I restrict my attention to the Lorentz and demagnetising contributions, since the main aim is to study the gen-

eral behaviour of magnetised samples without any *a priori* knowledge about their chemical and structural details, which are required to evaluate the dipolar and hyperfine field contributions. In the following I assume, in line with the previous work of this chapter, that the sample acquires a uniform magnetisation $\mathbf{M}$ along the direction of the external field $\mathbf{B}_{ext}$, taken to be along $\hat{\mathbf{z}}$, in which case the Lorentz field becomes $\mathbf{B}_L = \mu_0 \mathbf{M}/3$ and the demagnetising field is given by $B_{D,i}(\mathbf{r}) = -\mu_0 N_{ij}(\mathbf{r}) M_j$, where the demagnetising tensor N_{ij} is in general given by equation (5.1). Note that even if the sample is not ferromagnetic, it will acquire a magnetisation $\mathbf{M} = \chi \mathbf{B}_{ext}/\mu_0$, where χ is the susceptibility. Therefore, in practice a full demagnetising field characterisation will require prior magnetisation or susceptibility measurements. Note that all fields calculated and plotted below are expressed in units of $\mu_0 \mathbf{M}$, allowing simple scaling using either of these two quantities.

In the following sections I first focus on cylindrically shaped samples, utilising the solution 5.35 derived above, before also considering different polyhedral objects, including two examples of single crystal samples I have previously measured.

5.4.1 Cylindrical samples

In this section I will assume a cylindrical geometry with a uniform magnetisation of magnitude $|\mathbf{M}| = M$ along the cylindrical axis, taken to be the z -axis, and the muons being implanted along the same axis. Furthermore, I will assume a typical experimental sample with a radius R of 10 mm, a height h of 2 mm, and a muon implantation depth of 0.1 mm, in line with the stopping range of surface muons of about 110 mg cm^{-2} and a typical sample density of order 10 g/cm^3 (appropriate for many metals). Figure 5.2 shows a schematic of the experimental setup at hand.

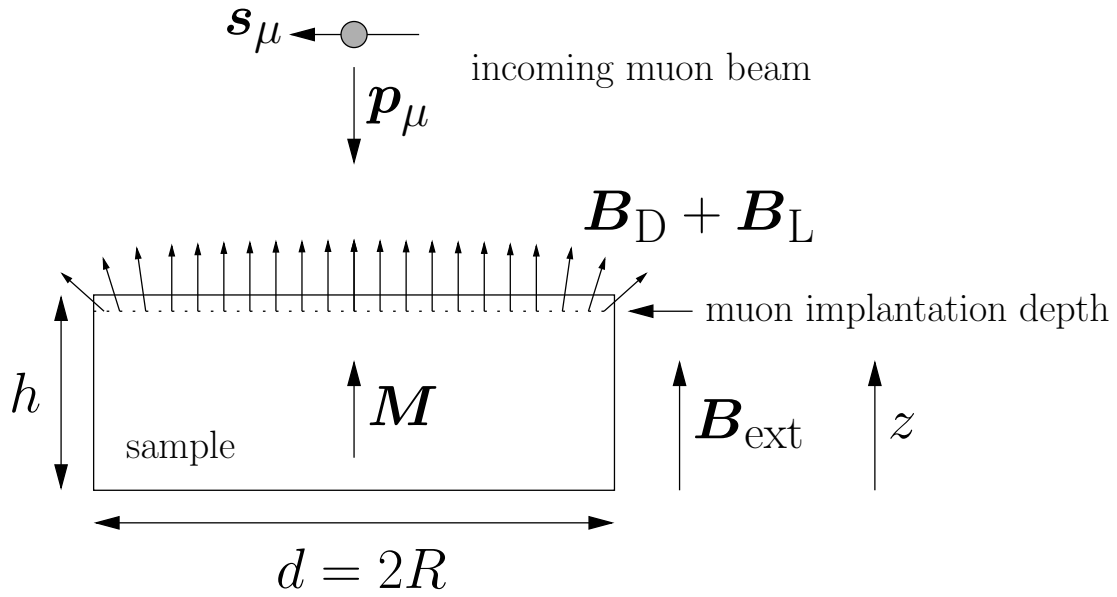


Figure 5.2: Schematic of high-field TF- μ^+ SR experiment, showing schematically the demagnetisation field variation within a cylindrical sample (shown in cross section) at the muon implantation depth.

Demagnetising Field Distribution

Using the analytic solution for the demagnetisation tensor of a cylinder from equation (5.35), the demagnetising field can be computed at the stopping depth of the muons as a function of the radial position. The resulting fields are plotted in Figure 5.3 for the demagnetising field and the sum of Lorentz and demagnetising field, and also their respective z -components. The reason for plotting the z -components is that the large external field is applied along $\hat{z}$ and therefore $(\mathbf{B}_D + \mathbf{B}_L) \cdot \hat{z}$ will add to the total field strength in first order, whereas the components perpendicular to $\hat{z}$ add in second order. Thus, the former will have the largest effect in a transverse field (TF) μ^+ SR experiment.

Figure 5.3 demonstrates that the demagnetising field is position dependent and more importantly that its z -component almost vanishes near the radial boundary, while the overall field strength does not. Qualitatively, this is due to a realigning of the field to satisfy the boundary condition $B_{\perp,\text{in}} = B_{\perp,\text{out}} = 0$ at the radial edge. This bending of the field lines is schematically indicated in Figure 5.2 and will lead to discrepancies between the fields experienced by muons near the centre

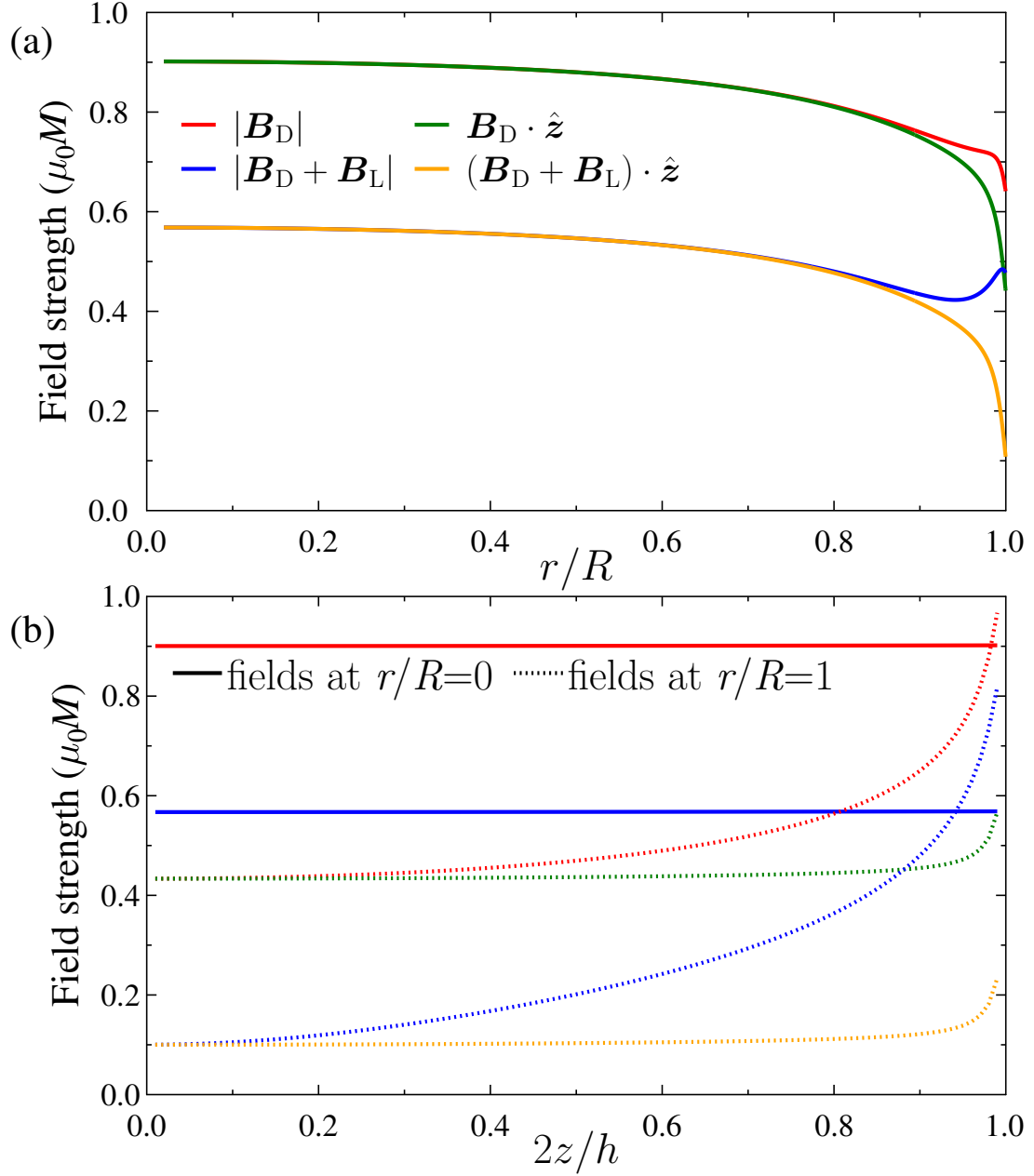


Figure 5.3: Magnetic field strengths and components along the cylinder axis. Panel (a) presents the radial dependence at the muon stopping depth. Panel (b) shows the depth (z) dependence of the fields at the centre and edge of the cylinder, with the colour coding the same as in panel (a). Note that the solid lines in (b) are the same for colours red/green, and blue/orange. R and h are the cylinder radius and height respectively; the cylinder centre is taken to be at $z = r = 0$. Note that the Lorentz field $B_L = \mu_0 M/3$ is homogeneous and that the demagnetising field B_D is not.

of the sample and those near the boundary. An important realisation is that the region near the radial edge actually constitutes a significant portion of the total volume (recall the area between circles of radii r and $r + dr$ scales as $2\pi r dr$). Hence, even though the field realignment only happens close to the boundary, it can be a significant effect due to the volume weighting of the edge regions.

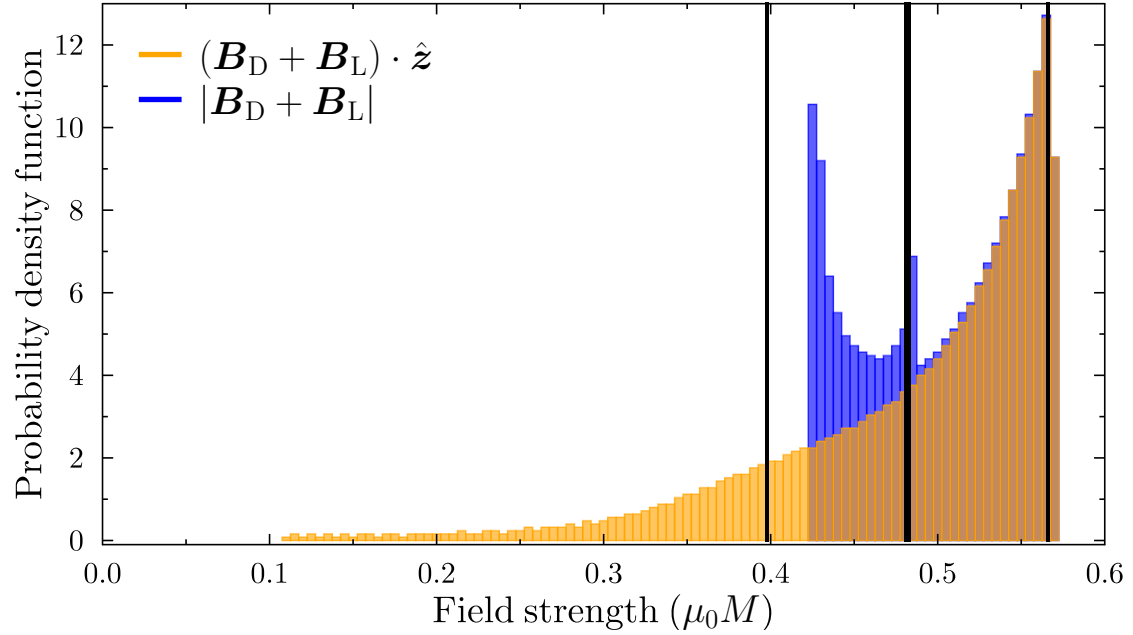


Figure 5.4: Probability density plot of the magnetic fields at the muon stopping depth. The black vertical lines indicate the mean and standard deviation of the z -component’s distribution (orange histogram).

The impact of the demagnetising field becomes apparent in the probability distributions, which are plotted in Figure 5.4 and demonstrate a clear and sizeable broadening of the magnetic field. The discrepancy between the two distributions for the field strength and its z -component has its origin in the realigning of the field near the radial boundary and the fact that the demagnetising field is stronger near the flat z -boundary in general. This is often qualitatively explained by modelling the flat boundaries to contain “magnetic charges” induced by the external field, which in turn induce the demagnetising field.

The calculations described above assume all muons to stop precisely at a depth of 0.1 mm and in a radially uniform way, which is a good approximation if the muon beam covers the entire sample. However, when one repeats the above cal-

culations and includes a Gaussian profile for the stopping distance centred around this implantation depth, the outcomes are effectively unchanged. In fact, the field distribution results were largely insensitive to all stopping profiles I tested. Thus, I restrict the subsequent discussion to a delta-function stopping profile and simply change the delta-function depth.

Effect of aspect ratio

I now examine the impact of the edge effects on the field broadening as a function of the cylinder's aspect ratio τ , defined as the ratio of height h to diameter $d = 2R$ (the calculations above assumed $\tau = h/d = 0.1$). Computing the field distributions at the muon stopping depth for different values of h/d yields the results shown in Figure 5.5. Plotted in the figure are the mean and standard deviation of both the field strength and its z -component. Figure 5.5 shows that the correct results are recovered in the limits of a flat cylinder (disc: $h/d \rightarrow 0$, $\mathbf{B}_D = -\mu_0\mathbf{M}$, $\mathbf{B}_D + \mathbf{B}_L = -2\mu_0\mathbf{M}/3$) or long cylinder (wire: $h/d = \infty$, $\mathbf{B}_D = 0$, $\mathbf{B}_D + \mathbf{B}_L = \mu_0\mathbf{M}/3$). Furthermore, it illustrates that the field broadening, characterised by the standard deviation, is strongest when the aspect ratio is of order 0.1–1, which applies to most experimental samples. Moreover, in this range the broadening even becomes comparable to the actual demagnetising field strength, as demonstrated in the inset of Figure 5.5 which plots the ratio of the two.

Therefore, I conclude that the field broadening due to the demagnetising response and edge effects will in general be most significant for the dimensions of typical μ^+ SR samples and should thus be considered in earnest for most high-field TF- μ^+ SR experiments. Additionally, one possible way to decrease the impact of the demagnetising fields is to reduce the cylinder aspect ratio to 0.01 or lower by either making the sample thinner or wider. However, this might not always be experimentally feasible, which applies to the option of increasing the aspect ratio above 10 as that would require too large a sample space in virtually all scenarios.

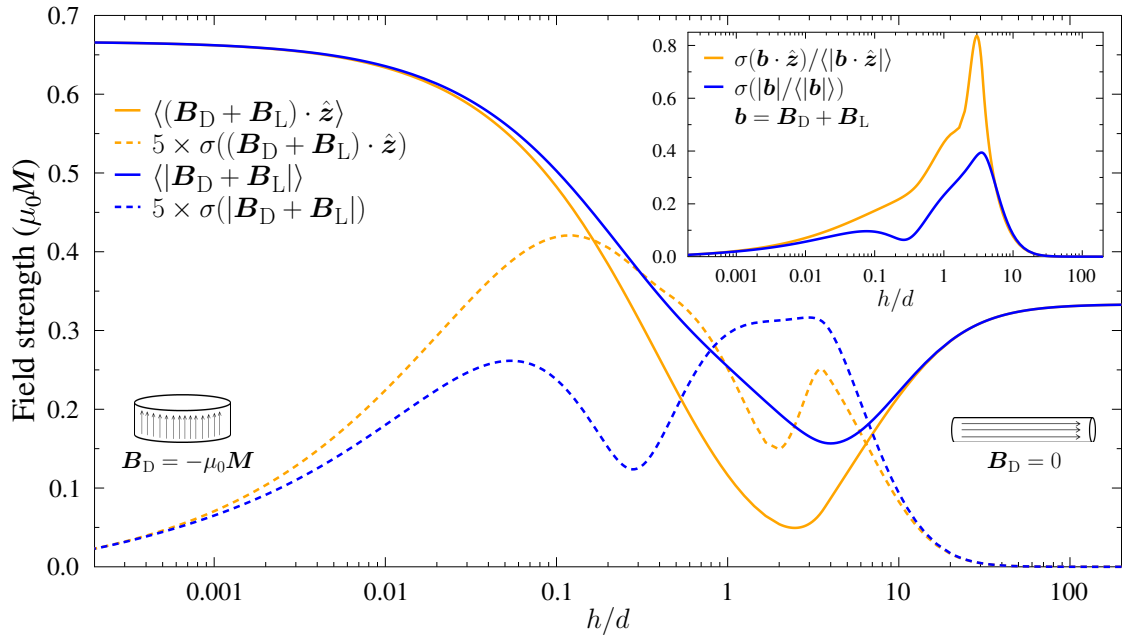


Figure 5.5: Demagnetising field distribution as a function of cylinder aspect ratio. Plotted are the averages and standard deviations (scaled up by a factor of 5 for readability) for both the total field and its component along z . The inset graph shows the ratio of standard deviations and mean values.

Effect of muon stopping depth

Another possible way of influencing the effect of the demagnetising field experienced by the muons, besides changing the aspect ratio of the sample, is to reduce the implantation depth of the muons by placing a degrader on top of the sample. This has the effect that more muons stop in regions closer to the flat z -boundary than the radial edge. Figure 5.6 illustrates the two main resulting consequences for the case $\tau = h/d = 0.1$. Firstly, the average demagnetising field strength increases as the stopping distance is reduced, which shows that the field is stronger near the cylinder's flat surfaces where $\nabla \cdot \mathbf{M} \neq 0$. Secondly, the broadening of the field distribution decreases as the implantation depth is shortened. Therefore, by adding a degrader it can be possible to reduce the field broadening at the expense of raising the average demagnetising field strength.

Discussion: identifying and reducing demagnetising effects

My investigations show that the demagnetising response of typical cylindrical samples can be significant due to edge effects. If one assumes the external field $\mathbf{B}_{ext} \parallel \hat{z}$

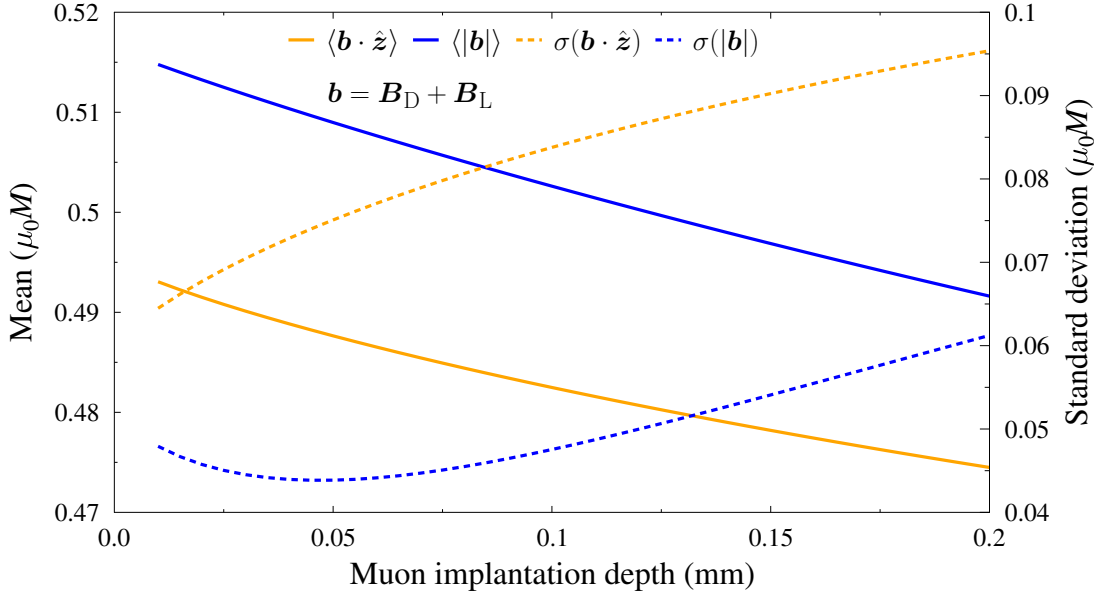


Figure 5.6: Field distribution dependence on the muon implantation depth for the case $h/d = 0.1$. Solid lines and the left hand axis correspond to mean values, dashed lines and the right hand axis to standard deviations.

to be very large then to a good approximation the demagnetising and Lorentz field components parallel and perpendicular to $\hat{\mathbf{z}}$ add to the total field in first and second order respectively. In this case, a possible signature that an observed broadening may be caused by the demagnetising field is a field distribution resembling that of the z -component of $\mathbf{b} = \mathbf{B}_D + \mathbf{B}_L$ shown in Figure 5.4, which has a long low-field tail due to the radial edge behaviour and a sharp high-field cut-off (this behaviour is reversed if $\chi < 0$, i.e. for diamagnets). If an experimentally observed field distribution resembles this characteristic behaviour the impact of the demagnetisation response should be considered more closely.

Additionally, there are three potential ways of influencing the demagnetisation effects experimentally that present themselves. While changing the aspect ratio of the sample is in theory a potential option, a practically more feasible possibility is the addition of a degrader on top of the sample. This in effect shortens the muon implantation depth and subsequently reduces the demagnetising field broadening as discussed above. This has the disadvantage of introducing additional field contributions due to muons stopping in the degrader and the demagnetising response

of the degrader itself. Another option to reduce the demagnetising field broadening is to place a thick circular mask with radius $< R$ in front of the sample, such that the muons that would stop in the regions near the radial boundary are completely stopped in the mask. In Figure 5.3 this would correspond to only considering regions away from the radial edge, thereby shortening the low-field tail of the b_z distribution shown in Figure 5.4. However, the presence of the mask will lower the data rate and potentially shift the background signal experienced by muons. An alternative to such a mask, which should have similar effects, could be to reduce the muon beam spot radius below the sample radius, while simultaneously ensuring that the sample is well centred in the beam.

5.4.2 Other sample shapes

So far I have focussed on the effect of demagnetising fields in cylindrical samples only. In this section I give two examples of how they can be calculated for the cases of non-circular and segmented samples, and highlight similarities with the edge effects observed in the cylindrical case. In both scenarios I make use of the principle of superposition of shape functions, which allows us to “build” complex sample shapes out of simpler ones. This is elaborated on in section 5.2 and illustrated in Figure 5.1 and is a direct corollary of the Fourier transform expression for the demagnetising tensor in equation (5.1).

In the following, I also utilise the analytical solution for the demagnetising tensor in rectangular prisms (cuboids) published by Joseph and Schlömann [75]. Alternative approaches due to Engel-Herbert and Hesjedal [90] as well as Smith *et al.* [91] exist for this geometry, including relaxation of the uniform magnetisation assumption.

Polyhedral sample shape

Figure 5.7(a) depicts a single crystal of $\text{Sr}_3\text{Ru}_2\text{O}_7$ I have previously measured on the high field HAL9500 spectrometer at the Swiss Muon Source. In order to compute

the demagnetising fields in this sample I decomposed it into a set of rectangular prisms, which are outlined in red in panel (a) of Figure 5.7, and added their respective demagnetising tensors. The prisms only serve as an approximation to the actual sample shape, but in theory their number can be increased to improve the accuracy of the computation. The density of $\text{Sr}_3\text{Ru}_2\text{O}_7$ can be calculated from crystal structure measurements [92, 93] to be about 6150 mg/cm^3 , which gives an estimate for the muon stopping distance of roughly 0.18mm from the sample surface. Using the measured thickness of the single crystal of about $1.90(5)\text{mm}$ results in the demagnetising fields at the muon implantation depth shown in Figure 5.7. Panels (b) and (c) of the figure comprise the magnitude of the demagnetising field components parallel and perpendicular to the externally applied field, which in this case is perpendicular to the plane of the plots. It can be observed that, just like in the case of the cylindrical samples considered in the previous section, there is appreciable bending of the demagnetising field near the boundary of the sample. Whereas the field is nearly uniform and parallel to the external field in the central regions of the crystal. Thus, we expect a very similar response in high magnetic fields as those predicted for cylindrical samples in section 5.4.1 with a low field tail and sudden high field cut-off. It should be noted that the plots in Figure 5.7 do not take into account the Lorentz field or the demagnetising field of the silver sample holder and furthermore require knowledge of the sample magnetisation (or susceptibility) as a function of applied field to ascertain the actual size of the demagnetising fields.

Multiple co-aligned crystals

In the case of an experimental sample comprising multiple separate parts the principle of superposing shape functions can also be applied to determine the demagnetising field. An example of this is shown for a set of co-aligned EuS single crystals in Figure 5.8. In panel (a) of the figure the individual crystals can be seen, as well as the approximated cuboids for each. The density of EuS is about

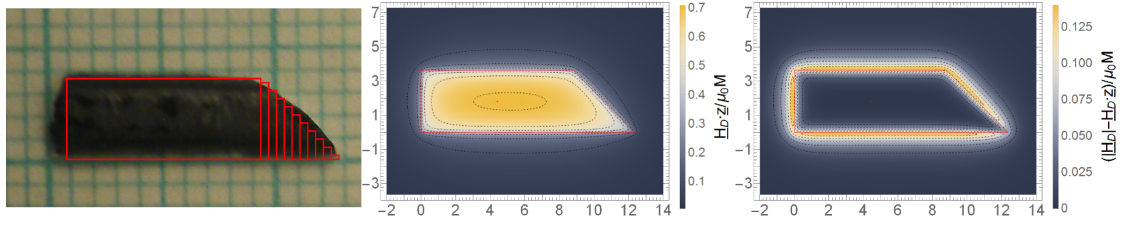


Figure 5.7: Single crystal sample of $\text{Sr}_3\text{Ru}_2\text{O}_7$ and approximate demagnetising fields. Panel (a) shows the sample of thickness 1.90(5)mm, with the red outlines representing the sum of cuboids used to approximate its shape. Panels (b) and (c) show the demagnetising fields calculated at the muon stopping depth of about 0.18mm.

5750 mg/cm^3 [94] and thus the muon stopping distance is roughly 0.2mm in this material. Taking the average height of the crystals to be very roughly 1mm this yields the demagnetising field plots in panels (b) and (c) of Figure 5.8. As before, only the regions close to the sample boundaries have appreciable bending of the demagnetising field and are therefore subject to significant effects on the muons that stop in those regions. Consequently, the impact on the field distribution is expected to be comparable to that found in the cylindrical case, i.e. a low field tail with a high field cut-off. It should be noted that the assumption of uniform height of the crystals that I used above can be relaxed in general, but at the expense of additional complexities.

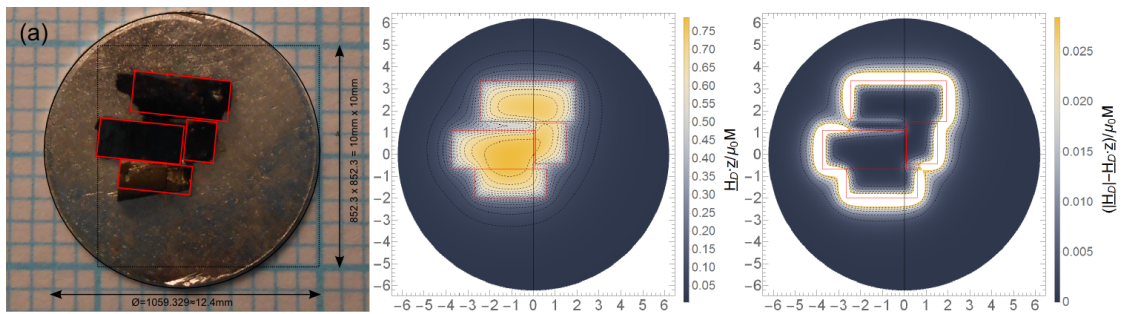


Figure 5.8: Single crystal sample of EuS and approximate demagnetising fields. Panel (a) shows the coaligned single crystals of EuS, with the red outlines highlighting the cuboids used to calculate the demagnetising fields presented in panels (b) and (c). The fields were calculated at the muon stopping depth of about 0.2mm, assuming all crystals to be the same height (1mm) for simplicity.

5.5 Outlook

Better understanding of how demagnetising fields impact μ^+ SR measurements and potentially overshadow intrinsic sample behaviour is becoming increasingly important. While in this chapter I have made attempts at helping elucidate demagnetising effects and identifying possible countermeasures, there are still many aspects that can be improved and expanded.

One important undertaking for the future is the creation of a “library” of shapes for which the demagnetising tensor is analytically described, as this would allow decomposing complex shapes much more straightforwardly. One particular shape we are interested in is that of a cylindrical rod with hemispherical ends, as this is an excellent approximation to some pulsed field powder probes. In this case the demagnetising tensor of a hemisphere could be numerically computed from equation (5.52) (it’s unlikely but not impossible that an analytical solution might emerge) and suitably combined with that for a cylinder.

Another aspect pertaining to μ^+ SR measurements specifically is the incorporation of muon beam and stopping profiles. In all the above simulations I assumed the muons to uniformly illuminate the entire area of the sample and stop at the same penetration depth. However, in reality the beam profile is roughly Gaussian and the stopping depth varies as a function muon energy, which can be investigated via a technique called projected range imaging [95]. In theory both these aspects could and should be considered for the most accurate analysis of demagnetising field effects on a set of μ^+ SR data, and a future task will be their incorporation into demagnetising field simulations.

Chapter 6

Pyrochlores

A crucial question when conducting μ^+ SR experiments is whether the muon acts as an “innocent” probe or not, i.e. to what extent the measurements reflect the influence of the muon on its local environment rather than the intrinsic behaviour of the sample. This chapter concerns a μ^+ SR investigation of the magnetic behaviour of two families of pyrochlores: $\text{Pr}_2\text{B}_2\text{O}_7$ (B=Sn, Hf, Zr, Ir) and $\text{A}_2\text{Ti}_2\text{O}_7$ (A= Dy, Ho). In both scenarios I employ DFT calculations to determine the most likely muon stopping sites and analyse and quantify the local distortions induced by the muons. I subsequently argue that crystal field calculations based on the locally perturbed ion environments show strong evidence that in the case of the Pr-based pyrochlores our experimental μ^+ SR observations, which we find inconsistent with any previously reported behaviour, have their origin in muon induced effects rather than any intrinsic properties. I identify the crystal field splitting of the doublet ground state of the Pr^{3+} ions caused by the change of the local oxygen environment as the most likely origin of the experimental behaviour. I further reason that the sensitivity to local perturbations in this family of compounds is rooted in the fact that the Pr ions are non-Kramers ions and hence not symmetry protected from being split. Subsequently I argue, using an essentially identical methodology, that in stark contrast the μ^+ SR experiments on the titanate pyrochlores $\text{A}_2\text{Ti}_2\text{O}_7$ do indeed reflect the intrinsic sample behaviour qualitatively and that the reported

thermally activated behaviour may be linked to the details of the crystal field levels.

Much of the work on the Pr-based pyrochlores in this chapter has been published in Physical Review Letters [96]. My contributions to this project are centred around the DFT calculations of the muon sites and the local muon induced distortions, which are also the focus of this chapter. While I will cover all the relevant aspects required to follow my argumentation, most of the experimental data analysis and modelling is due to Francesca Foronda, whose thesis will cover many of the experimental aspects in much more detail [97].

My personal contributions to this research project include: help with conducting the μ^+ SR experiments on $\text{Pr}_2\text{B}_2\text{O}_7$ (B=Sn, Hf, Zr) and $\text{Dy}_2\text{Ti}_2\text{O}_7$ and preliminary data analysis; calculation of the muon stopping sites and the muon induced distortions of the local crystal environment, and writing the associated segment in the PRL publication [96]; assistance with the implementation of the hyperfine enhancement model.

This project was made possible through a great collaborative effort: The μ^+ SR experiments and detailed data analysis were carried out by F. Foronda with experimental assistance by J.S. Möller, S. Blundell, T. Lancaster, S. Giblin, F.L. Pratt, S. Cottrell and C. Baines. The samples were provided by D. Prabhakaran and the crystal field calculations were performed by A. Boothroyd. A Pr pseudopotential containing 4*f* valence electrons was kindly provided by D. Ceresoli. The hyperfine enhancement model and the main text of the PRL publication are due to F. Foronda and S. Blundell.

6.1 $\text{Pr}_2\text{B}_2\text{O}_7$

In this section I present an investigation of the magnetic behaviour of the family of Pr-based pyrochlores $\text{Pr}_2\text{B}_2\text{O}_7$ (B=Sn, Hf, Zr, Ir) using the μ^+ SR technique. After giving a brief overview of the most important known properties and the scientific

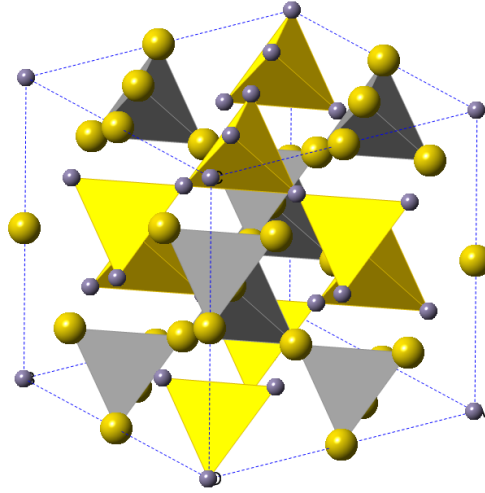


Figure 6.1: Pyrochlore tetrahedral structure. Grey (yellow) atoms correspond to site A (B). Oxygen atoms and tetrahedra formed by two ions of type A and B each are omitted.

interests in these compounds, I summarise the results of the μ^+ SR experiments we performed. I highlight the discrepancies between the theoretically predicted and previously reported behaviours and our observations, in addition to an unexpected similarity of the μ^+ SR data for all the Pr pyrochlores investigated. I subsequently present a detailed study employing DFT calculations to determine the muon stopping sites in these compounds and furthermore analyse the distortions of the local crystal environment induced by the muon presence. This is followed by a computation of the crystal field levels of the Pr ions closest to the muon, which shows that the local perturbations due to the muon causes the Pr doublet ground state to split. I examine this splitting as a function of proximity to the muon and subsequently argue that all the μ^+ SR observations of this family of materials can be explained by hyperfine enhanced Pr nuclear moments. I then demonstrate that a hyperfine enhancement modelling of the experimental data yields expected ground state splittings in fair agreement with those predicted by the combination of DFT and crystal field calculation, thus corroborating the proposition of purely muon induced effects being observed instead of any intrinsic behaviour. Finally, I present an explanation for the sensitivity of these compounds to the perturbations caused

by the muons, and discuss these findings in the context of past and future $\mu^+\text{SR}$ experiments and offer guiding suggestions for identifying scenarios in which muon induced effects might be significant and should be considered.

6.1.1 Introduction

Pyrochlore oxides have the chemical formula $\text{A}_2\text{B}_2\text{O}_7$, with A a rare-earth ion and B typically a transition metal. Their structure (space group 227: $Fd\bar{3}m$), depicted in Figure 6.1, is such that both A and B sites form interlacing lattices of corner-sharing tetrahedra, which is a common ingredient for frustrated magnetic systems, as highlighted in chapter 2.2. Consequently, a plethora of interesting magnetic structures can be realised in the pyrochlores, such as spin glasses, spin liquids and spin ices [98]. Spin-ice behaviour, already discussed briefly in chapter 2.2.1 is characterised by what is called a “2in-2out” ground state in which two of the Ising spins at the corner of each tetrahedron point inwards along the local (111) direction and two spins point outwards. This phenomenon has been extensively studied – including $\mu^+\text{SR}$ measurements – for example on $\text{Dy}_2\text{Ti}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$ [4, 5]. Recently it has been proposed that placing a lanthanide ion with fewer f -electrons and a smaller magnetic moment, such as Pr^{3+} , on the A sites could result in a novel type of quantum spin liquid ground state referred to as *quantum* spin ice [99]. The subsequent combination of extended $4f$ -wavefunction and weaker dipolar interaction is predicted to allow quantum tunnelling between different spin ice configurations; hence the name quantum spin ice. Such systems are of special interest as they could be hosts to unconventional magnetic excitations, which have been theorised to provide a real lattice analogue of quantum electromagnetism [100, 101].

Previous susceptibility and neutron studies of one of these quantum spin ice candidates, $\text{Pr}_2\text{Sn}_2\text{O}_7$, discovered evidence for a dynamic spin ice state at low temperatures and confirmed a weaker dipolar interaction [102–104]. Additionally, the studies revealed an increased zero-point entropy compared to the classical spin

ices $\text{Dy}_2\text{Ti}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$ (about 25% higher) and furthermore the persistence of relaxation down to about 200 mK, thereby exposing the dynamic nature of the Pr spins. A more recent neutron investigation mapped out the crystal field levels of the Pr^{3+} ions in the Sn and Zr members of the family in detail and found them to comprise a non-Kramers doublet ground state with a large Ising-like anisotropy [104, 105]. Additionally, both studies also presented evidence for strong fluctuations that persist to low temperatures and thus corroborating the existence of a quantum spin ice state.

6.1.2 μ^+ SR measurements

We performed ZF μ^+ SR measurements of polycrystalline samples of $\text{Pr}_2\text{B}_2\text{O}_7$ (B=Sn, Hf, Zr) at both the EMU spectrometer at the ISIS muon facility, RAL (UK), and the GPS spectrometer at the Swiss Muon Source, PSI (Switzerland). The data were collected in the temperature range 0.05–280 K using ^3He cryostats and ^4He dilution refrigerators. X-ray characterisation of the samples, prepared by standard solid-state reactions, confirmed the existence of a single phase in each one of them.

Figure 6.2 shows representative low and high temperature data of the ZF measurements for all three samples. We observe that at 1.5 K the asymmetry follows an initial Gaussian like depolarisation before recovering to a roughly constant value that is about 1/3 of the initial asymmetry. This behaviour is characteristic of a static Kubo-Toyabe relaxation function due to a random distribution of static local fields (see chapter 3.6.1 and Figure 3.6 there) with mean square width $B_{\text{rms}} = \Delta/\gamma_\mu$ and static relaxation rate Δ . Thus, the muons predominantly experience a static, random distribution of local fields with no significant dynamical fluctuations. In order to incorporate any potential slow dynamics, we fit the asymmetry data to a product of the ZF Kubo-Toyabe function (3.11) and an exponential relaxation $\exp(-\lambda t)$ with dynamic relaxation rate λ . This fitting can be employed for all measured temperatures, the results of which are presented in Figure 6.3.

Figure 6.3 allows a few important observations. First of all both Δ and λ increase smoothly upon cooling, likely due to the magnetic moments increasing, and neither shows evidence of a magnetic phase transition. We further note that at all temperatures the static relaxation rate is significantly larger (by about an order of magnitude) than the dynamic one, and that both are roughly temperature independent below 1 K. Besides, the relaxation rates appear to track each other, indicating that the increase in spin dynamics may be linked to the growth of the magnetic moment size. These observations are in direct contradiction to the strong dynamical fluctuations that were observed by neutron scattering to persist to temperatures below 1 K. Additionally, the compounds all exhibit a surprising similarity between their behaviours. Remarkably this includes the iridate sample, which contrary to the other compounds is a metal and thus is not expected to follow the same quantitative trends. Furthermore, we can estimate the rms value of the magnetic field $B_{\text{rms}} = \Delta/\gamma_\mu$ to be roughly 2–5 mT, which is about an order of magnitude too high to stem from isolated nuclear spins of the Pr^{3+} ions [106, 107]. Another detail that can be noted from Figure 6.2 is that the asymmetry displays a small but very fast relaxing component in the first few $0.1 \mu\text{s}$. While the origin of this fast relaxing volume fraction is not entirely understood, we believe it possibly originates from a short-lived muonium state.

In conclusion, our ZF μ^+ SR data do not reveal any fluctuation driven phenomena but instead a static distribution of fields too large to be caused by isolated nuclear spins, thus contradicting all previously observations using alternative experimental probes. To investigate this conundrum further, I now employ DFT calculations to determine the muon stopping sites and their local environments.

6.1.3 DFT+ μ

In this section I give a detailed account of the “DFT+ μ ” calculations I performed on two members of the Pr based pyrochlores: $\text{Pr}_2\text{Sn}_2\text{O}_7$ and $\text{Pr}_2\text{Zr}_2\text{O}_7$. The various steps involved in the computations of each compound are entirely analogous,

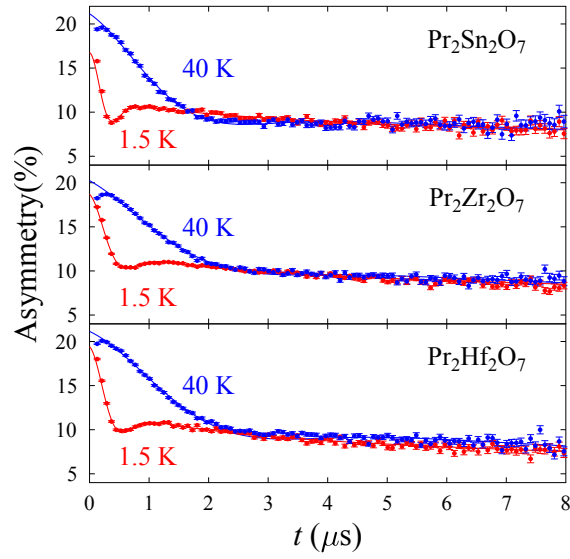


Figure 6.2: Representative low and high temperature asymmetry data of ZF μ^+ SR measurements of the Pr based pyrochlores. Solid lines represent fits to the data. From Ref. [96].

and hence I restrict in-depth discussions to $\text{Pr}_2\text{Sn}_2\text{O}_7$ and only present the final results for $\text{Pr}_2\text{Zr}_2\text{O}_7$. Note that due to the strong similarities obtained for these two materials, and furthermore because the Ti-based pyrochlores (see section 6.2 below) also yield qualitatively equivalent results, we expect our conclusions to also be applicable for $\text{Pr}_2\text{Hf}_2\text{O}_7$. The calculations presented here were all performed with the plane-wave software QUANTUM ESPRESSO [71].

Computational details

The first major step in the process of determining the potential muon sites in a system is to reproduce the bulk properties of the material within DFT. To that end I created ultrasoft pseudopotentials of Pr, Sn and O using the PSlibrary available within Quantum Espresso. I employed the general gradient approximation due to Perdew, Burke and Ernzerhofer [60] in addition to the formalism developed by Rappe, Rabe, Kaxiras and Joannopoulos [108] for creating such ultrasoft potentials. Most calculations presented in this chapter employ a Pr pseudopotential in which the $4f$ electron shells are incorporated into the pseudised core, such that they are not treated as valence electrons. The expectation is that because the $4f$ orbitals have smaller radii than the $6s$ -shells (in fact $r_{4f} \approx r_{6s}/2$) this approxi-

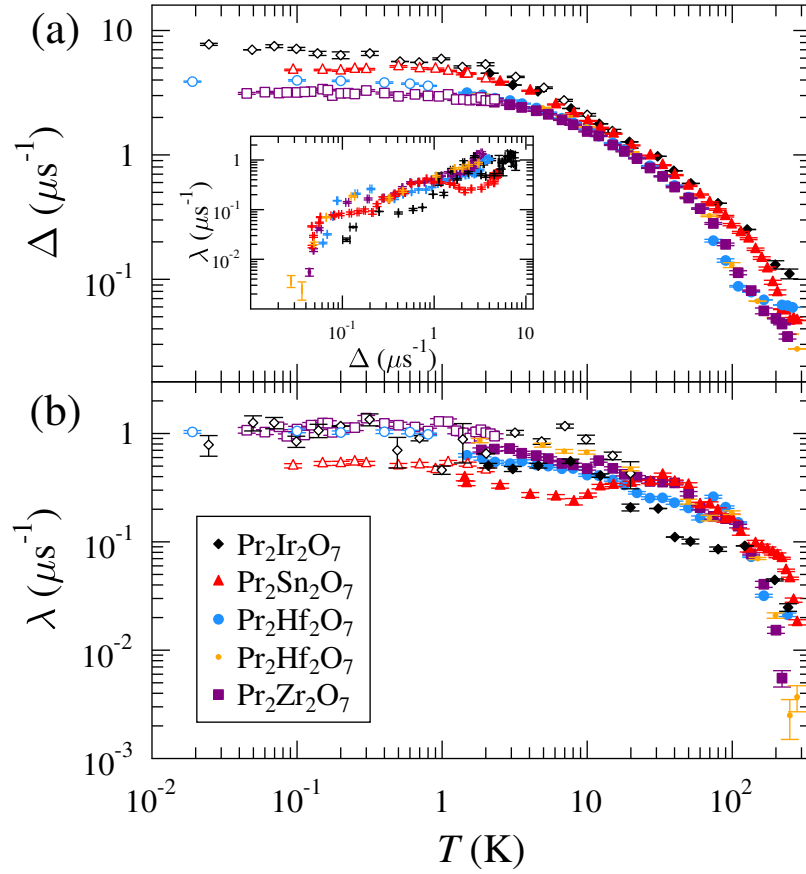


Figure 6.3: Temperature dependence of the static (Δ) and dynamic relaxation rates (λ) in panels (a) and (b), respectively, obtained from fits of a product of Kubo-Toyabe and exponential relaxation. The results shown are for zero applied field. Data for $\text{Pr}_2\text{Ir}_2\text{O}_7$ was extracted from Ref. [106]. Note that the $\text{Pr}_2\text{Hf}_2\text{O}_7$ sample was measured twice to demonstrate reproducibility. From Ref. [96].

mation will not compromise the accuracy of the calculations while reducing the computational costs. Nevertheless, I also performed test calculations with a Pr pseudopotential with the $4f$ electrons in valence, which reproduced all the results presented here and thereby confirmed their validity.

One way to test the convergence of the DFT calculations is to compute the total energy of the system at hand for the experimentally measured crystal structure with lattice parameter $a = 10.6 \text{ \AA}$ for $\text{Pr}_2\text{Sn}_2\text{O}_7$ [109] and a slightly compressed unit cell ($a = 10.5 \text{ \AA}$ in this case). The resulting energy difference is plotted for a range of energy and density cut-offs, and k -point grid sizes in panels (a)–(c) in Figure 6.4, indicating convergence for cut-offs of 60 Ry (energy) and 300 Ry (density) and a $2 \times 2 \times 2$ Monkhorst-Pack k -grid. These values are tabulated in Table 6.1 together with those obtained for $\text{Pr}_2\text{Zr}_2\text{O}_7$. The lattice parameter can subsequently be obtained through two methods: either by allowing the ionic positions and unit cell size to change according to the Hellmann-Feynman forces acting on them, which yields $a = 10.736 \text{ \AA}$ and atomic positions in very good agreement with the experimentally determined ones. Alternatively one can minimise the pressure in the system by fitting a Birch-Murnaghan equation of state [110] to the energy curve as a function of lattice parameter, displayed in panel (d) of Figure 6.4. This is equivalent to minimising the total energy and results in $a = 10.798 \text{ \AA}$. This demonstrates a sufficient agreement of the atomic positions and the lattice parameter calculated through DFT with the experimentally determined ones. Additionally, a calculation of the band structure yields a band gap of about 3.1 eV which agrees with the insulating nature of the compounds at hand (recall that DFT underestimates band gaps) and thus further corroborates the conclusion that the bulk properties are adequately reproduced within the DFT computations.

This now allows the next step of the “DFT+ μ ” process to be taken: the introduction of the muon into the unperturbed unit cell. Since DFT simulations of bulk

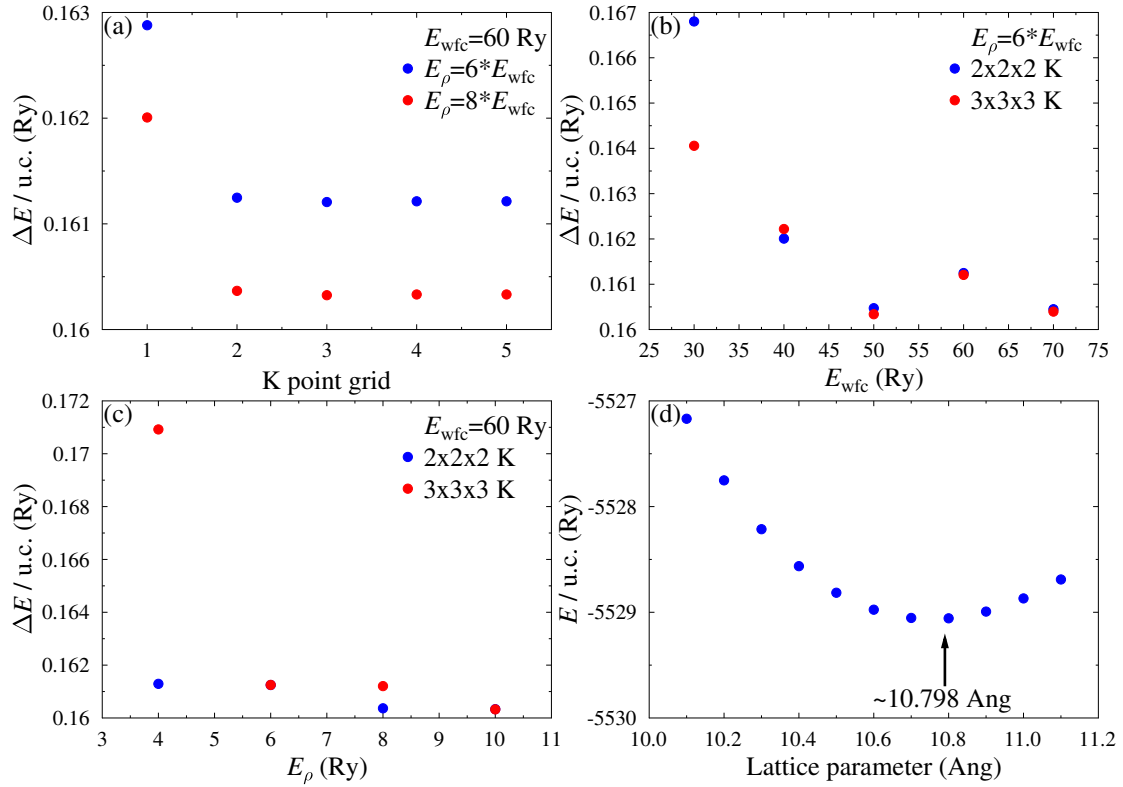


Figure 6.4: Conversion study of DFT parameters for $\text{Pr}_2\text{Sn}_2\text{O}_7$. Panels (a)–(c) show the total energy difference between the experimentally determined unit cell and a slightly compressed one. E_{wfc} and E_{ρ} are the cut-offs for the kinetic energy and electron density, respectively, and the k-point grid is of the form $A \times A \times A$. Panel (d) shows the total energy per unit cell as a function of the lattice parameter and the equilibrium value obtained via a Birch-Murnaghan equation of state.

systems assume a lattice, i.e. translational invariance, in general the muon needs to be added into a larger supercell to maximise the distance between muons. This is in line with the very dilute limit we operate in experimentally, where even at pulsed sources there are only a few thousand to tens of thousands of muons at most in the sample at any one time. In the case at hand the unit cell is sufficiently large ($a = 10.6 \text{ \AA}$ with 88 atoms) [109] that no supercell is needed or even computationally viable. I introduced the muon, modelled via a hydrogen pseudopotential, onto a $10 \times 10 \times 10$ grid of points from which I selected only those that were symmetry inequivalent, and furthermore not on a point of high symmetry to remove the possibility of metastable solutions. For each of the remaining points, supplemented by a few hand-picked ones, I carried out a relaxation DFT calculation in which all atoms, including the muons, were allowed to change position until the forces

	E_{wfc} (Ry)	E_{ρ} (Ry)	k -grid	functional	comments
$\text{Pr}_2\text{Sn}_2\text{O}_7$	50	300	$2 \times 2 \times 2$	GGA	ultrasoft, $4f$ in core
	50	550*	$2 \times 2 \times 2$	GGA	ultrasoft, $4f$ in valence
$\text{Pr}_2\text{Zr}_2\text{O}_7$	60	360	$2 \times 2 \times 2$	GGA	ultrasoft, $4f$ in core

Table 6.1: Summary of the computational details employed in this chapter. These parameters produce well converged results in agreement with bulk properties of the shown compounds. E_{wfc} and E_{ρ} represent the cut-offs for the kinetic energy and the charge density, respectively. The GGA functional is that of Ref. [60] and the ultrasoft potentials were created following the formalism of Ref. [108]. *Explicit treatment of the $4f$ orbitals requires significantly higher cut-offs due to their more complex spatial nature.

acting on them had converged to an accuracy within 10^{-3} Ry/a.u.

Muon stopping site

The relaxation calculations converge on three separate crystallographic positions for a bare μ^+ site, two of which are higher in energy by about 0.45 eV and 0.91 eV per unit cell. Thus, there is one energetically favoured stopping site for the muons. This site is shown in Figure 6.5 together with the distances to the nearest O and Pr ions. An important thing to note is that the muon forms an O–H like bond with an oxygen on the $48f$ Wyckoff position (labelled O1) with a bond length of 1.0 Å. This bond formation has been observed in previous μ^+ SR studies [70, 111–114] and appears to be a very robust occurrence in oxides.

Another crucial observation is that the muon site is located on a mirror plane defined by the oxygen it bonds to and the two Pr ions this oxygen is linked to, and it is almost perfectly opposite one of the Pr ions with the μ –O–Pr bond angle (indicated by the longest blue arrow in Figure 6.5) being about 167.7° . In fact the muon site is located at Wyckoff position $96g$ and therefore it does not satisfy the local 3-fold symmetry of the unperturbed system and hence necessarily breaks the local symmetry of its environment. The fractional coordinates of the muon sites are documented in Table 6.2 for both the Sn and Zr members of the Pr based pyrochlores.

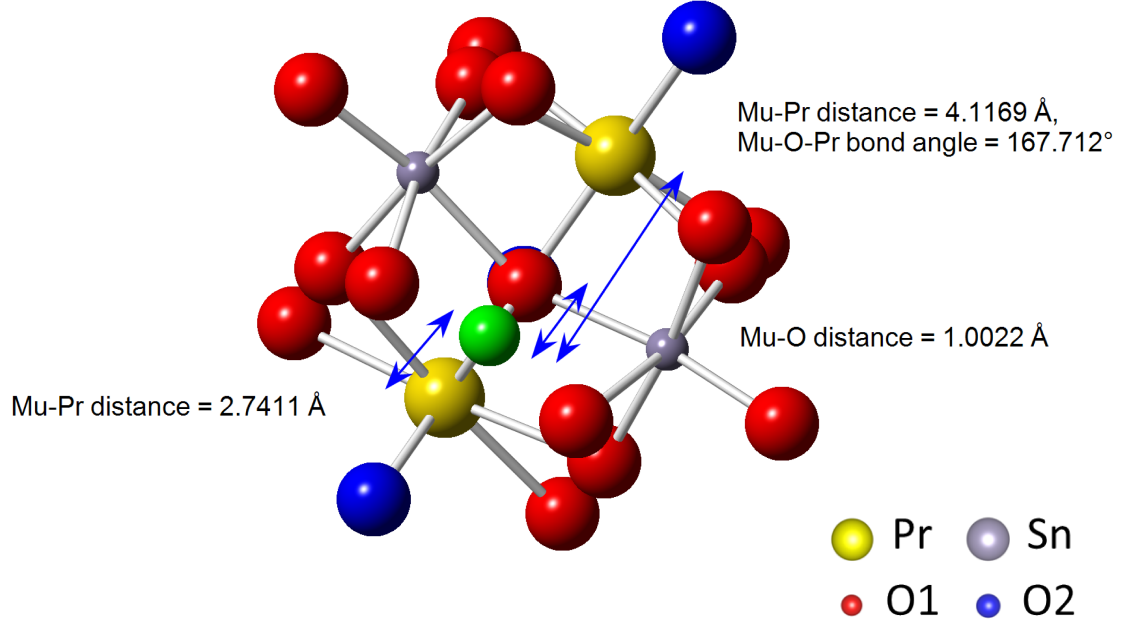


Figure 6.5: Muon stopping site in $\text{Pr}_2\text{Sn}_2\text{O}_7$. The positive muon is indicated by the green sphere and label Mu, and the distances to the nearest ions are illustrated by the blue arrows. The given bond angle is measured along the $\mu\text{-O-Pr}$ bonds which roughly follow the longest blue arrow.

Fract. Coords.	x	y	z	WP
$\text{Pr}_2\text{Sn}_2\text{O}_7$	-0.0125	0.0471	0.2028	96g
$\text{Pr}_2\text{Zr}_2\text{O}_7$	-0.0115	0.0465	0.2035	96g

Table 6.2: Fractional coordinates of the muon sites and their Wyckoff positions (WP) as calculated by DFT relaxation calculations. The unit cells are taken to be the experimentally measured cubic ones with lattice parameters $a_{\text{Sn}} = 10.6 \text{ \AA}$ [109] and $a_{\text{Zr}} = 10.69 \text{ \AA}$ [115]. Note that the origin of the unit cell was chosen such that the fractional coordinates for the different atoms are Sn/Zr:(0, 0, 0), Pr:(1/2, 1/2, 1/2), O2:(3/8, 3/8, 3/8), O1:(x , 1/8, 1/8), where the parameter x for the two compounds presented here was measured to be $x_{\text{Sn}} = 0.33148(5)$ [109] and $x_{\text{Zr}} = 0.335$ [115].

Electrostatic potential

An alternative method to investigate the possible muon site candidates is by considering the electrostatic Coulomb potential of the system at hand. In particular regions of high potential are of interest, because they correspond to the lowest energy required to add a positive charge such as the muon in those regions. The Coulomb potential for $\text{Pr}_2\text{Sn}_2\text{O}_7$ is shown in Figure 6.6 with the maximum potential regions coloured in blue and an isosurface at 3 eV below the maximum plotted in red. Suitable cuts through the unit cell have been chosen to highlight the most relevant regions. When comparing the global maxima of the electrostatic potential with the muon sites determined through the full DFT relaxation technique employed in the previous section an excellent agreement is observed. This correspondence is consistent throughout all the muon site calculations presented in this chapter, and has also been found in previous “DFT+ μ ” studies [70, 116]. Thus confirming the suitability of the electrostatic potential as an indicator of possible muon sites. However, it should be noted that considerations of the Coulomb potential do not account for any local distortions and therefore should only be seen as a first order approximation of the actual muon sites and as a method for double checking the plausibility of results obtained from full relaxation computations.

Muonium

As mentioned in chapter 3.3 the muon typically comes to rest at an interstitial site in either a bare, positively charged μ^+ state or through electron capture alternatively forms a hydrogen like state called muonium (Mu). I repeated the procedure of the previous sections in the case of a unit cell of neutral charge to check the possibility of a muonium stopping site. The subsequent DFT relaxation computations yield one candidate site for a muonium state, which is about 0.76 eV higher in energy per unit cell than the previously determined μ^+ stopping site. Investigating the local spin density, plotted in Figure 6.7, further reveals a hydrogen like s -orbital for which a population analysis yields a total Löwdin charge [118, 119]

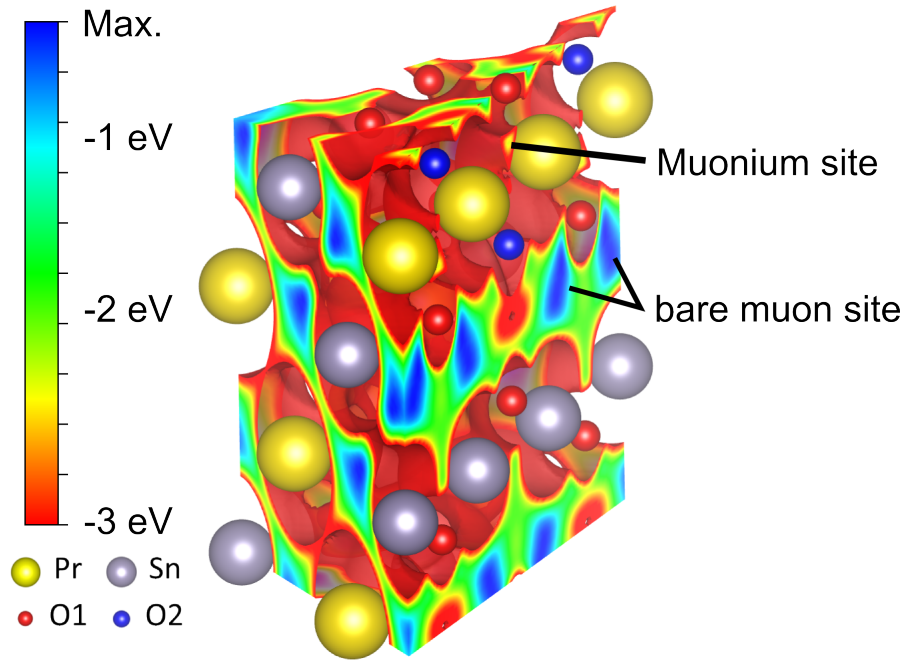


Figure 6.6: Electrostatic potential for $\text{Pr}_2\text{Sn}_2\text{O}_7$. The maximum potential, shown in blue, is chosen as the reference value and an isosurface at 3 eV below this maximum is plotted in red. The sites for μ^+ and muonium states obtained through DFT relaxation calculations are indicated. The VESTA [117] software suite was employed for the visualisation.

of $s = 0.86$. Importantly in this scenario there is no formation of a O–H like bond and in fact the nearest oxygen ions are at a distance of about $2.2 \text{ \AA}$ to the muonium, indicating no bond formation. Furthermore, it can be noted that the muonium is located on both a 3-fold axis and a mirror plane, and thus it does not break the local symmetry of its environment. The fractional coordinates of the muonium state in $\text{Pr}_2\text{Sn}_2\text{O}_7$ are $(0.013, 0.013, 0.737)$ with Wyckoff position $32e$ in the coordinate system described in the caption of Figure 6.5. The location of this site is also indicated in the electrostatic potential plot presented in Figure 6.6, although muonium sites due to their neutral charge do not allow a straightforward identification via the Coloumb potential. In conclusion, the formation of a muonium state is possible in the compounds at hand but it is very energetically unfavourable and hence will not be considered further in the following discussions.

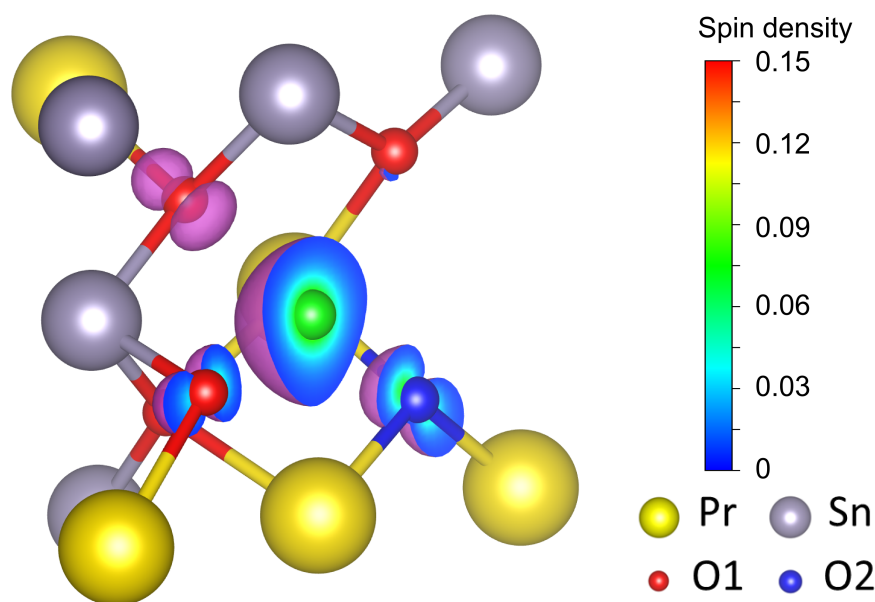


Figure 6.7: Spin density plot around the muonium site in $\text{Pr}_2\text{Sn}_2\text{O}_7$.

Muon induced distortions

Now that the location of the muon site within the unit cell is established it is instructive to consider the perturbation to the local environment caused by the presence of the muon. In Figure 6.8 the distortions of all the atoms in the unit cell are plotted as a function of the final distance from the muon site. A few insightful observations can be made, one of which is that the oxygen that the muon forms a 1 Å O–H like bond with is distorted the most and is almost “pulled” towards the muon. Additionally, we can also notice that the two Sn and two Pr ions that initially form a tetrahedron with this oxygen are all strongly “pushed” away by the positively charged muon as well. Furthermore, we note that the distortions decrease as the distance to the muon increases. This is as one would expect due to the system trying to recover to its bulk structure. However, it is important to bear in mind that all the DFT calculations assume a lattice in which each unit cell contains one muon and therefore the large distance results shown in Figure 6.8 are likely overestimating the distortions because the atoms in those regions are potentially affected by muons in the adjacent unit cells as well.

A three-dimensional illustration of the muon induced distortions is presented in

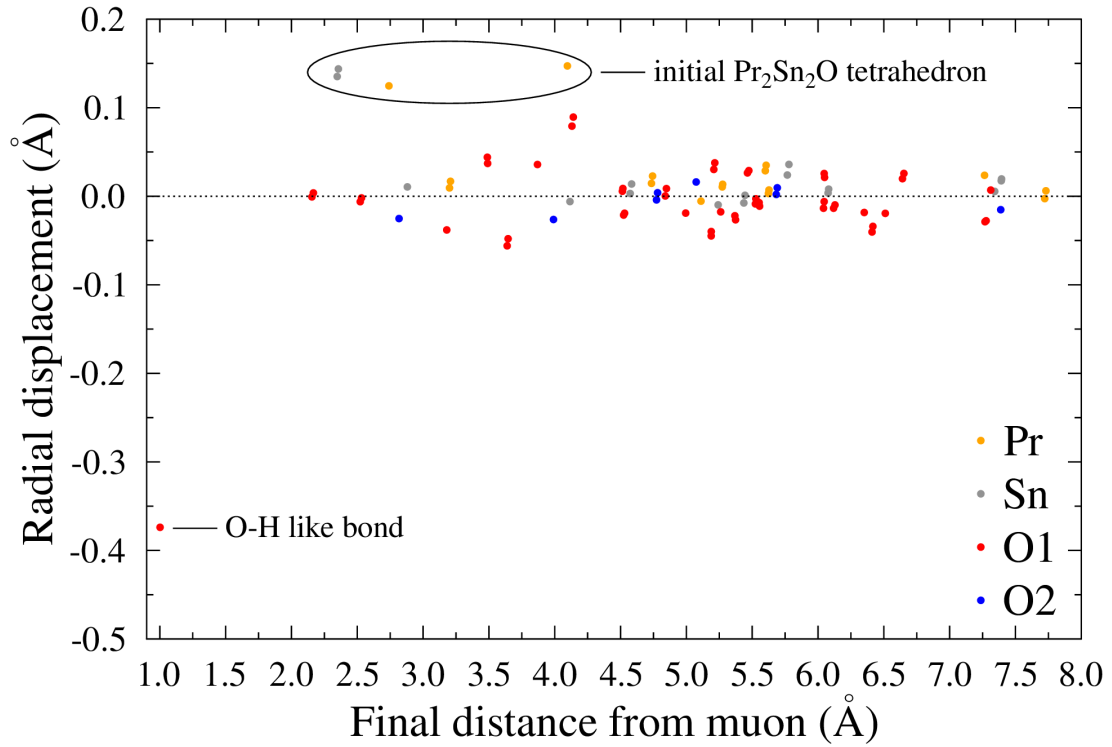


Figure 6.8: Distortions of the atomic positions in $\text{Pr}_2\text{Sn}_2\text{O}_7$ due to the presence of a positive muon. Radial displacement here refers to the change in distance to the muon site. The oxygen that forms an O-H like bond with the muon is indicated, in addition to the two Sn and two Pr ions it initially forms a tetrahedron with.

Figure 6.9. This figure focusses on the Pr ions and their respective O environments as they turn out to be the crucial elements in exposing the muon induced effects in our experimental $\mu^+\text{SR}$ data. We can observe from Figure 6.9 that the effect of the muon is to “pull” in one of the oxygens and thereby stretch the Pr-O bond with the ion labelled Pr3 and rotate the Pr-O bond with ion Pr1. The remaining positions appear much less significantly distorted, which agrees with the results shown in Figure 6.8 above.

In the subsequent sections I will argue that the change of the PrO_8 unit will result in a change of the Pr crystal fields which in turn is responsible for our experimental observations. Therefore, it is at this point instructive to investigate the extent of the distortion of each Pr ion’s local oxygen environment. I parametrise the perturbation of each PrO_8 unit by adding the distance changes between the oxygens and the Pr atom in quadrature. The resulting quantity has the dimension

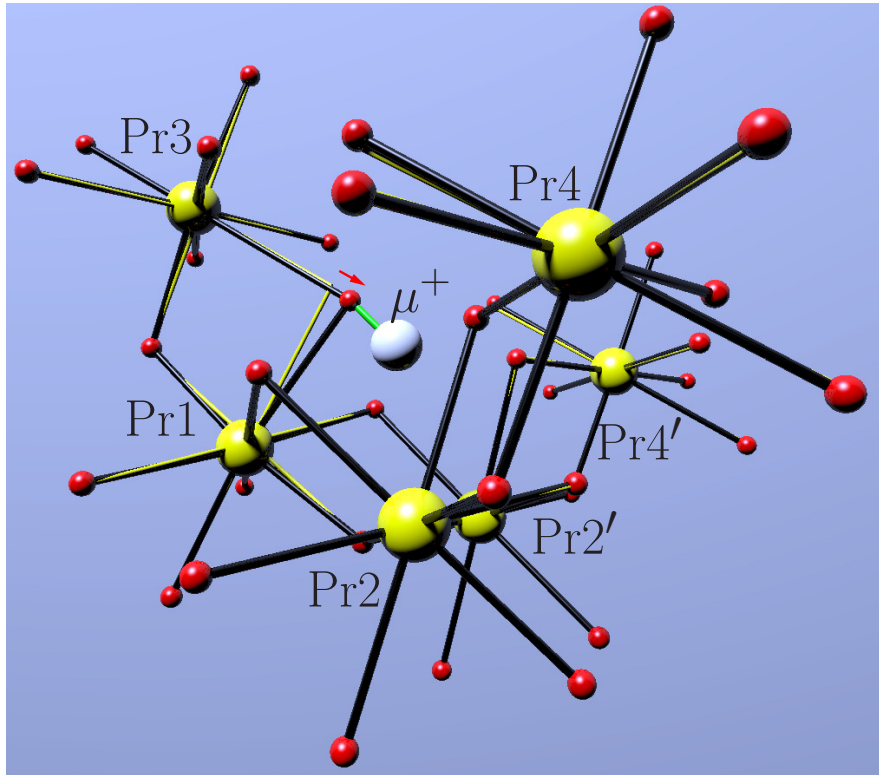


Figure 6.9: Three-dimensional illustration of the local muon induced distortions. Yellow, red and grey spheres denote Pr and O ions and the muon (Sn ions are omitted for visibility). The black and yellow bonds represent the atomic positions with and without the presence of the muon, respectively. The nearest Pr ions are labelled and numbered according to their distance to the muon, with primes denoting equidistance (see Figure 6.10 below as well). From Ref. [96].

of a length and is plotted in Figure 6.10 as a function of the Pr- μ distance. From this figure we can confirm the earlier qualitative observation based on Figure 6.9 that indeed the most distorted PrO_8 units are those of the two Pr ions associated with the oxygen the muon bonds to. We furthermore notice that the most perturbed PrO_8 environment is not particularly close to the muon stopping site and that in fact two less distorted Pr ions, labelled Pr2 and Pr2' in Figures 6.9 and 6.10, are considerably closer. This suggests that the muon induces highly anisotropic distortions and that the most severe impacts of muon induced effects are not necessarily located closest to the muon site.

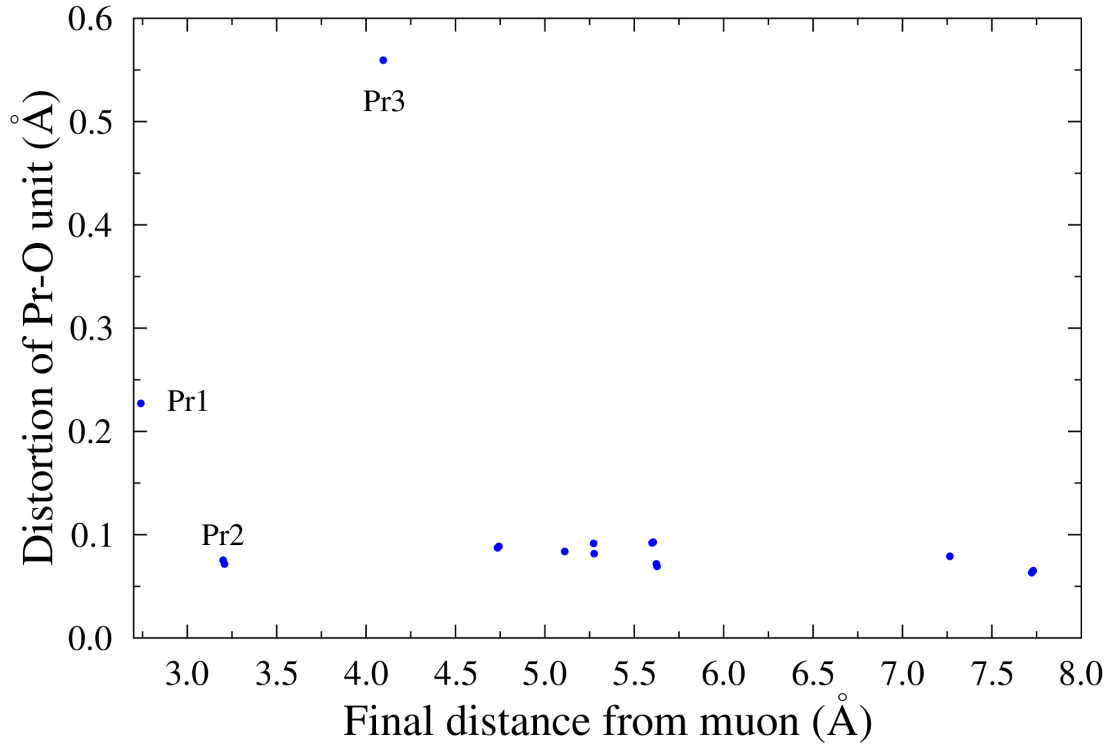


Figure 6.10: Distortion of the PrO_8 units as a function of distance from the muon site. The distortion is calculated by adding all Pr-O distance changes in quadrature. The four nearest Pr ions are labelled and numbered according to their distance to the muon, in line with the notation in Figure 6.9. The unlabelled points correspond to further out Pr ions.

6.1.4 Crystal fields

After having calculated the oxygen environments of each Pr ion and their change upon addition of an implanted muon, it is now possible to investigate the changes

of the crystal field levels of each Pr ion. The procedure for calculating the crystal fields adopted here is the following: first of all point charges are placed at the relative positions of all the eight oxygens neighbouring each Pr ion as determined through experimental measurements. The oxygen charges are then augmented from their usual $-2e$ values to produce crystal field levels of the Pr^{3+} ions commensurate with those determined through previous neutron experiments [104]. Subsequently, the oxygen positions are amended to those calculated for the case of a muon being implanted and the crystal field levels of each individual Pr ion is recalculated. The obtained results are summarised in Figure 6.11 for the Pr atoms closest to the muon stopping site.

Two important observations present themselves in Figure 6.11. Firstly, the doublet ground state is split into two singlets. This is possible because the Pr^{3+} are non-Kramers ions, which means that any multiplet crystal field levels are not symmetry protected from being split. Because the implanted muons necessarily break the local symmetry, as I established in section 6.1.3, they also unsurprisingly lead to this splitting of the doublet ground state. Secondly, we can further note that the splitting is largest for the two Pr ions (labelled Pr1 and Pr3) associated with the oxygen that bonds to the muon, in agreement with the results of Figure 6.10. However, as already suggested in the previous section there are two additional Pr ions (labelled Pr2 and Pr2') which are in fact closer to the muon than the most severely affected one (Pr3). The resultant ground state splittings of the Pr crystal fields are summarised in Table 6.3 together with the distortions of the associated PrO_8 units and the $\text{Pr}-\mu$ distances calculated in the previous section.

Pr atom	1	2,2'	3	4,4'
$\text{Pr}-\mu$ separation (Å)	2.7	3.2	4.1	4.7
PrO_8 unit distortion (Å)	0.23	0.07	0.56	0.09
Splitting ϵ (meV)	4.8	1.3	11.4	4.0

Table 6.3: Parameters obtained from DFT and crystal field calculations in the case of a muon having implanted into $\text{Pr}_2\text{Sn}_2\text{O}_7$ and perturbing its local environment. The values are given for the Pr ions closest to the muon, numbered according to their $\text{Pr}-\mu$ separation. Adapted from Ref. [96].

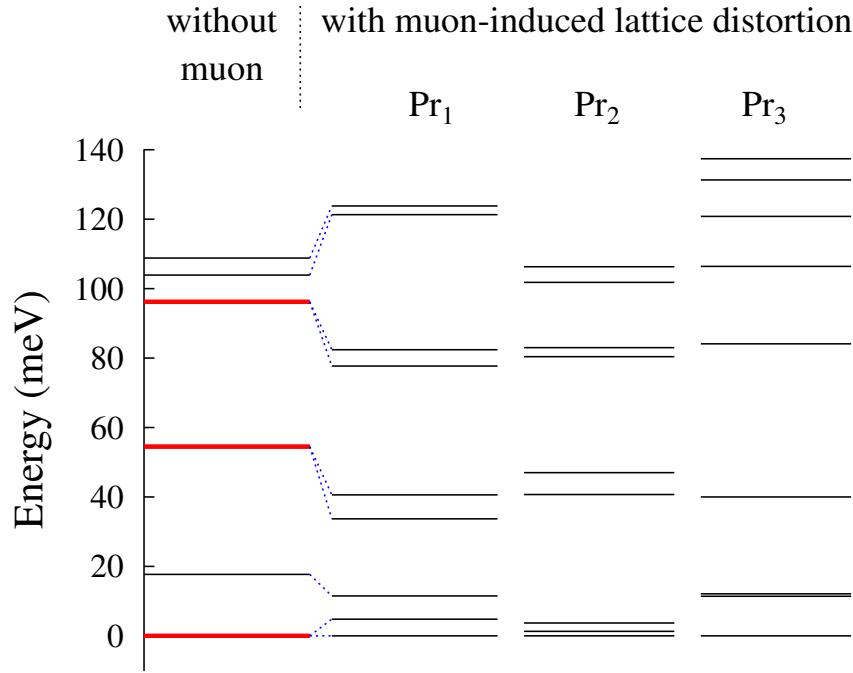


Figure 6.11: Crystal field levels of the Pr^{3+} ions in $\text{Pr}_2\text{Sn}_2\text{O}_7$. Thick red lines denote doublets and the dotted blue lines indicate the changes of the individual levels. The unperturbed values (without the muon) shown on the left were established via neutron measurements [104]. From Ref. [96].

6.1.5 Hyperfine enhancement

The main aim of this section is to establish the last corner stone in our explanation for the experimental $\mu^+\text{SR}$ observations of the Pr based pyrochlores. We can recall from section 6.1.2 that the $\mu^+\text{SR}$ data revealed a static distribution of moments with a mean square width an order of magnitude too large to originate from Pr nuclear moments. Here I will present an interpretation based on a distribution of hyperfine enhanced nuclear moments.

Hyperfine enhancement describes a phenomenon commonly encountered in NMR investigations, in which the nuclear moment of an ion is increased through the splitting of its magnetic doublet ground state. The subsequent enhancement is greater the larger the energy gap between the two split singlets is. Therefore, this phenomenon presents itself naturally as a possible mechanism that can occur

in $\text{Pr}_2\text{Sn}_2\text{O}_7$, whereby the splitting of the doublet ground state is induced through the presence of a positive muon distorting the crystal field environments of its neighbouring Pr ions.

A possible theoretical model for hyperfine enhancement in a two state system has previously been developed by Bleaney [120]. Consider the general Hamiltonian for a nucleus with spin $\mathbf{I}$ in an external field $\mathbf{B}$

$$H = H_X + g_I\mu_B\mathbf{B} \cdot \mathbf{J} + A_J\mathbf{J} \cdot \mathbf{I} - g_J\mu_B\mathbf{B} \cdot \mathbf{I}, \quad (6.1)$$

where H_X incorporates the energy splitting ϵ between the two singlet states. By forming the partition function and subsequently differentiating it, the magnetic moment $m = k_B T (\partial \ln Z / \partial B)_T$ can be evaluated. After defining the electronic matrix element $\alpha = \langle E | \hat{J}_z | G \rangle$ that mixes the two singlets $|G\rangle$ and $|E\rangle$ via the usual angular momentum operator, the resulting expression for the moment in the case of no applied field becomes [96]:

$$m = m_0 + \frac{\eta}{\tilde{\epsilon}} \tanh\left(\frac{\tilde{\epsilon}}{k_B T}\right). \quad (6.2)$$

Additionally, the following parameters have been defined here:

$$m_0 = g_J \mu_B I_z \quad (6.3)$$

$$\eta = g_J \mu_B \alpha^2 A_J I_z \quad (6.4)$$

$$\tilde{\epsilon} = \sqrt{(\epsilon/2)^2 + (\alpha A_J I_z)^2}. \quad (6.5)$$

The enhanced magnetic moment is then expected to be proportional to the static field width via $\Delta \propto m$, and we furthermore can substitute the values $A_J/h = 1.093 \text{ GHz}$ [120] and $I_z = 5/2$ for the Pr nuclei in this case.

The above scenario describes the enhancement of a single magnetic moment due to a splitting of size ϵ . However, in the case of $\text{Pr}_2\text{Sn}_2\text{O}_7$ we showed that the Pr ions

experience different ground state splittings depending on their relative position to the muon. For simplicity we can choose a model that is restricted to two differently split moments contributing to Δ . This restriction is based on the observation that the muon only has three nearby Pr ions (labelled Pr1, Pr2 and Pr2' in the previous sections, with Pr2 and Pr2' behaving equivalently) which are likely to dominate the dipole interaction, since the dipole-dipole coupling falls off as r^{-3} . Taking the two moments to add in quadrature ($\Delta \propto \sqrt{m_1^2 + m_2^2}$) the resulting model can be fitted to the measured ZF μ^+ SR data. The results of this fitting are plotted in Figure 6.12 and demonstrate an excellent applicability of the two moment model to our data. Furthermore, the energy splittings that can be extracted for the two moments from the model are summarised in Table 6.4. Comparing these values with those obtained from the crystal field calculations presented in Table 6.3 we observe that they are in fair agreement with the theoretically calculated splittings for the Pr1 and Pr2 sites. Especially considering the sensitivity of the crystal field levels to the positions of the oxygen atoms surrounding each Pr ion, any small discrepancies between the theoretically predicted and experimentally fitted energy splittings is expected to be well within the inherent uncertainties.

Compound	B_{rms}	ϵ_1	ϵ_2
Pr ₂ Sn ₂ O ₇	5.65(5) mT	6(1) meV	0.6(1) meV

Table 6.4: Energy gaps extracted from a two moment hyperfine enhancement model (see the main text) fitted to the experimentally observed μ^+ SR relaxation rate. The corresponding data is shown in Figure 6.12. Adapted from Ref. [96].

6.1.6 Conclusions

In conclusion, the detailed analysis of the μ^+ SR measurements of the Pr based pyrochlores reveals that in certain circumstances it is possible for a μ^+ SR experiment to reflect the response to the implantation of the positive muons rather than any intrinsic sample behaviour. In the case of Pr₂B₂O₇ these muon induced effects dominate because the Pr³⁺ are non-Kramers ions with a high symmetry doublet ground state that is split through the local distortions caused by the muons. By

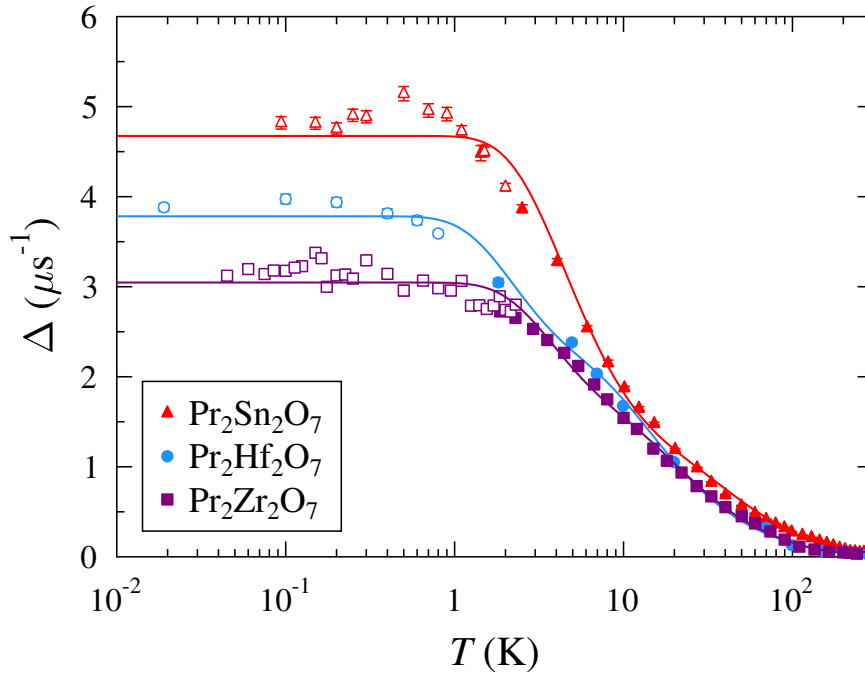


Figure 6.12: Static relaxation rate Δ observed in μ^+ SR measurements of the Pr based pyrochlores. The solid lines represent fits employing the model of two differently enhanced magnetic moments described in the main text. From Ref. [96].

combining DFT and crystal field calculations to determine the muon stopping sites and to quantitatively evaluate the shifts of the Pr crystal field levels I demonstrated that the experimentally observed static distribution of moments is well explained by a hyperfine enhancement of the Pr nuclear moments. This enhancement originates from the ground state splitting caused by the local symmetry breaking muon presence. Furthermore, the work presented here implies that the muon induced distortions are highly anisotropic and can in general be significant in oxides due to the formation of an O–H like bond of length 1 Å. However, in magnetically ordered systems this is expected to have a minimal if not negligible effect as the muon is expected to predominantly couple to the local magnetic field in that case. Nonetheless, if the system studied via μ^+ SR is in a delicately balanced ground state, be it because of low dimensional or frustrated magnetism for example, or especially in the case of a highly symmetric non-Kramers multiplet ground state, the possibility of muon induced effects should be considered. A viable procedure to

quantitatively investigate such possible effects has been demonstrated here through the utilisation of DFT computations.

6.2 $A_2Ti_2O_7$

6.2.1 Introduction

After the realisation that the μ^+ SR experiments performed on the Pr based pyrochlores $Pr_2B_2O_7$ ($B = Sn, Zr, Hf, Ir$) do not exhibit any of the previously observed phenomena attributed to a quantum spin ice ground state but instead reflect purely muon induced effects, the question arises naturally whether earlier μ^+ SR measurements of the structurally very similar Ti based pyrochlores $A_2Ti_2O_7$ ($A = Dy, Ho$) might have been affected in analogous ways. $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$ are counterparts to the $Pr_2B_2O_7$ with experimentally confirmed classical spin ice ground states, as already discussed in sections 2.2.1 and 6.1.1 above. Especially $Ho_2Ti_2O_7$ warrants a detailed investigation due to the Ho^{3+} also being non-Kramers ions with a magnetic doublet ground state. This doublet in theory could and should be split by the anisotropic perturbations caused by the implantation of a muon. Although the Dy^{3+} ions on the other hand are Kramers ions with a set of symmetry protected doublet crystal levels, the changes of the energy gap between the ground state and the first excited state are of particular interest in this case as experimentally a thermally activated behaviour was observed [121] that may be related to this energy gap.

6.2.2 Muon stopping site

The implantation sites of the muon and the consequently distorted atomic positions were determined in a series of DFT calculations entirely analogous to those I presented in detail for the Pr based pyrochlores in section 6.1. After confirming that the chosen pseudopotentials and energy and density cut-offs, summarised in Table 6.5, reproduce the crystal structures to an adequate accuracy and yield

a sufficiently large band gap, the muon site was determined through structural relaxation calculations. The resulting muon stopping sites are recorded in Table 6.6 and are entirely consistent with electrostatic potential considerations. Moreover, all the properties of the muon sites discussed in detail in section 6.1.3 for the case of $\text{Pr}_2\text{Sn}_2\text{O}_7$ are also found in $\text{Dy}_2\text{Ti}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$, namely the formation of a 1 Å long O–H like bond and local distortions equivalent to those presented in Figures 6.8 to 6.10.

	E_{wfc} (Ry)	E_{ρ} (Ry)	k -grid	functional	comments
$\text{Dy}_2\text{Ti}_2\text{O}_7$	50	300	$2 \times 2 \times 2$	GGA	ultrasoft, 4 <i>f</i> in core
$\text{Ho}_2\text{Ti}_2\text{O}_7$	60	360	$2 \times 2 \times 2$	GGA	ultrasoft, 4 <i>f</i> in core

Table 6.5: Summary of the DFT computational details for the Ti based pyrochlores. These parameters produce well converged results in agreement with bulk structural properties of the shown compounds, including their lattice parameters $a_{\text{Dy}} = 10.124$ Å and $a_{\text{Ho}} = 10.104$ Å [122]. E_{wfc} and E_{ρ} represent the cut-offs for the kinetic energy and the charge density, respectively. The GGA functional is that of Ref. [60] and the ultrasoft potentials were created with the formalism of Ref. [108].

Fract. Coords.	x	y	z	WP
$\text{Dy}_2\text{Ti}_2\text{O}_7$	-0.007	0.048	0.202	96 <i>g</i>
$\text{Ho}_2\text{Ti}_2\text{O}_7$	-0.006	0.046	0.204	96 <i>g</i>

Table 6.6: Fractional coordinates of the muon sites and their Wyckoff positions (WP) as calculated by DFT relaxation calculations. The unit cells are taken to be the experimentally measured cubic ones with lattice parameters $a_{\text{Dy}} = 10.124$ Å and $a_{\text{Ho}} = 10.104$ Å [122]. Note that the origin of the unit cell was chosen such that the fractional coordinates for the different atoms are Ti:(0, 0, 0), Dy/Ho:(1/2, 1/2, 1/2), O2:(3/8, 3/8, 3/8), O1:(x , 1/8, 1/8), where the parameter x for the two compounds presented here was measured to be $x_{\text{Dy}} = 0.3275(5)$ and $x_{\text{Ho}} = 0.3285(5)$ [122].

6.2.3 Crystal fields

Using the atomic positions calculated via DFT in the presence of the positive muon one can then determine the crystal field levels of the Dy and Ho ions. The point charge model employed to this end is generated following the same procedure described in section 6.1.4 and it produces the crystal field levels presented in Figures 6.13 and 6.14 for $\text{Dy}_2\text{Ti}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$, respectively. It should be noted that just like in $\text{Pr}_2\text{Sn}_2\text{O}_7$ the muon has a set of neighbouring moment bearing

ions for which the crystal field levels are displayed in the figures. These ions are numbered according to their distance to the muon site and correspond directly to the Pr ions labelled similarly in section 6.1.4.

The crystal fields of the Dy ions, shown in Figure 6.13, confirm that the Kramers doublets are not split and thus no hyperfine enhancement can occur in this material. However, the energy gap between the ground state and the first excited state is decreased significantly. The corresponding energy gaps obtained for the Dy ions closest to the muon are indicated in the figure. It is important to note that they are in decent agreement with the thermal activation energy of about 210 K observed experimentally [121, 123]. Therefore, the activated behaviour observed in the μ^+ SR experiments could potentially be affected quantitatively by the muon induced distortions decreasing the energy gap of the lowest lying crystal field levels.

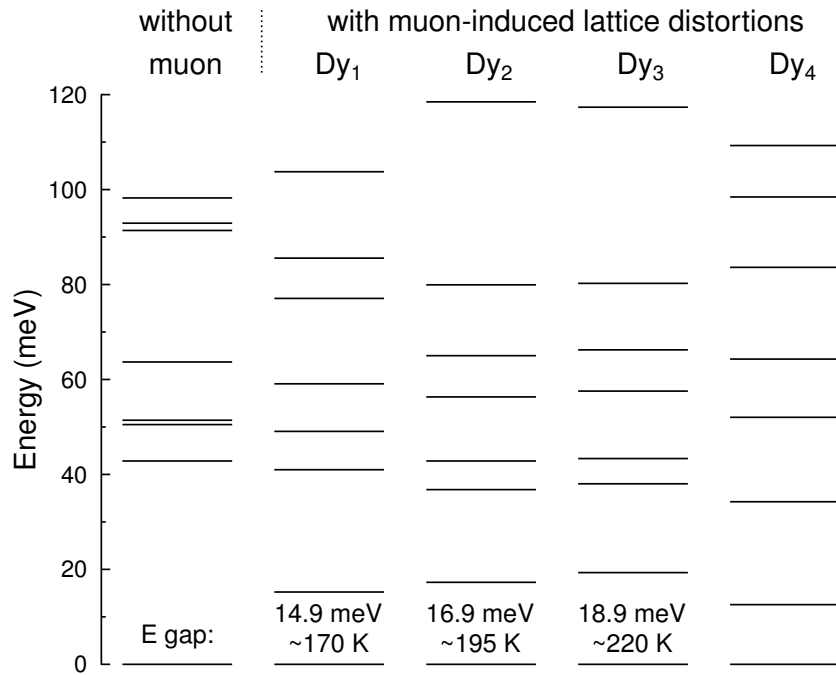


Figure 6.13: Crystal field levels of the Dy^{3+} ions in $Dy_2Ti_2O_7$. The unperturbed values (without the muon) shown on the left were determined by scaling the experimentally determined crystals fields in $A_2Ti_2O_7$ ($A=Ho, Tb$) [124]. Note that each level represents a Kramers doublet. The energy gap between the ground and first excited states is also indicated.

Figure 6.14 presents the crystal field levels of the Ho ions in $Ho_2Ti_2O_7$ both

without and including muon induced distortions. It can immediately be observed that any doublet states are split due to the muon lowering the symmetry of its environment, which is possible because the Ho^{3+} are non-Kramers ions. However, the splittings of the doublet ground states are only of the order of 0.01 meV and thus –surprisingly– negligibly small for all the Ho ions nearest to the muon. Therefore, any hyperfine enhancement caused by this splitting will be insignificant and cannot negatively affect the μ^+ SR measurement. We can additionally consider the energy gaps to the next highest lying crystal levels, since this gap has previously been suggested to be at the heart of an observed activated behaviour [121, 125]. The obtained gaps are in the range 10.9–12.4 meV (125–145 K) and thus considerably smaller than the previously reported value of about 210 K [121, 125]. Nonetheless, we can say with confidence that the observed μ^+ SR behaviour in $\text{Ho}_2\text{Ti}_2\text{O}_7$ cannot be attributed to muon induced effects but reflects the intrinsic sample behaviour (albeit the quantitative details may be marginally affected by the muon presence).

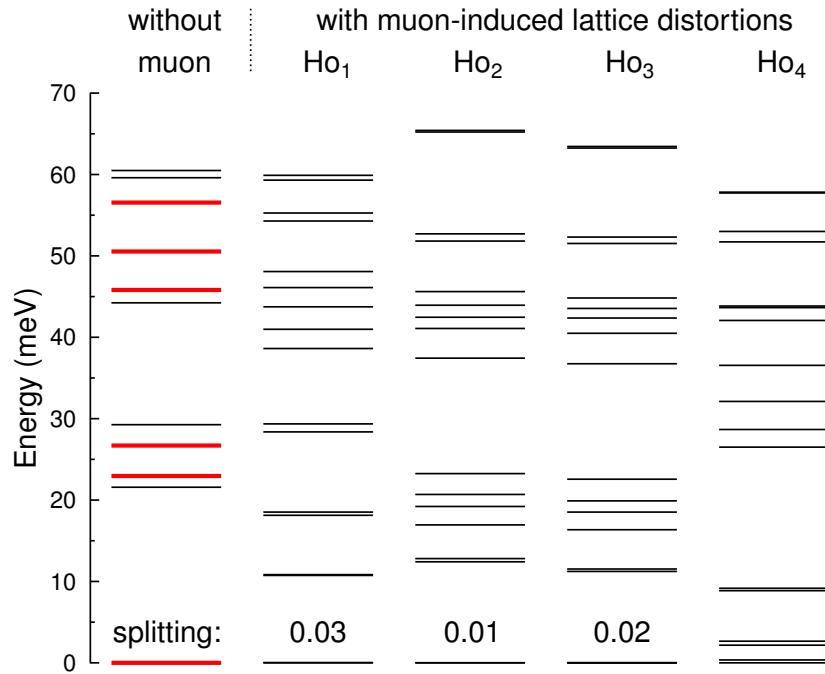


Figure 6.14: Crystal field levels of the Ho^{3+} ions in $\text{Ho}_2\text{Ti}_2\text{O}_7$. Thick red lines denote doublets. The unperturbed values (without the muon) shown on the left were established via neutron measurements [124]. The very small splittings of the ground state double (in meV) are indicated in the plot. The energy gaps to the next higher lying excited state are in the range of 10.9–12.4 meV (125–145 K) for Ho1 to Ho3.

6.2.4 Conclusions

In summary, I determined via DFT calculations the muon sites in the spin ice pyrochlores $\text{Dy}_2\text{Ti}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$ and the distortions of the local crystal structure that the muons cause. The results are entirely consistent with and very similar to those obtained for the Pr based pyrochlores presented earlier in this chapter. The subsequently evaluated crystal field levels of the perturbed ions reveal that in the two compounds at hand the energy splitting of the doublet ground state is negligibly small, which is the case for the Ho non-Kramers ions, or identically zero, which is the case for the Dy Kramers ions. Thus, we can conclude that the experimentally observed behaviour in the $\mu^+\text{SR}$ experiments cannot be influenced by any hyperfine enhanced nuclear moments and therefore they are expected to qualitatively reflect the intrinsic sample behaviour. Nevertheless, an analysis of the higher lying excited crystal field levels reveals that the energy gap between the ground state and the first excited state is roughly in line with an thermal activation barrier reported for $\text{Dy}_2\text{Ti}_2\text{O}_7$ and smaller than a corresponding activation energy proposed for $\text{Ho}_2\text{Ti}_2\text{O}_7$.

6.3 Outlook

The insights gained into muon induced effects in $\text{Dy}_2\text{Ti}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$ are currently in the process of being combined with recently performed single crystal $\mu^+\text{SR}$ measurements. A corresponding publication is in preparation.

A potential future addition to the “DFT+ μ ” tool set I am interested in is the possibility of employing Wannier orbitals to determine the crystal field levels of the ions using *ab initio* calculations.

Chapter 7

α -RuCl₃

This chapter presents an investigation of the magnetic behaviour of a powder of α -RuCl₃ using μ^+ SR measurements in combination with dipolar field and DFT calculations. Most of the work presented in this chapter has been published as a Rapid Communication in Physical Review B [126].

After giving a brief account of existing publications and the current state of research on α -RuCl₃ I summarise the most important aspects of the synthesis and structural analysis of our powder sample. I then present the results of μ^+ SR experiments, which reveal two oscillation frequencies with distinct transitions at around 11 K and 14 K. Subsequently, I utilise DFT calculations to identify likely muon stopping sites and combine these with dipolar field calculations to show that the two measured muon rotation frequencies are consistent with two inequivalent muon sites within a zig-zag antiferromagnetic structure proposed previously. Additionally, I argue that the two distinct transitions can be interpreted as originating from a temperature regime (11–14 K) in which static correlations are established within the two-dimensional Ru layers, but interlayer correlations are not significant, with full three-dimensional order setting in below the lower 11 K transition.

My contributions include conducting the μ^+ SR experiments at the Swiss Muon Source, analysis and fitting of the μ^+ SR data sets obtained at both the ISIS muon facility and the Swiss Muon Source, analysis and visualisation of the electrostatic

potential obtained via DFT, prediction of muon site candidates and calculations of dipole fields for different magnetic structures and subsequently drawn conclusions.

My collaborators helped make this project possible in various ways. A. Haghighirad synthesised the sample and performed the x-ray structural analysis; P. Baker and S. Blundell carried out the μ^+ SR measurements at the ISIS muon facility; R. Valentí and Y. Li performed the DFT calculations; my supervisor S. Blundell helped carry out the dipole field calculations and the muon experiments.

7.1 Introduction

α -RuCl₃ is a layered material in which Ru ions are arranged on a nearly geometrically perfect honeycomb lattice, making it one of the many solid-state systems with triangular architectures that can realise novel magnetically frustrated states, as discussed in chapter 2.2. This compound is thought to be a spin-orbit assisted Mott insulator [127, 128], in which both the near two-dimensionality of the separate honeycomb layers and bond-dependent interactions are proposed to be major ingredients [129]. Furthermore, this material has attracted great interest since unconventional excitations observed via Raman [22] and inelastic neutron scattering [23] (INS) have been presented as evidence that α -RuCl₃ may be close to a realisation of the coveted Kitaev quantum spin liquid ground state. A subsequent study of the magnetic response function measured via INS also reported signatures of Majorana fermion excitations that were predicted to occur in Kitaev’s quantum spin liquid [24].

There is however a history of conflicting reports about the crystal and magnetic structures and magnetic phase transitions. Although the crystal structure has now largely been accepted to be monoclinic (spacegroup $C2/m$) [130], there are still open questions regarding the unconventional magnetism occurring in this compound. While early studies pointed towards an antiferromagnetic transition with numerous reported temperatures of 13 K [131], 15.6 K [132] or even 30 K [133],

later investigations proposed a potential second transition around 8 K [134–136] thought to originate from low-moment magnetism. Recent neutron powder diffraction provided evidence for a single transition to a zig-zag antiferromagnetic state with 2-layer stacking at $T_N = 13$ K [130], though a later single crystal neutron study has proposed a single transition at 8 K to a 3-layer stacking magnetic order in pristine single crystals and a change of T_c to 14 K upon mechanical deformation of the crystals [137]. These differences in observed properties are thought to originate from the propensity of this compound to exhibit stacking faults between the weakly coupled honeycomb layers [130].

Positive muons as local magnetic probes have been extensively utilised in studies of various layered magnets [138–140], including Na₂IrO₃ [16] which has a layered honeycomb structure similar to α -RuCl₃. Therefore muons are an ideal tool to help with the investigation of the magnetic behaviour of α -RuCl₃.

7.2 Sample synthesis and stacking faults

Polycrystalline samples of α -RuCl₃ were synthesised by vacuum sublimation ($p \approx 10^{-5}$ mbar) from commercial RuCl₃ powder in a three-zone furnace with a hot and cold end of 650 °C and 450 °C, respectively. Those temperatures were chosen in order to obtain phase-pure α -RuCl₃ (the β -polytype transforms irreversibly into the α -phase above 395 °C) and to keep the Cl₂ gas pressure in the ampoule below atmospheric pressure. The polycrystalline material harvested from the ampoule contained many plate-like shiny crystals of hexagonal shape.

The structure was analysed using single crystal X-ray diffraction measurements ($\lambda = 0.71073$ Å) using an Agilent Supernova diffractometer equipped with an Atlas detector. The data integration and cell refinement were performed with the CrysAlis Pro Software, the structure analyzed using SIR-2011 in WinGX, and the data were refined with the SHELXL 2014 software package [141–144]. Visualisation of the crystal structure (Figure 7.1) was carried out in VESTA [117].

The observed diffraction pattern of a small single crystal, picked out of the polycrystalline batch used for our μ^+ SR measurements, is fully consistent with the structural model of Ref. [130], whereby honeycomb layers of edge-sharing RuCl_6 octahedra are vertically stacked with an offset along $-\mathbf{a}$ in a monoclinic crystal structure (spacegroup $C2/m$). In the diffraction patterns, presented in Figure 7.2, diffuse scattering is visible, in addition to sharp Bragg-reflections, along $\mathbf{c}^*$. This diffuse scattering has been attributed to the occurrence of stacking faults [130], whereby a Ru layer is in-plane shifted by $\pm\mathbf{b}/3$ as highlighted in Figure 7.1 (b). The associated energy cost is minimal as the Cl positions are unchanged upon such a shift, plausibly explaining the propensity of them to occur in $\alpha\text{-RuCl}_3$. In the structural refinement of the sharp diffraction peaks such $\pm\mathbf{b}/3$ stacking faults were parametrised by allowing Ru atoms to partially occupy the honeycomb center site $(0.5, 0, 0)$ at the expense of the nominal Ru site $(0.5, 0.33325, 0)$. The most important results of the converged structural refinement at room temperature are summarised in Table 7.1, with the complete set of fitting parameters available in Ref. [126]. The fractional site occupancies for the two Ru positions in Table 7.1 show that there is roughly one stacking fault every six Ru layers on average in our powder samples.

Space group	$C2/m$					
Unit cell	$a = 5.985 \pm 0.005 \text{ \AA}$, $b = 10.355 \pm 0.005 \text{ \AA}$, $c = 6.049 \pm 0.005 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 108.830^\circ$					
Wyckoff Positions	Atom	Site	x	y	z	occupancy
	Ru	4j	0.50	0.33325	0	0.864
	Ru	2b	0.50	0	0	0.13578
	Cl	8j	0.2501	0.17107	0.76279	1
	Cl	4i	0.2359	0	0.23865	1

Table 7.1: Structural parameters of $\alpha\text{-RuCl}_3$ at room temperature from single crystal X-ray diffraction. Note that the fractional coordinates are in agreement with previously published ones [130, 137] upon a change of origin by $(0.5, 0, 0)$.

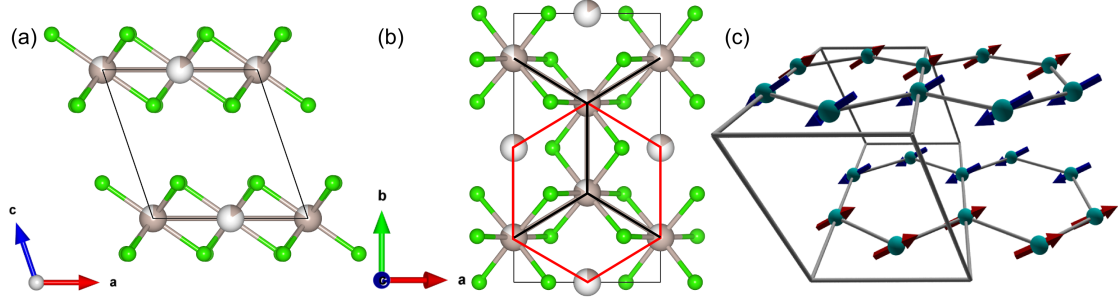


Figure 7.1: Crystal and magnetic structure of α -RuCl₃, showing Ru atoms as grey spheres, Cl as green spheres and the unit cell as a black outline. The partial coloring of the grey spheres indicates the occupational fraction of the corresponding Ru site, with which the stacking faults by $\pm \mathbf{b}/3$ of the Ru layers was modelled. Panels (a) and (b) show projections along the b and c axes, respectively. The red and black outlines in (b) illustrate the Ru honeycombs for a layer with and without a stacking fault, respectively. Panel (c) illustrates the antiferromagnetic state reported by Johnson *et al.* [130] combined with the moment direction found by a theoretical study [20].

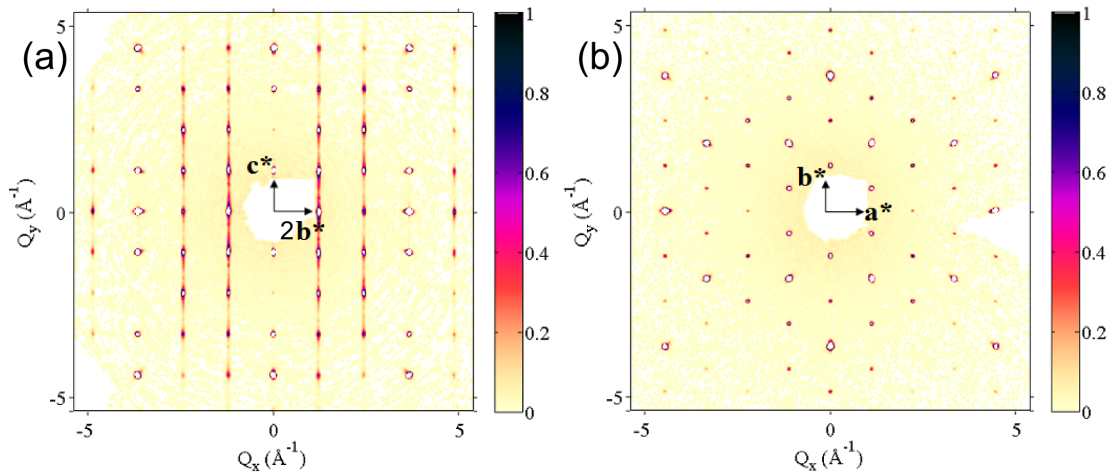


Figure 7.2: X-ray diffraction patterns of a α -RuCl₃ crystallite, showing the $0kl$ and $hk0$ planes in panels (a) and (b), respectively. The diffuse scattering rods due to the structural stacking faults are clearly visible in (a). This figure and the corresponding data are courtesy of A. Haghigirad and are comparable to Figure 1 in Ref. [130].

7.3 μ^+ SR measurement

We conducted ZF μ^+ SR measurements of our powder sample of α -RuCl₃ on the EMU spectrometer at the ISIS muon facility, RAL (UK), as well as the GPS spectrometer at the Swiss Muon Source, PSI (Switzerland). Data were collected in the temperature range 1.5 K to 40 K using ⁴He cryostats. Representative raw data obtained are plotted in Figure 7.3 (a) with Fourier transform spectra presented in Figure 7.3 (b). The measurements reveal oscillations below 14 K with two clearly separate frequencies at low temperatures around 1 MHz and 2.5 MHz, resulting from two inequivalent muon stopping sites with local fields of 7.5 mT and 18.5 mT, respectively.

The μ^+ SR data can be well fitted below 11 K with a sum of two oscillating functions $A_i \cos \omega_i t e^{-\lambda_i t}$, where the exponentials allow for relaxation caused by slow dynamics of the magnetic moments. In addition, a very slowly relaxing background term $A_b e^{-\lambda_b t}$ is included to account for muons stopping in the sample holder. In the range $11 \text{ K} \lesssim T \lesssim 14 \text{ K}$ only one oscillating component (plus background term) is required to fully describe the muon asymmetry. Figure 7.4 presents the resulting frequencies ω_i , relaxation rates λ_i and oscillation amplitudes of the precession signals for the data collected on the GPS spectrometer. The fits were performed in the time-range $t < 3 \mu\text{s}$, chosen as a compromise to extract both the oscillation frequencies (short times) and relaxation rates (longer times) accurately. The goodness of fit is $\chi^2=1.03(5)$ per degree of freedom averaged over all fits. Essentially identical results were obtained on the same sample in a separate experiment using the EMU spectrometer at the ISIS muon facility, demonstrating reproducibility. The fitted parameters can be modelled with a phenomenological order parameter equation of the form $y^2 = y_0^2(1 - (x/T_c)^\alpha)^\beta + c^2$ from which critical temperatures of 11.0(5) K and 14.3(3) K can be extracted for the high and low frequency components, respectively. Additionally, the ratio of the amplitudes yields a volume fraction ratio of roughly 4:2 for the two oscillating signals. Un-

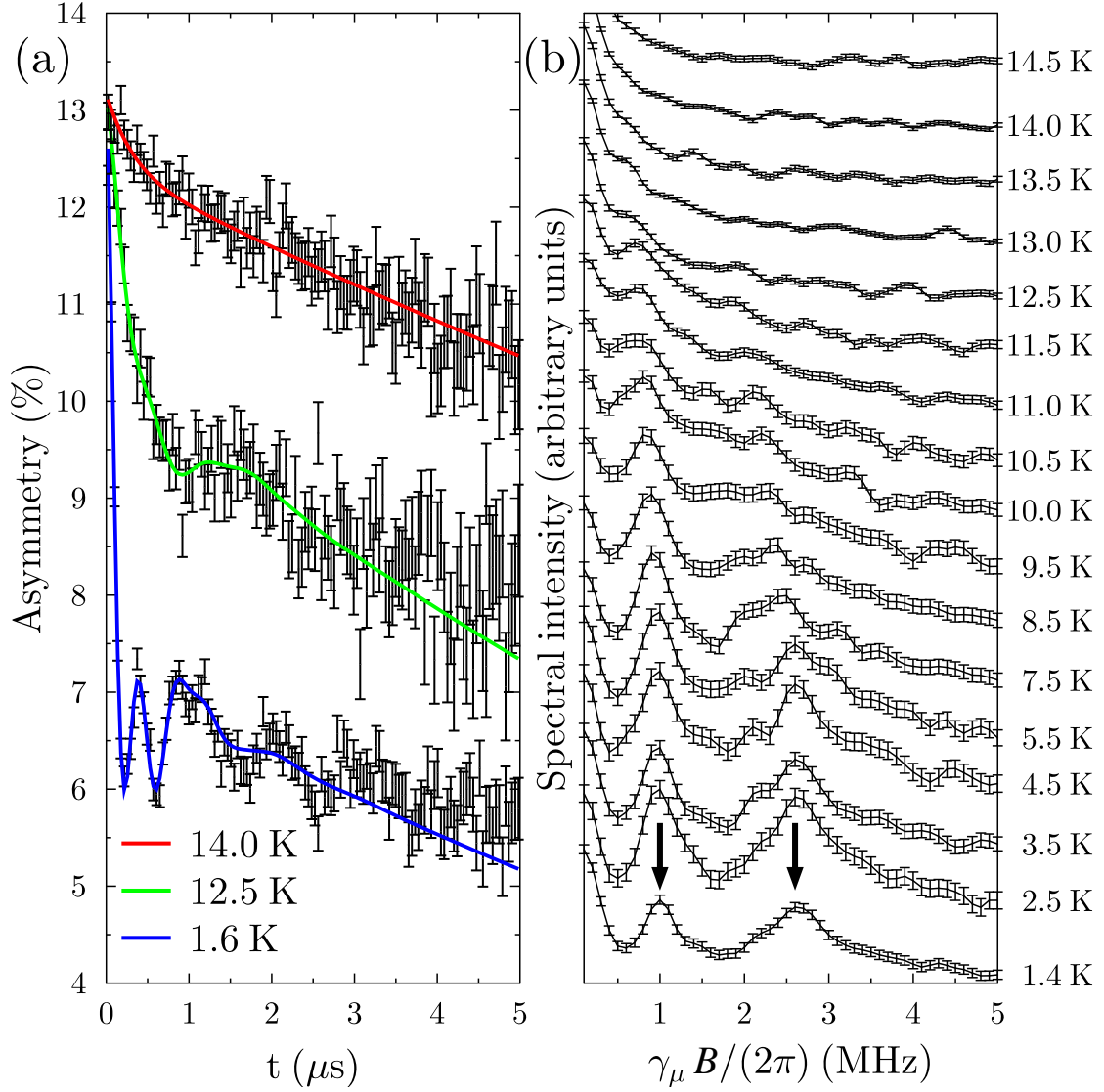


Figure 7.3: Panel (a): Muon asymmetries at selected temperatures. Solid lines represent fits using two ($T \lesssim 11$ K) or one ($11 \text{ K} \lesssim T \lesssim 14$ K) oscillating components with a Lorentzian relaxation. Panel (b): Fourier transform spectra of the muon asymmetries (vertically displaced for clarity).

fortunately, the values for the critical exponents α and β cannot be determined precisely enough from our data to unambiguously link them with theoretical values. It should also be noted that the amplitude of the higher frequency falls to zero, even while its frequency is non-zero. The presence of two μ^+ SR precession signals necessitates two inequivalent muon stopping sites in the magnetic phase of our sample, whose origins I discuss in the next sections.

7.4 Muon stopping site

Further analysis requires the knowledge of the potential muon stopping sites. To ascertain these we employ DFT calculations to map out the electrostatic Coulomb potential of α -RuCl₃ throughout its unit cell. The maxima of such a potential map have been a reliable approximation to the muon sites in previous more in-depth “DFT+ μ ” calculations, which also accounted for local distortions of the lattice caused by the muon presence, see for example Refs. [96, 116, 145] or chapter 6 above.

The DFT calculations were performed within the generalised gradient approximation [146] by employing the full potential linearised augmented plane wave (LAPW) basis as implemented in WIEN2k [147]. The RK_{max} parameter was set to 9 and a mesh of 800 **k** points in the first Brillouin zone was used. The electrostatic (Coulomb) potential was calculated from the converged electron density and the three-dimensional electrostatic potential maps were obtained with the XCrySDen package [148] and visualised with the Vesta software [117].

The Coulomb potential of α -RuCl₃ calculated via DFT is plotted in Figure 7.5, with the global maximum of the potential chosen as the reference value. A large Coulomb potential corresponds to a low energy required to add a positive charge. Therefore, by considering regions of high electrostatic potential, and particularly local maxima, we can identify plausible regions for a muon to stop in. When additionally taking into account that we expect a μ^+ to implant near a Cl⁻ ion,

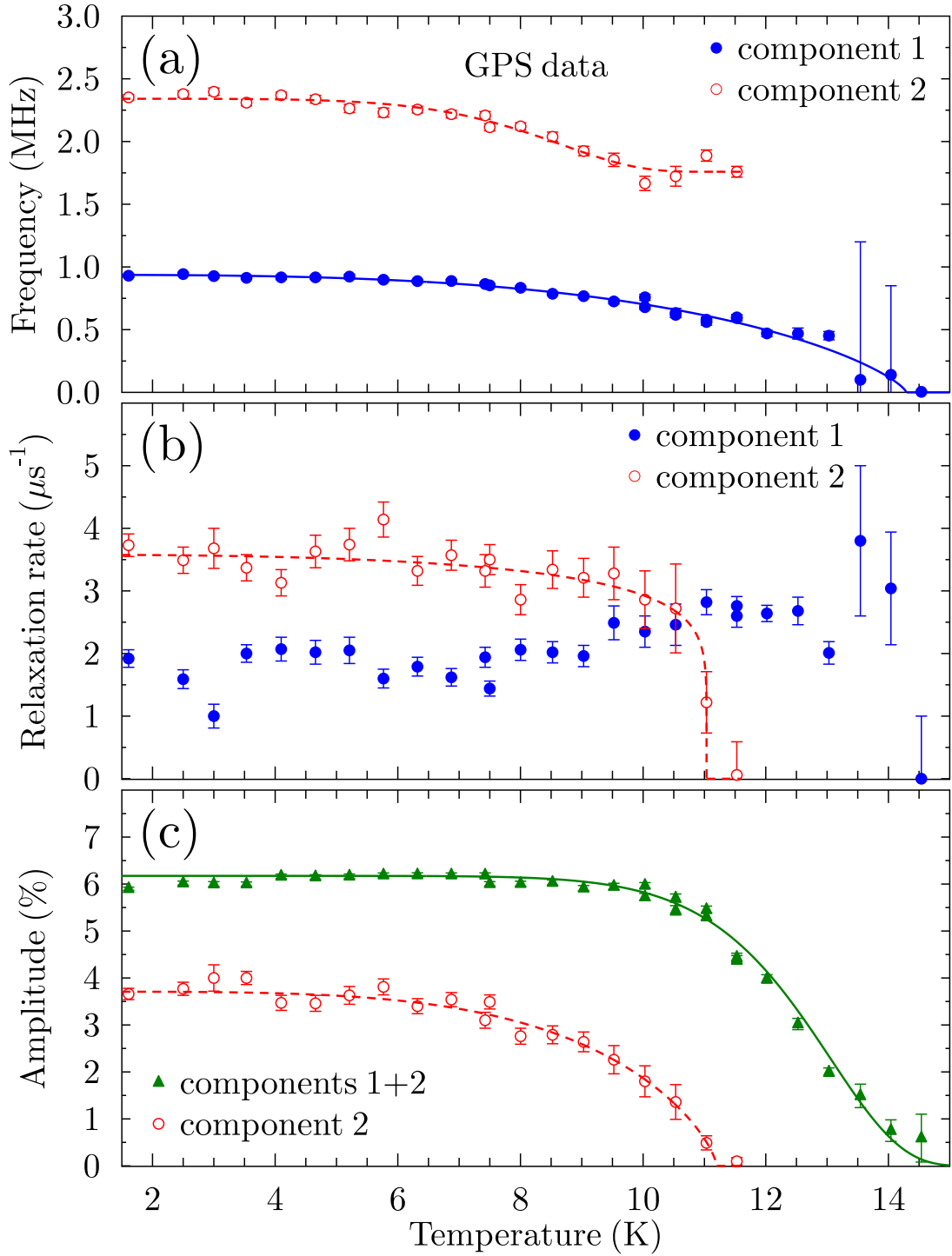


Figure 7.4: Results of fitting two oscillation frequencies with Lorentzian relaxation to the muon asymmetry. The lines represent order parameter fits of the form $y^2 = y_0^2(1 - (x/T_c)^\alpha)^\beta + c^2$.

four plausible muon site candidates are found, which are shown in Figure 7.5 and summarised in Table 7.2. These candidate sites are separated by up to 0.4 eV in their Coulomb potential values, with the origin (Mu1) being the lowest. The expectation of the formation of a Cl- μ bond in α -RuCl₃ stems from previous μ^+ SR measurements involving compounds containing fluorine and oxygen [145], where the muon is known to form hydrogen-like bonds with the highly electronegative F and O ions. We can estimate the Cl- μ bond length using the known lengths for H-F (0.92 Å), H-Cl (1.27 Å) and H-O (0.96 Å) bonds and simply scaling, using the bond lengths of F- μ (1.14–1.21 Å) [149] and O- μ ($\approx$ 1.0 Å) [96, 149]. As a result we obtain a likely Cl- μ bond length of roughly 1.5–1.6 Å.

While the muon will generally perturb its local environment, as mentioned in chapter 3.7 and studied extensively in chapter 6, its effect is short-ranged and significant only for the nearest neighbor ions [96, 145], and in the present case we anticipate only a small displacement of a nearest Cl⁻ ion and negligible effects on the magnetic moment carrying Ru³⁺ ions. As a result, we do not expect distortions to have a significant impact on the bulk magnetism probed in our μ^+ SR measurement, unlike for the case of the Pr based pyrochlores discussed in chapter 6.

Atom	WP	SS	x	y	z
Ru	4g	2	0	0.33441	0
Cl	4i	m	0.73023	0	0.23895
Cl	8j	1	0.75138	0.17350	0.76619
Mu1	2a	2/m	0	0	0
Mu2	4i	m	0.14	0	0.36
Mu3	4g	2	0	0.2	0.5
Mu4	2d	2/m	0.5	0	0.5

Table 7.2: Fractional coordinates of atoms and muon site candidates determined through DFT calculations. Abbreviations stand for Wyckoff position (WP) and site symmetry (SS). The fractional coordinates of α -RuCl₃ originate from Ref. [130] and are compatible with our x-ray diffraction characterisation (Table 7.1).

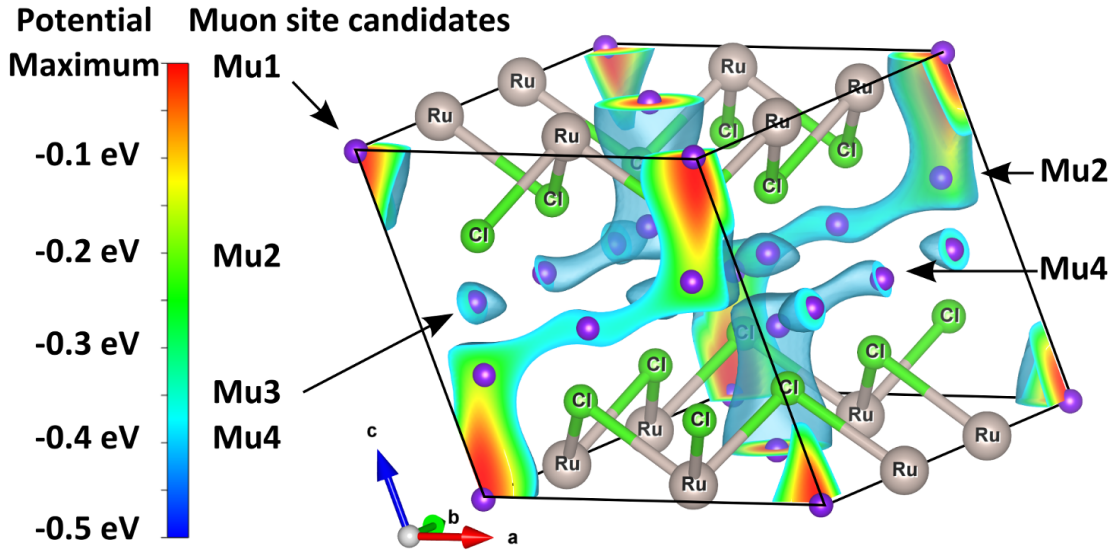


Figure 7.5: Coulomb potential of α -RuCl₃ calculated via DFT. The blue isosurface plotted is at 0.4 eV below the maximum. The purple spheres indicate the muon site candidates we identified. Their labels are placed next to the colour scale to indicate the approximate value of the potential at the sites. Please note that the colour scale is inverted compared to Figure 6.6 for readability.

7.5 Dipolar field calculations

Having obtained a set of plausible muon stopping sites it is now possible to calculate the local magnetic field experienced by an implanted muon stopping on these sites. This field is in general a sum of contributions due to dipolar couplings, demagnetising and Lorentz fields and hyperfine interactions, as discussed in chapter 3.4. Since α -RuCl₃ orders antiferromagnetically the magnetisation and thus the demagnetising and Lorentz fields are trivially zero. We expect the μ^+ to stop near a Cl^- ion and thus direct overlap with any Ru^{3+} electron spin density will be insignificantly small and so we can also neglect any hyperfine contribution [145, 149]. Therefore, we focus on the dominant dipole field only, which for a muon at position $\mathbf{r}_\mu$ and magnetic moments $\boldsymbol{\mu}_i$ at $\mathbf{r}_i$ is given by

$$\mathbf{B}_{\text{dip}}(\mathbf{r}_\mu) = \sum_i \frac{\mu_o}{4\pi|\Delta\mathbf{r}_i|^3} \left[\frac{3(\boldsymbol{\mu}_i \cdot \Delta\mathbf{r}_i)\Delta\mathbf{r}_i}{|\Delta\mathbf{r}_i|^2} - \boldsymbol{\mu}_i \right], \quad (7.1)$$

where $\Delta\mathbf{r}_i = \mathbf{r}_i - \mathbf{r}_\mu$ (see also chapter 3.4).

To compute this sum, we make use of the substantial knowledge about the

magnetic structure of α -RuCl₃ extracted from previous neutron diffraction experiments. One neutron powder study provided evidence for a zig-zag antiferromagnetic order within each Ru honeycomb layer with an additional antiferromagnetic stacking between the layers. Panel (c) in Figure 7.1 illustrates this state. The corresponding propagation vector is $\mathbf{k} = (0, 1, 0.5)$, and moreover the moments are constrained to lie in the ac plane and the lower limit of the moment size is $0.64(4)\mu_B$ [130]. However, another recent single crystal measurement proposed an alternative zig-zag antiferromagnetic ordering with 3-layer stacking ($\mathbf{k} = (0, 1, 1/3)$) in pristine single crystals with moments aligning in the ac plane in a spiral or collinear pattern [137]. Investigations using *ab initio* and model calculations, focussing on intra-layer interactions, also find an in-plane zig-zag antiferromagnetic order [20, 150] and predict the magnetic moments to make an angle of roughly 30° with the ab plane [20, 151], as shown in Figure 7.1 (c) above.

7.5.1 Two-layer magnetic order

Using the known crystal structure and the proposed 2-layer magnetic ordering [130] the dipole field strength can be computed at the candidate muon sites obtained through the DFT simulations. Figure 7.6 displays the resulting Larmor frequencies and how they change as a function of the magnetic moment direction within the ac plane. The first thing to note is that the dipole field vanishes due to the local symmetry at candidate site Mu1, which is the electrostatically most favourable one and is located at the centre of the Ru hexagons. Besides, Figure 7.6 also reveals that there is no single moment direction within the ac plane for which we obtain precession frequencies that agree with both the experimentally observed ones. However, it is important to bear in mind that so far we did not account for any local distortions due to the presence of the muon. To approximate such perturbations we can incorporate the fact that we expect the muon to form a bond with a nearby Cl⁻ ion of length $\approx 1.5 \text{ \AA}$. To revise our model accordingly, we considered each muon site to be displaced from our earlier candidate sites towards

each of the nearest Cl⁻ ions. Figure 7.7 presents the resulting muon precession frequencies as a function of the magnetic moment direction. It shows that if we take the moment to be at $\approx 30^\circ$ with the ab plane [20] and small distortions towards the nearest neighbor Cl⁻ ions both the Mu1 and Mu3 site candidates are compatible with the experimentally observed frequencies of about 1 MHz and 2.5 MHz.

It should be noted that both the Mu1 and Mu3 sites have six nearby Cl⁻ ions, four of which are at the $8j$ Wyckoff positions and two of which are at the $4i$ Wyckoff positions (see Table 7.2). Consequently, if either Mu1 or Mu3 is indeed close to the correct muon stopping site we would expect two muon precession frequencies with an amplitude ratio of 2:1. Even though this is roughly in line with the two experimentally observed oscillation amplitudes, this would however not explain why the two frequencies disappear at different temperatures. To this end I explore a range of possible scenarios below.

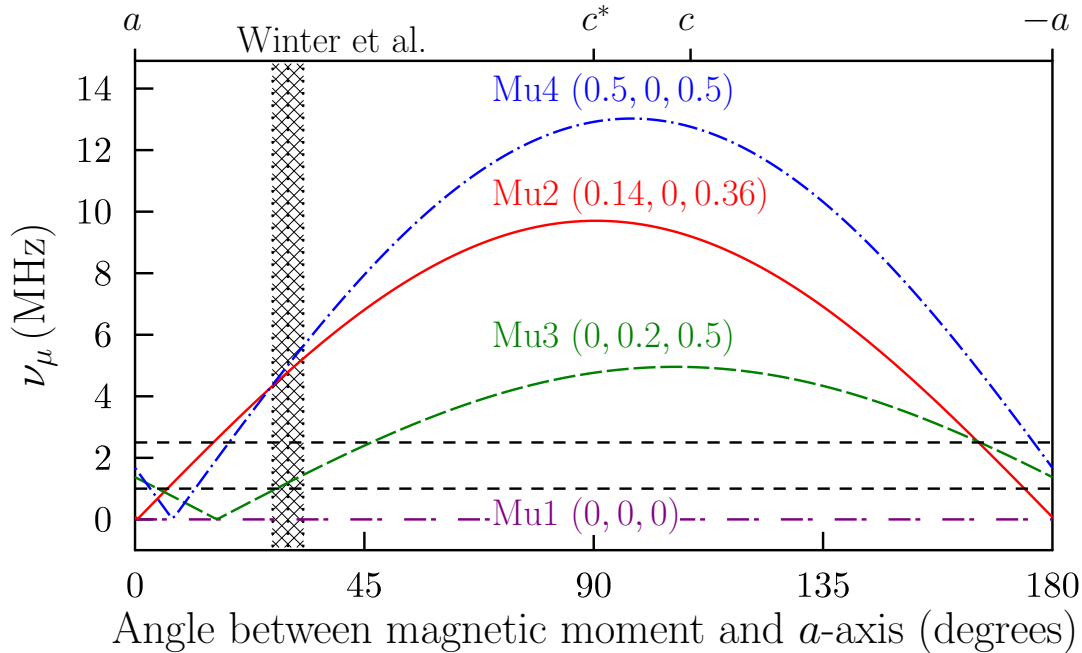


Figure 7.6: Muon Larmor precession frequencies due to dipolar fields at the four muon site candidates as a function of the magnetic moment direction in the ac -plane. Directions parallel to crystallographic axes are indicated at the top of the plot. The magnetic structure was taken to be the 2-layer ordering proposed by Johnson *et al.* [130] and the approximate moment direction predicted by Winter *et al.* [20] is indicated by the vertical shaded area. Horizontal dashed lines mark the two measured frequencies.

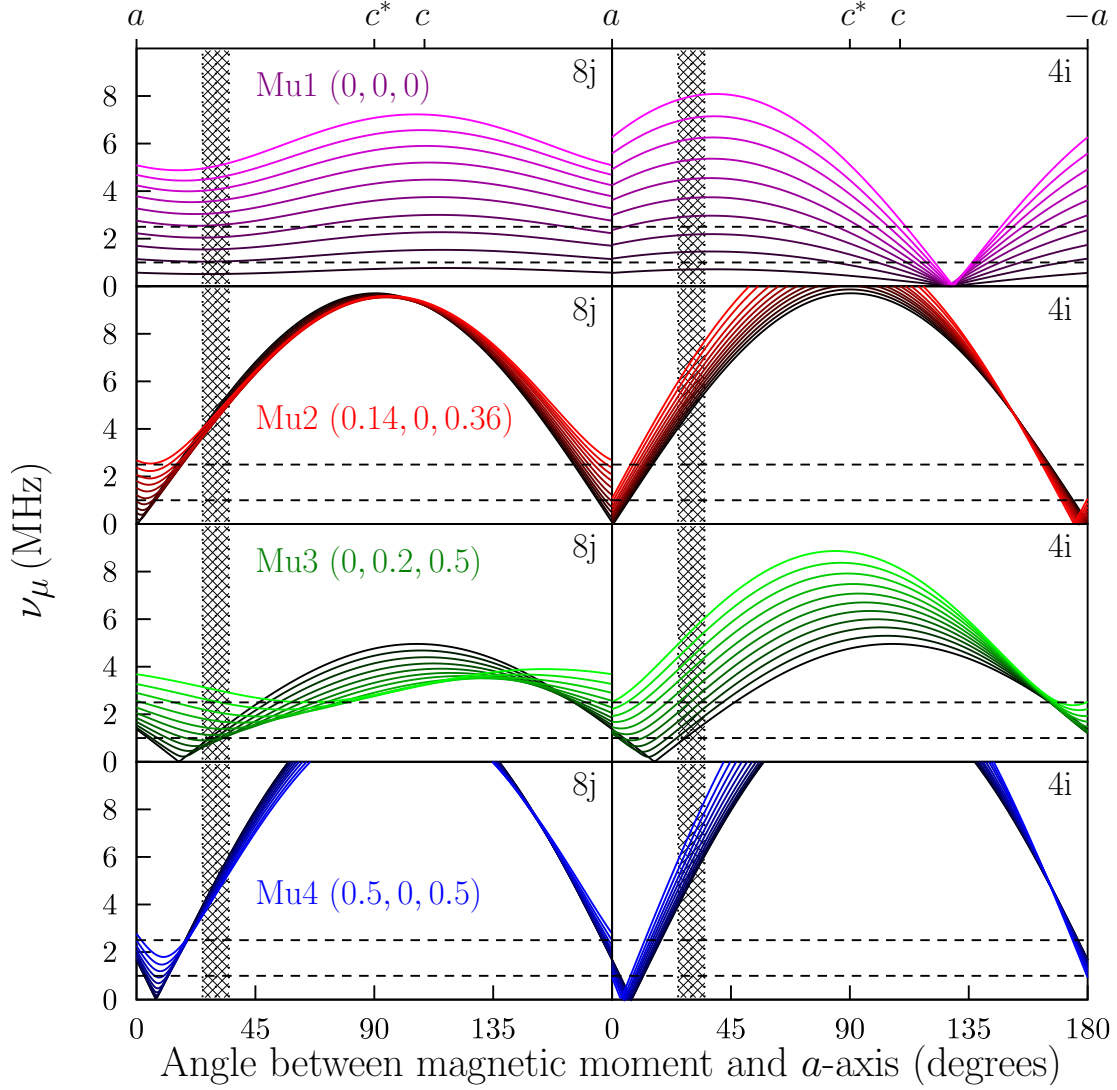


Figure 7.7: Muon Larmor precession frequencies at the muon site candidates (black curves) and for ten positions ($0.1 \text{ \AA}$ between each) along a straight line towards the nearest Cl^- ions (coloured curves), as a function of the magnetic moment direction in the ac plane. Positions further away from the undistorted muon site candidates are displayed with a deeper colour tone. The left and right columns show distortions towards Cl^- ions on the $8j$ and $4i$ Wyckoff positions, respectively (see Table 7.2). The magnetic structure was taken to be the 2-layer ordering proposed by Johnson *et al.* [130]. Moment directions parallel to crystallographic axes are indicated at the top and the approximate angle predicted by Winter *et al.* [20] is marked by the vertical shaded area. Horizontal dotted lines indicate the two measured frequencies.

Effect of stacking faults

One potential origin for the two observed μ^+ SR signals we considered are the structural stacking faults occurring in $\alpha\text{-RuCl}_3$. To study their effect we calculated the dipolar field at our candidate muon sites assuming a nearby Ru layer

being translated by $\pm \mathbf{b}/3$. For these calculations, we chose the magnetic structure depicted in Figure 7.1 [130] and fixed the Ru moment direction, following Ref. [20], to lie at 30° to the a -axis in the ac plane. We calculated our results assuming that the muon site was somewhere between the sites identified by our electrostatic calculations and the nearest Cl^- ion, parametrising these sites by the distance along this line from 0–1 Å (the likely site is expected to lie between these limits given the predicted μ –Cl bond length). In the presence of stacking faults the local symmetries are broken, so that it becomes necessary to calculate the dipolar field for our candidate muon sites distorted towards all the neighbouring Cl ions. The results are shown in Figure 7.8. The first column of panels shows the results without stacking faults, i.e. a projection of the graphs in Figure 7.7 along the vertical shaded lines, while subsequent columns contain results for stacking faults at the z -values shown. Since the Ru layers occur at integer z , we indicate the location of the stacking faults by half-integer z .

The graphs in Figure 7.8 demonstrate that stacking faults only have a significant effect on the precession signals if the muon is directly adjacent to the fault. For example Mu1, which is at $z = 0$, is affected by stacking faults at $z = \pm \frac{1}{2}$, whereas Mu3 and Mu4, which are at $z = \frac{1}{2}$, are primarily affected by a stacking fault at $z = \frac{1}{2}$. However, we can also notice that different symmetry equivalent sites (which result in identical traces for the case without stacking faults) become inequivalent when a stacking fault is nearby, resulting in a range of local fields. This could be a source of broadening in the experimentally observed μ^+ SR data, because the slightly different frequencies will sum together to produce a damped signal.

In addition it is also possible that at a stacking fault the magnetic moments reverse in sign. While this cannot be determined from the relevant neutron data in Ref. [130], it is a possible scenario given that the fault alters the local exchange pathways and thus interlayer interactions. We have considered this possibility and

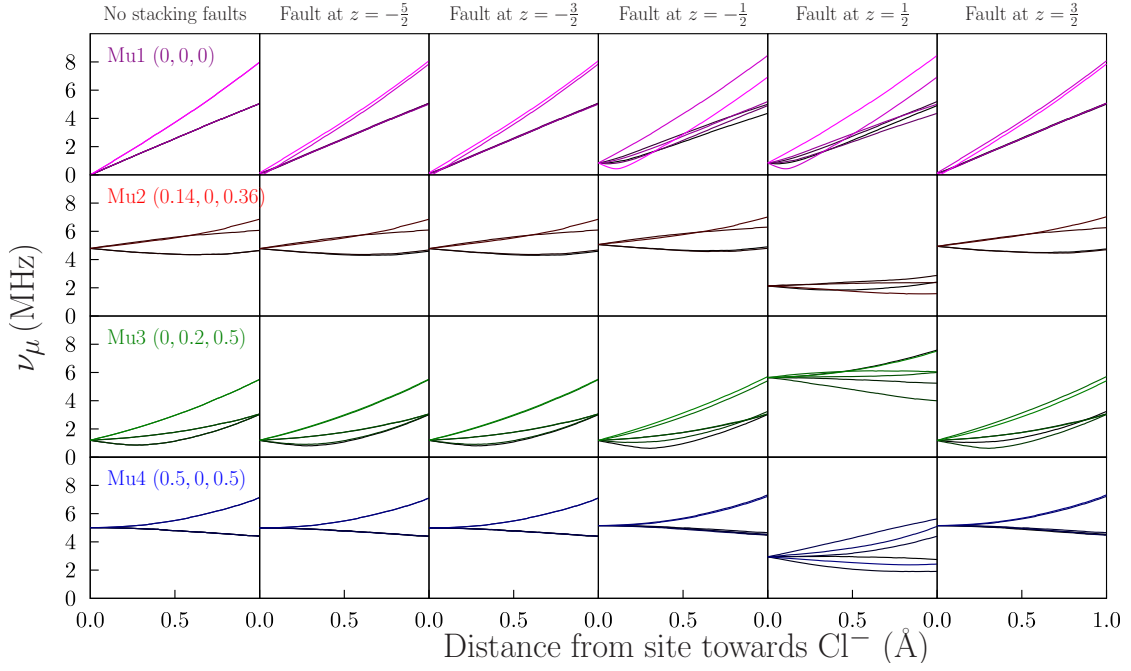


Figure 7.8: Muon precession frequencies for muon site candidates near a stacking fault. See the main text for details.

repeated the above calculations for the case in which all magnetic moments are reversed ($\mathbf{m} \rightarrow -\mathbf{m}$) below the stacking fault. The corresponding calculations are shown in Figure 7.9. The results are quite similar, but there are noticeable differences when the fault is close to the muon, and in particular in this case the Mu2 to Mu4 sites have slightly higher precession signals while those at Mu1 have less of a spread.

Thus we can conclude that stacking faults can have a significant effect on the precession signal of a muon, but only if the muon is directly adjacent to the fault. Since a stacking fault occurs roughly only every 6 Ru layers in our powder sample we thus expect that our measured muon Larmor frequencies are not significantly affected by the stacking faults directly.

In-plane order and out-of-plane disorder

In the magnetic structure proposed in Ref. [130], which is depicted in Figure 7.1, the Ru layers are stacked antiferromagnetically. Motivated by the idea that the structural stacking faults may locally affect the interlayer ordering, we examined the scenario of in-plane order with a lack of order between the planes. To this end

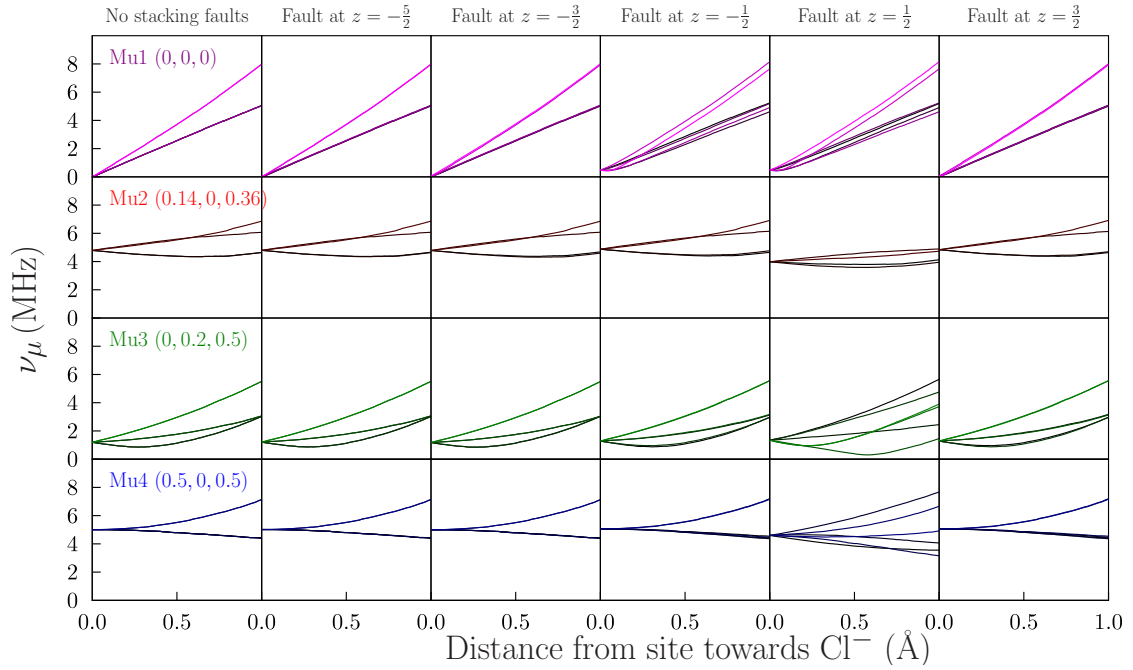


Figure 7.9: Muon precession frequencies as for Figure 7.8, but with spins reversed at a stacking fault.

we calculated the dipole fields at the candidate muon sites with different ordering configurations along the c -axis. These are shown in Figure 7.10, with the first two columns representing the cases of antiferromagnetic and ferromagnetic stacking of the Ru layers, respectively, while the other columns correspond to more randomised stackings. The results demonstrate that the precession signals at Mu1 are largely unaffected by any c -axis order or lack thereof, whereas the precession signals corresponding to the other sites are more strongly affected, with a range of local fields and thus broadening in the case of interlayer disorder. Within this picture, the appearance of the two experimentally observed transitions at different temperatures could plausibly be explained by the development of significant 2D intra-layer correlations (giving a coherent signal at the Mu1 site) before the phase transition to full 3D order at a slightly lower temperature (giving a second signal due to possibly the Mu3 site). This interpretation is not inconsistent with the neutron powder data obtained on these samples [130], because the structural stacking faults and magnetic disorder along the c -axis both manifest themselves in diffuse scattering along $\mathbf{c}^*$. Such diffuse scattering was indeed observed, but the quality

of the data does not allow a clear identification whether it was caused by either the stacking faults or disorder or both. In addition, the fact that susceptibility measurements show a single broad feature at 14 K [130] can also be explained, since the Ru spins are expected to shed the majority of their entropy upon ordering within the layers and therefore the lower temperature phase transition would probably lead to a feature too small to detect.

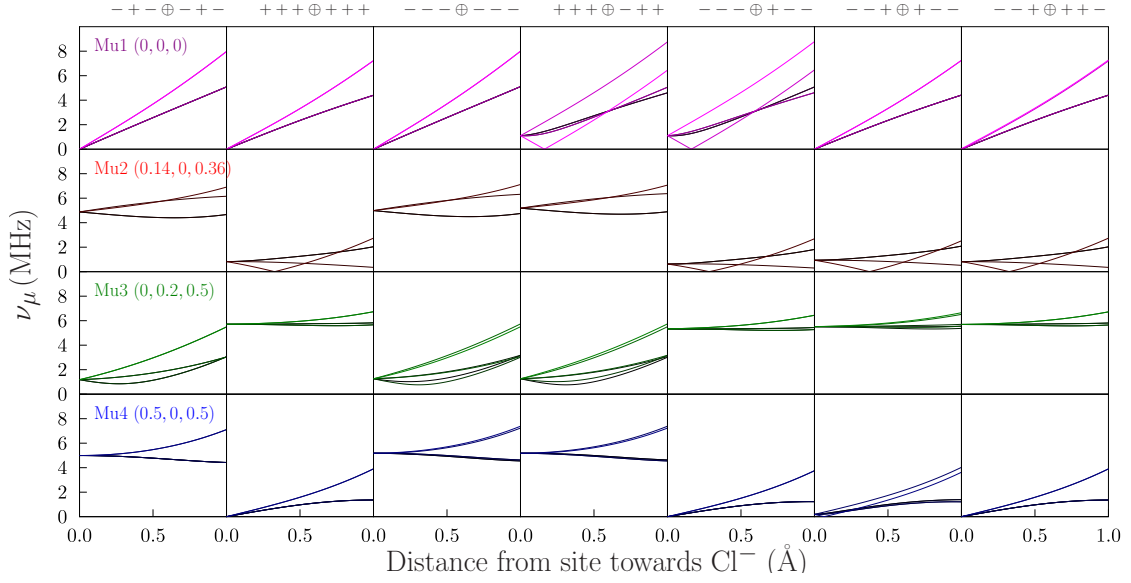


Figure 7.10: Muon precession frequencies as for Figure 7.8, but now with different c -axis ordering configurations. These are indicated schematically by the sequence above each column, with the muon in the layer indicated by $\oplus$ and the nearby layers indicated with $+$ and $-$. The column on the left corresponds to the low-temperature magnetic structure proposed in Ref. [130] (see Figure 7.1).

7.5.2 Alternative structural and magnetic phases

A potential explanation for the two observed μ^+ SR signals to appear at slightly different temperatures is the presence of two magnetic phases in our sample. Although x-ray, neutron and susceptibility measurements on samples grown in the same manner as ours only show evidence for a single phase, we nevertheless considered two alternative crystal and magnetic structures that have been proposed previously.

AB stacking of Ru layers

Alternative arrangements of the Ru layers that have been proposed previously [23, 137] are summarised in Figure 7.11. It should be noted that the ABC labelled stacking [130] is nearly identical to the AB one, since the geometry of the monoclinic unit cell yields $a/3 \approx -c \cos \beta$. To investigate the feasibility of the AB stacking, which Banerjee *et al.* [23] highlight as the root for the higher temperature transition ($T_N \approx 14$ K) they observed, we performed test DFT calculations for both the ABC and AB stacking orders shown in Figure 7.11 using the two full potential all-electron codes WIEN2K [147] and FPLO [152, 153]. For these calculations we prepared an AB unit cell out of the ABC unit cell (see Figure 7.11) and kept the same atom positions without further structural relaxations. The total energy of the AB stacking turns out to be higher than the ABC stacking by a few tens of meV per unit cell, making the AB stacking energetically less favourable. Additionally, we confirmed that the electrostatic potential predicts the muon site candidates to be unchanged in the AB stacking structure, indicating the robustness of the muon sites predicted by our DFT calculations. The resulting dipole fields expected at these muon sites are plotted in Figure 7.12 and show that the Larmor precession frequencies of the muons are essentially the same as those we calculated for the $C2/m$ structure. Therefore, it is unlikely that the existence of two different magnetic phases in our sample due to the two proposed stacking orders (ABC and AB) is at the root of the two frequencies we observed in our μ^+ SR experiment.

Three-layer magnetic structure

A recent neutron diffraction study reported a magnetic structure in pristine single crystals of α -RuCl₃ with zig-zag antiferromagnetic ordering within the Ru layers but with three-layer stacking periodicity that is either of spiral or collinear nature (see Figure 5 in Ref. [137]). Based on these two magnetic structures I have calculated the dipole fields at the muon site candidates obtained from the earlier DFT analysis. Figure 7.13 presents the resulting muon precession frequencies for

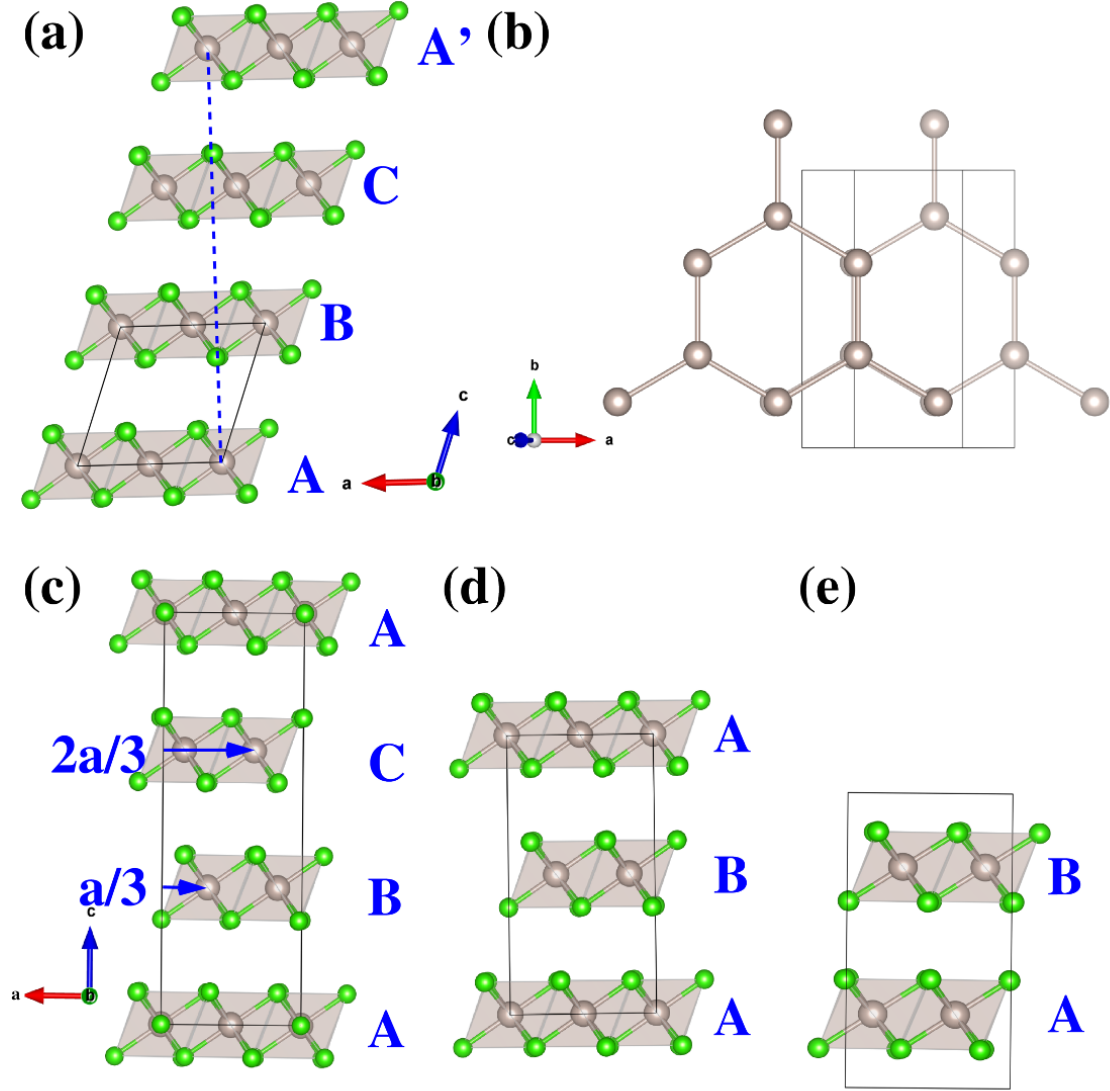


Figure 7.11: Structures and stacking orders proposed for α - RuCl_3 . Grey and green spheres represent Ru and Cl atoms, respectively. Panel (a) shows the $C2/m$ structure [128, 130, 137] with panel (b) highlighting that the A and A' layers almost overlap when viewed along the c^* direction. The angle between direction $\overline{AA'}$ and the a axis is 89.523° . Panel (c) presents the ABC stacking proposed in Ref. [137] (see Figure 1 (b) there), which is almost identical to the $C2/m$ structure since $a/3 \approx -c \cos \beta$. Panel (d) shows the AB stacking proposed in Ref. [137] (see Figure 1 (c) there) with panel (e) representing a unit cell for this AB stacking within the $C2/m$ symmetry obtained by allowing bond length differences of up to $10^{-4}\text{\AA}$.

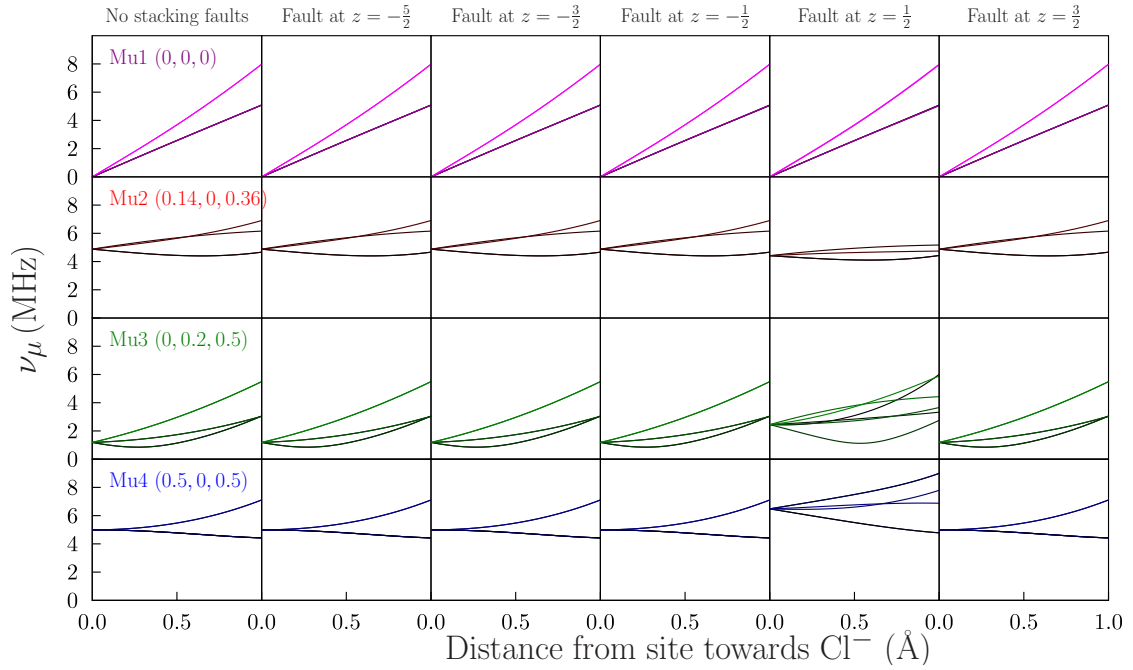


Figure 7.12: Muon precession frequencies as for Figure 7.8, but now with AB stacking order as shown in Figure 1(c) of Ref. [137].

the muon site candidates in each of the three distinct layers of both the proposed spiral and collinear spin configurations. We can note that the magnitudes of the frequencies are of the order of the observed ones and that a more realistic analysis including distortions of the muon sites towards the nearest Cl⁻ ions could potentially improve the quantitative agreement. However, the spiral and collinear ordering lead to three and two distinct frequencies, respectively, associated with muons stopping near the three different Ru layers. Additionally, including the more realistic distortions towards nearby Cl⁻ ions will in general lift the degeneracies of the frequencies associated with Cl⁻ ions that are symmetry equivalent in the crystallographic unit cell but are not equivalent in the larger magnetic unit cell. Therefore, the number of precession frequencies we expect to observe experimentally in such magnetic structures is larger than two. Hence, both of the three-layer magnetic structures proposed by Cao *et al.* for single crystals are very unlikely to be compatible with our μ^+ SR measurements of α -RuCl₃ powder. Nevertheless, another μ^+ SR measurement on pristine α -RuCl₃ single crystals is required to confirm whether the three-layer ordering is indeed the appropriate one and it might

provide valuable insights into why powder and single crystal measurements yield inconsistent observations.

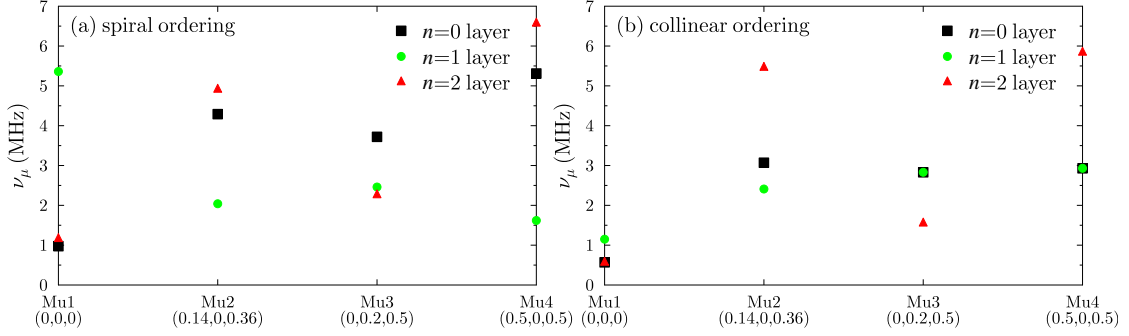


Figure 7.13: Muon precession frequencies at the muon site candidates for the 3-layer magnetic orders proposed by Cao *et al.* [137]. The parameter n labels the Ru layer within the 3-layer stacking, see Figure 5 (a) and (b) in Ref. [137].

7.6 Conclusion

In summary, we observed two precession frequencies in a μ^+ SR measurement of a powder of α -RuCl₃, indicative of long-range magnetic order, with two distinct transitions at 11.0(5) K and 14.3(3) K. Using DFT calculations we identified candidates for the muon stopping site and computed the muon precession frequencies due to dipolar fields at these sites. We used two zig-zag antiferromagnetic structures proposed by recent powder and single crystal neutron diffraction studies and *ab initio* calculations. After taking local distortions due to the muons and the expected μ -Cl bond into account, and also examining a number of possible scenarios to explain the two transitions, we find that our results are consistent with a two-layer ordering proposed by Johnson *et al.* [130]. Within this picture, we suggest an interpretation based on a temperature regime with well established static correlations within the two-dimensional layers but interlayer disorder, and the full three-dimensional order setting in below the lower transition. It should be noted that the higher temperature transition is really a cross over and not technically a phase transition. Our proposed interpretation including such a cross over regime is somewhat similar to a state recently proposed to exist in frustrated triangular Ising antiferromagnets [154], where weak interlayer couplings and frustrated

stacking of layers have now been shown to be major ingredients [155].

7.7 Outlook

The next stage in our investigations of the unconventional magnetic behaviour of α -RuCl₃ is to carry out μ^+ SR measurements of a single crystal of this compound. To this effect we are going to perform ZF μ^+ SR experiments at the ISIS muon facility in the autumn of 2016, with the main aim being to test whether recently grown single crystals indeed show different magnetic behaviour to their powder counterparts, and to also study the very intriguing report of changes to the behaviour upon application of mechanical deformations [137].

Additionally, it might be very interesting to reconsider the μ^+ SR measurements of Na₂IrO₃ [16] in the light of these results. Interestingly, Na₂IrO₃ also showed two oscillation frequencies, but with a single phase transition. However, the energetically most favourable muon site in α -RuCl₃ at the centre of the honeycombs (labelled Mu1 above) is occupied by a Na ion in Na₂IrO₃. Using the insights gained from the present investigation of muon sites in α -RuCl₃, it is hoped to reexamine the Na₂IrO₃ data and thereby deepen the understanding of both compounds.

Chapter 8

Summary and conclusions

This thesis comprises three main research projects, which are all aimed to complement the experimental μ^+ SR technique with a variety of theoretical calculations, in order to improve the level of understanding gained from experimental observations. These insights have been applied to explicit examples of experimental measurements, whenever possible and necessary.

In the first project I investigated the effects of demagnetising fields on high field μ^+ SR data. After deriving an analytic expression for the demagnetising tensor of a finite cylinder of uniform magnetisation, I subsequently performed calculations of the resulting demagnetising fields. I find that these fields have a significant impact in the regions close to the boundary of the shape, caused by bending of the demagnetising fields lines in these regions. This results in a characteristic broadening of the field one expects to observe experimentally, with a low field tail and high field cut-off. I showed that the broadening is in general significant for typical sample dimensions, and that the demagnetising field effects can be reduced by a variety of means. These include a decrease of the muon implantation depth, and preventing the muons from stopping in the boundary regions, either by applying a thick mask or reducing the muon beam spot size. Furthermore, I highlighted that similar demagnetising field effects, caused by boundary regions, is also expected in more complex polyhedral shapes. Finally, I identified a range

of possible improvements of my simple calculation models, such as including muon beam and stopping profiles.

The remaining two projects focussed on a combination of theoretical calculations that were used to shed important insights into experimental observation, which were exclusively seen in μ^+ SR measurements. In both scenarios I presented how density functional theory can be utilised as a tool to determine plausible muon stopping sites.

In the case of the investigated quantum spin ices $\text{Pr}_2\text{B}_2\text{O}_7$ (B= Sn, Zr, Hf, Ir) I argued that the muon induce distortions of their local crystal environments. This in turn results in a splitting of the Pr^{3+} doublet ground state, which I calculated using the perturbed ion positions as predicted by density functional theory. Crucially, I showed that the ground state splitting results in a hyperfine enhancement of the Pr nuclear moment, which is compatible with the experimental μ^+ SR behaviour. Thereby, I concluded that in the Pr based pyrochlores the μ^+ SR measurements reflect the local response of the sample to the muon presence, instead of intrinsic properties. Through an analogous analysis, I then showed that in the classical spin ices $\text{A}_2\text{Ti}_2\text{O}_7$ (A= Dy, Ho) the μ^+ SR experiments indeed probe the intrinsic ground state properties, and that only the higher temperature behaviour, due to higher lying crystal field levels, is affected.

The final project used a combination of density functional theory and dipolar field calculations, in order to understand the experimental μ^+ SR measurements of the layered honeycomb magnet $\alpha\text{-RuCl}_3$. By evaluating the local field at plausible muon stopping sites, I investigated the applicability of different reported crystal and magnetic structures. I found that the data is compatible with a previously reported antiferromagnetic state with two layer periodicity. However, I argued that the phase transition at 14 K seen in neutron and susceptibility studies corresponds to a cross over region, in which significant spin correlations within the Ru layers form. I reasoned that this temperature regime is however also characterised by

an absence of full three-dimensional order, which only appears at a slightly lower temperature of 11 K.

Overall, I presented how the μ^+ SR technique can be supplemented with a variety of theoretical calculations, in order to help understand experimentally observed behaviour, and increase the amount of information that can be extracted from a μ^+ SR measurement.

Appendix A

Standard integrals and expressions

This is a compilation of the standard integrals employed in chapter 5. The numbers in brackets refer to the equation numbers used in Ref. [84].

$$\begin{aligned}
 (3.721.1) : \int_0^\infty \frac{\sin(ax)}{x} dx &= \frac{\pi}{2} \text{sgn}(a), & \text{for } a \in \mathbb{R} \\
 (3.723.2) : \int_0^\infty \frac{\cos(ax)}{\beta^2 + x^2} dx &= \frac{\pi}{2\beta} e^{-a\beta}, & \text{for } a \geq 0, \text{Re}(\beta) > 0 \\
 (3.723.3) : \int_0^\infty \frac{x \sin(ax)}{\beta^2 + x^2} dx &= \frac{\pi}{2} e^{-a\beta}, & \text{for } a > 0, \text{Re}(\beta) > 0 \\
 (3.738.2) : \int_0^\infty \frac{x^{m-1} \cos(ax)}{x^{2n} + \beta^{2n}} dx &= \frac{\pi \beta^{m-2n}}{2n} \sum_{k=1}^n e^{-a\beta \sin\left(\frac{(2k-1)\pi}{2n}\right)} \\
 &\quad \times \sin \left[\frac{(2k-1)m\pi}{2n} + a\beta \cos\left(\frac{(2k-1)\pi}{2n}\right) \right], \\
 &\text{for } m = \text{odd}, a > 0, |\arg(\beta)| < \frac{\pi}{2n}, 0 < m < 2n + 1 \\
 (3.915.2) : \int_0^\pi e^{i\beta \cos(x)} \cos(nx) dx &= i^n \pi J_n(\beta), & \text{for } n \in \mathbb{Z} \\
 (5.52.1) : \int x^{p+1} Z_p(x) dx &= x^{p+1} Z_{p+1}(x), \\
 &\text{for } Z_p = \text{a Bessel function (1st, 2nd or 3rd kind)}
 \end{aligned}$$

$$(6.512.3^8) : \int_0^\infty J_\nu(\alpha x) J_{\nu-1}(\beta x) dx = \begin{cases} \frac{\beta^{\nu-1}}{\alpha^\nu}, & \beta < \alpha \\ \frac{1}{2\beta}, & \beta = \alpha, \\ 0, & \beta > \alpha \end{cases} \quad \text{for } \operatorname{Re}(\nu) > 0$$

The following two expressions concern the small argument expansion of Bessel functions of the first kind and Leibniz's Theorem for the differentiation of an integral. The numbers in brackets correspond to the equation numbers in Ref. [85].

$$(9.1.10) : \lim_{z \rightarrow 0} J_\nu(z) = \lim_{z \rightarrow 0} \left(\frac{z}{2}\right)^\nu \sum_{k=0}^{\infty} \frac{\left(\frac{-z^2}{4}\right)^k}{k! \Gamma(\nu + k + 1)} = c_\nu z^\nu + O(z^{\nu+2}),$$

for $\nu = 0, 1, \dots$ and c_ν constants

$$(3.3.7) : \frac{d}{dc} \int_{a(c)}^{b(c)} f(x, c) dx = \int_{a(c)}^{b(c)} \frac{\partial}{\partial c} f(x, c) dx + f(b, c) \frac{db}{dc} - f(a, c) \frac{da}{dc}$$

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