

Magnetism in
quasi-low-dimensional systems
investigated with muon spin
rotation and high magnetic fields



Isabel Franke

St John's College

University of Oxford

A thesis submitted for the degree of

Doctor of Philosophy

Michaelmas Term 2011

Magnetism in quasi-low-dimensional systems investigated with muon spin rotation and high magnetic fields

Isabel Franke
St John's College
Michaelmas Term 2011

Abstract of thesis submitted for the degree of Doctor of Philosophy

This thesis presents the investigation of magnetism in a selection of low-dimensional systems and its relation to other physical properties, such as superconductivity. The techniques employed are muon spin rotation and pulsed magnetic field magnetisation. The ability of muons to directly probe the local field is used to study SrFeAsF, which is a parent compound of the high-temperature superconducting pnictides. This revealed that the magnetic and structural transitions are separated in this system. I then demonstrate the coexistence of magnetism and superconductivity in NaFeAs for the first time. This discovery is of great interest since the interplay between magnetism and superconductivity is thought to play an important role for high-temperature superconductivity. I further investigate the effect of partially replacing Fe with Co in NaFeAs. I study the ordering and spin reorientation in the Mott insulator Sr₂IrO₄, which has been suggested as a possible high-temperature superconductor. The complex magnetism observed in this system is contrasted to that in related iridates Ca₄IrO₆, Ca₅Ir₃O₁₂ and Sr₃Ir₂O₇. By combining pulsed-field magnetization and low magnetic field experiments with μ SR on a series of coordination polymers. I am able to determine the size and direction of the magnetic exchange interaction. I demonstrate how it is possible to adjust the interactions by altering the molecular architecture of these Cu-based spin- $\frac{1}{2}$ compounds. This is a significant contribution since it will lead to the targeted design of magnetic systems that can be utilized to experimentally test fundamental theories of magnetism.

Acknowledgements

This thesis has only been possible with the support of many people whom I individually thank here. I would like to thank my supervisor, Professor Stephen Blundell for his patience, encouragement and time given in preparation of this thesis. I wish to thank Paul Goddard for his invaluable support throughout my time as a DPhil student at Oxford. I am also grateful to everyone who helped develop my ideas, discussed, commented on and read my work. I thank my research group at the University of Oxford. Special thanks are due to all my research participants for giving me their valuable time and resources: Tom Lancaster, Andrew Steele, Jack Wright, Saman Ghannadzadeh, Bill Hayes. This work could not have been done without the exceptional guidance and advice given by Peter Baker, Francis Pratt and John Singleton. For the provision of interesting samples I thank Simon Clarke and his group as well as Gang Cao and Jamie Manson. Thanks also to my family and Lionel for their love, encouragement and support. Anyone I may have missed in the acknowledgment is also thanked.

Contents

1	Introduction	1
2	Experimental techniques	5
2.1	Introduction	5
2.2	Muon Spin Rotation - μ SR	6
2.3	Magnetisation in pulsed magnetic fields	16
2.4	Low-field magnetic susceptibility, heat capacity and steady-field magnetisation	22
2.5	Participants involved in experiments	25
3	Fe-based superconductors	28
3.1	Introduction	28
3.2	Overview of Fe - based superconductors	29
3.3	Two-dimensional magnetism in SrFeAsF	32
3.4	NaFeAs and its phase diagram	43
4	Complex iridates	58
4.1	Introduction	58
4.2	Experimental methods	61
4.3	Ca_4IrO_6 and $\text{Ca}_5\text{Ir}_3\text{O}_{12}$	62

4.4	Sr_2IrO_4 and $\text{Sr}_3\text{Ir}_2\text{O}_7$	66
4.5	Conclusion	73
5	Low-dimensional coordination polymers	78
5.1	Introduction	78
5.2	Overview of low-dimensional magnetism	80
5.3	Exchange interaction and anisotropy of the coordination polymers [Cu(HF ₂)(pyz) ₂]X	85
5.4	Magnetism of [Cu(Y) ₂ (pyz) ₂](ClO ₄) _n	91
5.5	Tuning the dimensionality of coordination polymers	103
5.6	Halogen-halogen bonds in Spin- $\frac{1}{2}$ Heisenberg antiferromagnets . .	115
5.7	Q1D magnetism in Cu(2.5-me ₂ pyz) (CH ₃ SO ₃) (NO ₃) (H ₂ O) and [Cu(2.3-me ₂ pyz) (CH ₃ SO ₃) (H ₂ O) ₂](CH ₃ SO ₃)	126
5.8	Conclusion	131
6	Conclusion	133
	References	141

1

Introduction

During the last two decades solid state chemists and crystal growers have produced low-dimensional magnets with many interesting properties, such as the layered cuprate high-temperature superconductors or transition-metal compounds, some of which are described in this thesis. In such systems the interaction is not equal in all directions but is confined mainly along a chain or within a plane. Due to the combination of low-dimensionality, strong interactions and quantum fluctuations these materials exhibit a multitude of interesting phenomena, such as the Haldane gap or the spin-Peierls transition [10].

We define a low-dimensional magnetic system to be a material, characterized by anisotropic exchange interactions that lead to quasi-two-dimensional (Q2D) or quasi-one-dimensional (Q1D) magnetism. Q2D systems usually consist of layered structures in which the exchange coupling is much stronger than between the layers, whereas Q1D systems are mostly built out of chains which are only weakly coupled to each other, but exhibit strong exchange interactions within the chains [75].

The effect of reduced dimensionality is believed to be an important ingredi-

ent in systems such as the high temperature copper oxides and iron-arsenides. Although some families, such as the 122 pnictides, have more three-dimensional electronic structures, the low dimensionality in most of these systems is still thought to be of importance and the superconducting compounds studied in this thesis (see Chapter 3) exhibit two-dimensional magnetism.

The interplay between the magnetism and superconductivity under investigation in the high temperature superconductors is also one of the reasons that makes the iridate compound Sr_2IrO_4 , (presented in Chapter 4 particularly interesting. The quasi-two dimensional magnetism in this material is intriguing due to its similarity to the cuprate superconductor La_2CuO_4 and its contrasting behaviour compared to the more conventional iridates which exhibit three dimensional magnetism.

Coordination polymers have attracted much attention because they are, in principle, easier to treat theoretically than three-dimensional (3D) systems. These self-organising materials are based on the complex chemistry of carbon, and can be created with an increasing degree of control. They are ideal for the study of the quantum theory of magnetism, magnetic exchange and the dependence on dimensionality, as well as furthering our understanding of the competition between magnetism and superconductivity.

I principally used two techniques for the study of these compounds: muon spin rotation and pulsed magnetic field magnetisation experiments. Muons are positively charged particles which, in our experiments, are implanted inside the sample. They are used as a local probe of internal fields and make it possible to follow an order parameter as a function of temperature. In addition they are very sensitive to weak fields, which makes them perfect for the study of molecular

magnetic materials and superconductors,

The investigation of condensed matter materials generally involves the use of extreme conditions, such as low temperatures, high pressures and high magnetic fields. Pulsed magnets provide the highest possible non-destructive field in the world – 97.4 T at the National High Magnetic Field Laboratory in Los Alamos, New Mexico – and thus play an important role in condensed matter research. In this thesis I will use pulsed magnetic field experiments to bring molecular magnetic materials to magnetic saturation and use the high-field magnetisation experiments to demonstrate the effect of varying the dimensionality. The thesis is structured as shown in the thesis outline on the following page.

Thesis Outline

Chapter 2 : Experimental techniques The main techniques of muon spin rotation (μ SR) and pulsed magnetisation experiments are described in detail, including an overview of the facilities, the theoretical background and experimental considerations.

Chapter 3 : Magnetism in Fe-based superconductors The magnetic transition in the pnictide parent compound SrFeAsF and the magnetism in NaFeAs are investigated using μ SR. The study includes the effect of partially replacing Fe with Co in NaFeAs.

Chapter 4 : Magnetism in iridate compounds Exotic magnetism in the iridium oxide Sr₂IrO₄ is presented and compared to the more conventional iridates Ca₄IrO₆, Ca₅Ir₃O₁₂, Sr₃Ir₂O₇.

Chapter 5 : Low-dimensional coordination polymers A combination of pulsed field magnetisation experiments, μ SR and low field susceptibility measurements are employed to investigate the interaction strengths and effect of various changes of molecular architecture on the magnetism in coordination polymers.

Chapter 6 : Conclusion Overview of the results obtained in the different chapters and conclusions drawn from them

2

Experimental techniques

2.1 Introduction

This chapter contains a description of the experimental techniques that have been employed to obtain the results presented in this thesis. The experimental work was performed using two types of techniques, microscopic measurements in the form of muon-spin rotation (μ SR) and bulk measurements which include magnetisation in pulsed magnetic fields, as well as susceptibility and heat capacity measurements. I give an explanation of μ SR, detailing the properties and the production of muons as well as the stopping and decay processes involved. The experimental geometries and methods are described along with the limitations that have to be considered. Furthermore the magnets used to achieve high magnetic fields and the technique utilised to perform magnetisation measurements in these magnets is described. This chapter also contains a brief explanation of the principles involved in heat capacity and susceptibility measurements which were performed using the Superconducting QUantum Interference Device (SQUID) and the Physical Property Measurement System (PPMS).

2.2 Muon Spin Rotation - μ SR

μ SR is a technique that is based on the implantation of spin-polarised muons in matter. Its sensitivity to extremely weak fields makes it interesting for the investigation of structure and dynamics on the atomic scale. Muons are a local probe of internal fields, and are essentially used as sensitive magnetometers [11]. The principle of this technique is that the implanted muons in the system precess in the low magnetic field in the material. As we shall see, muons can be implanted with 100% spin polarisation and in this respect the technique is different from Electron Spin Resonance (ESR) and Nuclear Magnetic Resonance (NMR), although all three are local-probe techniques. The spatial and temporal characteristics of internal fields can be studied by measuring the change of the spin polarisation of the muons, making it possible to investigate problems in solid state physics that otherwise could not be addressed [9].

The muon

	q	S	m	μ (μ_b)	$\gamma/2\pi$ (MHz T $^{-1}$)	τ_μ (s)
e	-e	1/2	m_e	-1.0011	2802×10^{-3}	∞
μ	+e	1/2	$207 m_e$	4.88×10^{-3}	135.5	2.19×10^{-6}
n	0	1/2	$1840 m_e$	-1.713×10^{-3}	183.3	885

Table 2.1: Properties of electron, muon and neutron: charge, spin, mass, magnetic moment, gyromagnetic ratio and lifetime.

The properties of the muon are listed in Table 2.1 alongside the properties of an electron and a neutron. It is the particularity of these properties that makes μ SR such a useful technique for condensed matter physics. Muons are elementary spin $-\frac{1}{2}$ particles that have a mass between that of an electron and a

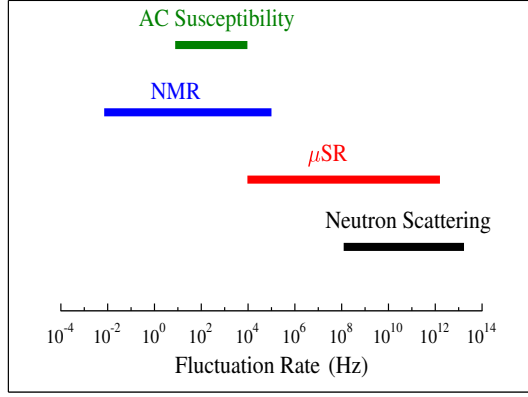


Figure 2.1: Range of fluctuation rates that can be measured with different techniques.

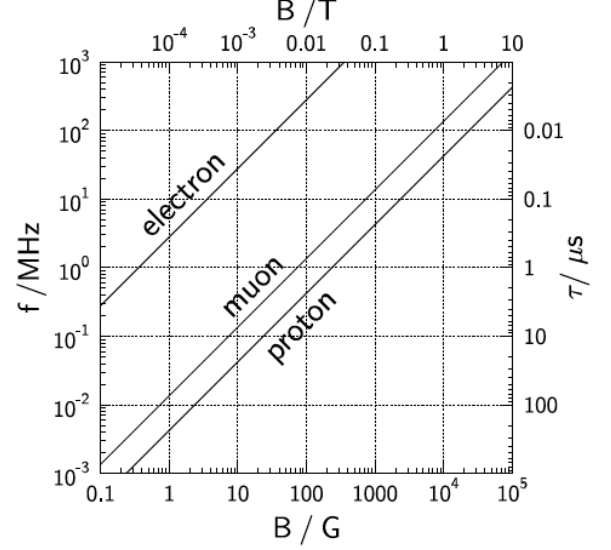


Figure 2.2: Larmor precession frequencies for electron, muon and proton [7].

neutron. Their spin-state of $\frac{1}{2}$ means that quadrupolar interaction does not occur, in contrast to NMR of $S > \frac{1}{2}$ where this can lead to broadening and weakening of the observed resonances. The lifetime of a muon is $2.19 \mu\text{s}$, which is comparatively long for a condensed matter process. This enables the measurement of fluctuation rates in the range of 10^4 to 10^{12} Hz. This time-window bridges the gap between NMR and neutron scattering as illustrated in Figure 2.1.

Muons can be either negatively or positively charged, but only the positive muon is of interest for most muon-spin rotation experiments. This is because this technique is based on the implantation of the muon at a specific site in the studied material. A negatively charged muon is attracted to the atomic nuclei and thus is not very sensitive to the magnetic properties of the system. However the positive muons are attracted to negative charge density, such as large areas of

electron density. So they are implanted at interstitial sites in inorganic materials or bond on to organic molecules [7]. Most importantly the large gyromagnetic ratio of the muon, which is proportional to its magnetic moment, results in a technique that is extremely sensitive and can detect fields down to 10^{-5} T.

Production of a muon beam

Muon spin rotation experiments are only possible in synchrotrons and cyclotrons. They provide high energy protons (~ 600 MeV) that are necessary for the production of muons. These protons are set to collide with a target (in most cases graphite), which contains protons and neutrons, which then creates pions:

$$p + p \rightarrow p + n + \pi^+ \quad (2.1)$$

$$p + n \rightarrow n + n + \pi^+ \quad (2.2)$$

$$p + n \rightarrow p + \pi^-, \quad (2.3)$$

where p , n and $\pi^\pm$ are a proton, a neutron and a positive or negative pion, respectively. Although there exist different techniques for muon production, for the one most commonly used the pions decay into muons $\mu^\pm$ and neutrinos, ν_μ and $\bar{\nu}_\mu$, while at rest in the surface layer of the target via the reactions:

$$\pi^+ \rightarrow \mu^+ + \nu_\mu \quad (2.4)$$

$$\pi^- \rightarrow \mu^- + \bar{\nu}_\mu. \quad (2.5)$$

The muons are 100 % spin polarised, because the spin of the neutrino is anti-parallel to its momentum; it has negative helicity; and the decaying pion has zero

spin. Therefore the spin of the muon has to be anti-parallel to its momentum, resulting in a spin-polarised particle [54]. The orientation of the muon spin can be rotated by 90° if it proves to be favorable for the experiment, using electric and magnetic fields, which are oriented perpendicular to each other as well as to the muon beam.

The high energy (4 MeV) muon beam produced is then guided to the sample through a combination of steering and focussing quadrupole magnets. Contaminating uncharged and negatively charged particles in the beam are separated off by a system of opposing electric and magnetic fields [8, 54].

Following implantation in the sample, the muons rapidly lose energy down to a few hundred eV, due to stopping processes such as ionization of atoms, scattering with electrons and series of electron capture and loss, whilst still retaining their polarisation [7].

Muon decay

The positive muon which has been implanted in the sample decays with a lifetime of $2.19 \mu\text{s}$ into a positron, an electron-neutrino and a muon-antineutrino:

$$\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu. \quad (2.6)$$

The decay occurs via weak interaction and violates parity, which means that the positrons produced in this reaction are emitted along the muon spin direction at the time of decay with an angular distribution given by:

$$N(\theta) = N_0(1 + \alpha \cos \theta), \quad (2.7)$$

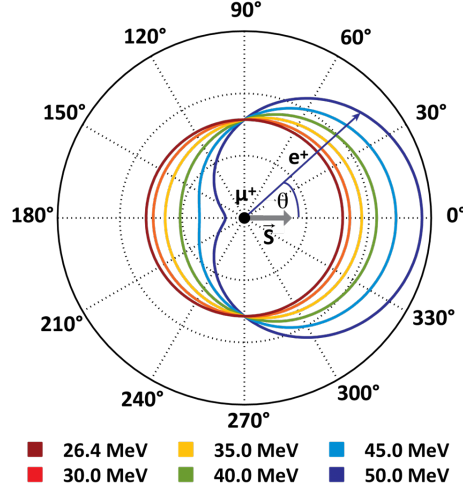


Figure 2.3: Angular distribution of positrons emitted when the muon decays. The emission distribution depends on the positron energy [68].

where θ is the angle between the muon spin and the direction in which the positron is emitted. The asymmetry factor α reflects the positron energy ϵ with $\alpha = 1$ for maximum energy and $\alpha = -\frac{1}{3}$ for $\epsilon = 0$. α takes the value of $\frac{1}{3}$ when all possible energies are averaged as shown in Figure 2.3 [68]. The detection of the positrons enables us to measure the polarisation of the muons at the moment of their decay.

Experimental procedure

The spin of the muon precesses in a magnetic field (internal or external) at the Larmor frequency $\omega = \gamma B$, where the gyromagnetic ratio of the muon is $\gamma = ge/2m\mu = 2\pi \times 135.5 \text{ MHz T}^{-1}$. The spin of the implanted muons will therefore precess in direct proportion with the magnetic field at the implanted muon site. Information on the effect of the field experienced by the muon spin in the sample is gained by recording the angle and time dependence of the positron emission

using scintillating detectors which are arranged around the sample.

There are essentially two different geometries for μ SR, as shown on Figure 2.5. In the longitudinal-field (LF) configuration the external magnetic field is applied parallel to the muon beam and the initial muon spin direction. For this geometry the detectors are at the front and the back of the sample and measure the rate at which the muon loses its initial polarisation. This experiment can also be performed in zero field, in which case the evolution of the muon polarisation only depends on local magnetic fields inside the sample.

In the most basic configuration the time evolution of the spin polarisation can be studied by obtaining the normalized difference of the counts in forward and backward detectors, which is defined by the asymmetry function

$$A(t) = \frac{N_F(t) - aN_B(t)}{N_F(t) + aN_B(t)}, \quad (2.8)$$

where a describes the difference in efficiency of the two detectors [8]. $A(t)$ is proportional to the muon polarisation along the z-axis, $p_z(t)$, which is the quantity of interest for this technique. As shown in Figure 2.4, $p_z(t)$ can be defined as follows:

$$p_z(t) = \cos^2 \theta + \sin^2 \theta \cos(\gamma B t), \quad (2.9)$$

The samples that are measured in this thesis are polycrystalline. Since the direction of the local field will only affect the amplitude of the frequencies and not the actual value (which only depends on the magnitude of the field), it means that we can take a “powder average” :

$$p_z(t) = \frac{1}{3} + \frac{2}{3} \cos(\gamma B t). \quad (2.10)$$

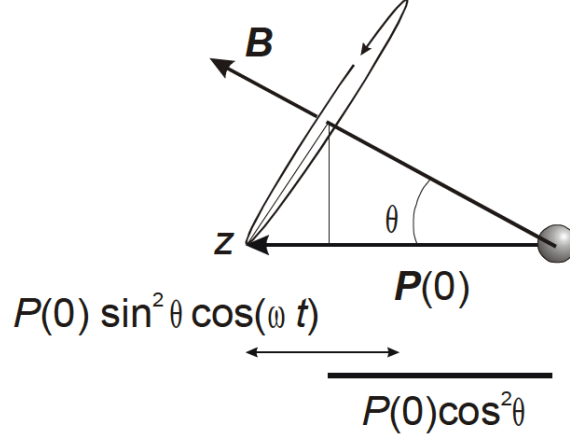


Figure 2.4: Muon spin precession around an internal field B at angle θ . The oscillating and non-oscillating components of the polarisation are shown are given.[1]

Through $\frac{1}{3}$ of the sample the local field will be parallel to the initial muon spin component, leading to the so-called “ $\frac{1}{3}$ - tail” in the data of powdered samples in the ordered state.

For the transverse-field geometry (TF) the external magnetic field is applied perpendicular to the muon beam and the muon spin direction. The detectors are placed around the beam, rather than intersecting it. This set-up is used to measure the precession frequencies of the muon spin as well as the broadening and dephasing observed in these.

For each set-up detectors at the right and at the left of the sample can also be added, in order to cover a larger solid angle. The raw positron spectra and asymmetry for both configurations is shown on Figure 2.6.

There are two different kinds of muon sources: continuous wave, in which the muons arrive in the sample one by one; and pulsed, in which the muons arrive in large numbers [3, 54]. In my project I have used both a continuous wave source (Paul Scherrer Institut, Switzerland) and a pulsed source (ISIS-UK).

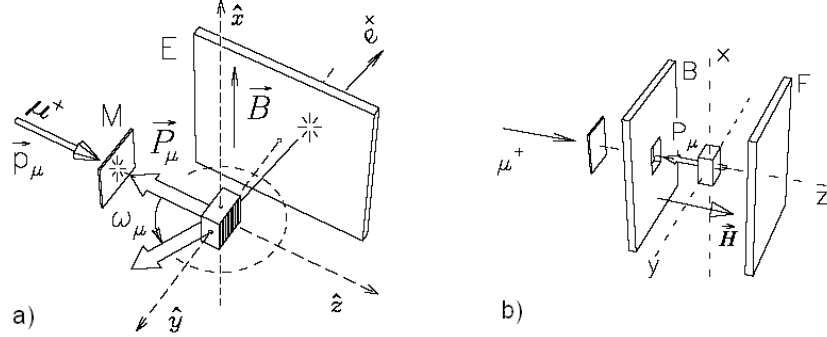


Figure 2.5: a) TF measurement configuration. b) ZF and LF configuration [20].

The swiss muon source at the Paul Scherrer Institut is the world's most intense continuous-beam muon source. It is powered by a 590 MeV cyclotron with a proton current of 2 mA. It has seven different beamlines for muon measurements, with a range of different instruments. Muon energies range from 0.5 keV to 60 MeV. A muon arrives at the sample at time intervals of on average 10 μ s. The arrival of the muon in the sample is detected, providing a start time for every event. Any second muon is prevented from entering the system before the first muon has decayed, so that the emitted positron can be ascribed to a specific muon. Continuous wave sources provide the means to achieve a high time resolution, which is interesting for the study of large magnetic fields and fast relaxation. However, this technique is restricted by the lifetime of the muon, which leads to a high background and a limited time-window.

The pulsed muon source at ISIS, Rutherford Appleton laboratory, provides the most intense pulsed muon beam in the world. It is powered by a synchrotron, which produces a proton current of 180 μ A at 800 MeV. At a frequency of 50 Hz a double pulse of protons is created by the synchrotron. 2 to 3 % of the beam is used to produce muons which are then distributed to the different muon beamlines,

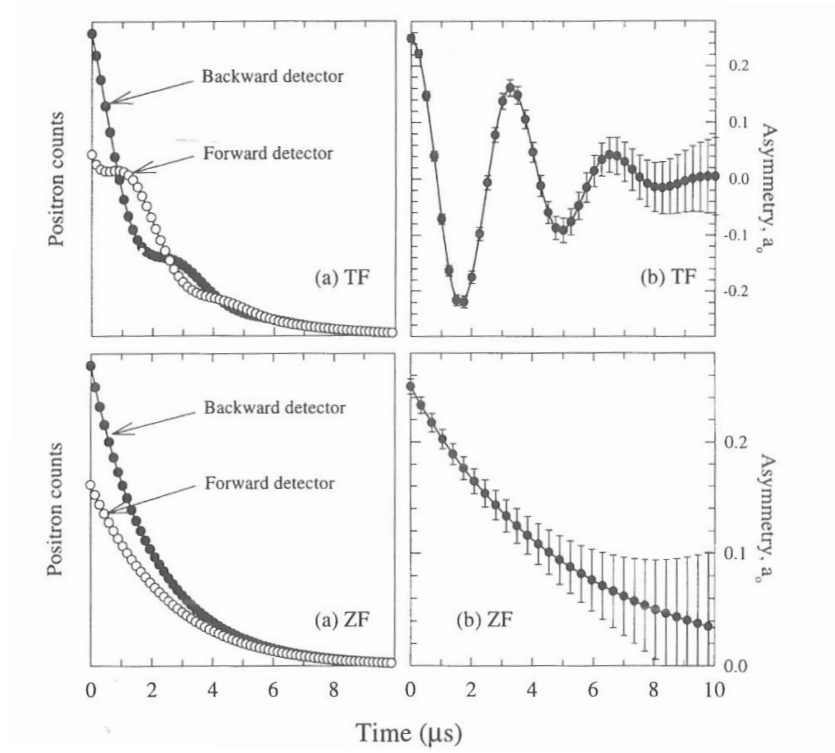


Figure 2.6: Raw positron spectra and associated asymmetry for transverse and longitudinal field configurations [48].

using a fast electrostatic kicker. Muons arriving in pulses lead to a higher count rate, but the experiment has to be adapted to the limitation resulting from the pulse width. The first event defines the start of the data collection. The t_0 is defined as the time when the centre of the pulse arrives at the sample and t_{offset} describes the time after t_0 at which reliable data can be recorded. These different values have to be kept in mind whilst analysing the data.

Pulsed muon sources enable us to measure long-lived muons (1 % of muons live longer than 10 μ s, 0.01 % of muons live longer than 20 μ s), resulting in very low background and a large time-window, which hence makes it very interesting for studies of the shape of the relaxation. But in contrast to continuous wave, pulsed

2.3 Magnetisation in pulsed magnetic fields

muon sources have a low time resolution and are limited to lower fluctuation rates. Combining both systems makes it possible to measure a large range of condensed matter phenomena.

I worked on various instruments to obtain the results presented here: GPS, LTF and DOLLY at the Paul Scherrer Institut and MuSR, EMU, ARGUS and HIFI at ISIS. Much of the work was performed primarily on GPS and MuSR, which is why I describe both of these instruments here.

The General Purpose Surface-Muon Instrument (GPS) in PSI is set-up for both LF and TF measurements with five positron detectors. The configuration consists of one muon detector (M), five positron detectors (forward (F), backward (B), up (U), down (D), right (R)), a backward veto detector (B_{veto}) and a forward veto detector (F_{veto}). The veto detectors discriminate against events not originating in the sample. The sample is cooled in a top-loading continuous-flow ^4He cryostat and fields of up to 0.6 T can be applied parallel to the beam.

The general purpose MuSR instrument in ISIS consists of 64 detectors. A rotation through 90° makes it possible to measure either in longitudinal field or transverse field configuration. The system works with variable-temperature cryostats that reach temperatures down to 40mK and fields up to 2500 G can be applied.

2.3 Magnetisation in pulsed magnetic fields

Pulsed magnetic fields

The need for high magnetic fields in condensed matter research is considerable. High magnetic fields are provided by electromagnets, using two different methods.

2.3 Magnetisation in pulsed magnetic fields

The DC method uses extremely high DC currents that flow in highly conducting materials to create magnetic fields up to 45 Tesla. These fields are limited by the power they are dissipating, by the cooling provided by high pressure water supplies around the coils and in the case of superconducting magnets by the critical current density and temperature [27, 41]. Resistive magnets reach fields of 33 T and superconducting magnets can provide fields up to 20 T. Combining both superconducting and resistive coils in one magnet makes it possible to optimize heat dissipation and stress levels, to achieve higher fields. The Hybrid magnet at NHMFL in Tallahassee produces DC fields up to 45 T.

Pulsed magnetic fields play an important role in high-field research, as they make it possible to create much higher fields than the DC magnets. The highest field in the world provided by non-destructive magnets is 97.4 T and is generated by a system of two coils, with a long and a short pulse respectively, in the National High Magnetic Field Laboratory (NHMFL), Los Alamos [66].

The work presented here has been obtained using mostly the pulsed field facility in Oxford, the Nicholas Kurti Magnetic Field Laboratory (NKMFL), which provides fields up to 55 T and the pulsed magnets at the NHMFL in Los Alamos which reach 65 T. The properties of the systems are detailed in Table 2.2.

The method with which the pulsed fields are generated in the two facilities is principally the same. The pulsed magnets consist of a coil of highly conducting and mechanically strengthened wire and are capacitor bank driven. The high voltage capacitor bank is rapidly discharged through the coil, which induces a magnetic field pulse. The coil has to be kept cooled to liquid nitrogen temperatures as the electric energy discharged into the coil is released not only in the form of magnetic energy but also in the form of heat. After each magnetic pulse the

2.3 Magnetisation in pulsed magnetic fields

	NHMFL (Los Alamos)	NKMFL (Oxford)
Peak field		
capacitor bank driven	50 T – 70 T	55 T
ac power driven	40 T – 60 T	—
capacitor and ac power	80 – 100 T	—
Pulse duration		
capacitor bank driven	20 – 800 ms	10 – 100 ms
ac power driven	2 s	—
capacitor and ac power	20 ms	—

Table 2.2: Properties of the pulsed magnetic field systems used in this thesis. There are a variety of different magnets at the NHMFL.

coil heats up and its resistivity increases. It is then allowed to cool back down to liquid nitrogen temperatures. The time-interval between two pulses depends on the cooling time of the coil and increases with peak field. The resistive magnets that are employed for this technique can withstand stress of 1 - 3 GPa. The stress increases with the square of the field strength [27].

The short time duration of the pulses means that fast electronics need to be used to read out data during a measurement. In addition, pulsed magnets generally have very small bores, which limits the size of the mechanical instrumentation that can be inserted into the magnet.

The typical shape of a pulse generated in the NKMFL, with a duration limited to $t \leq 100$ ms is shown in Figure 2.7. The stress created by the field on the material limits its strength to about 60 T.

Magnetisation

Pulsed magnetic fields are employed to measure various characteristics of materials, such as magnetic, transport and optical properties. This thesis concentrates

2.3 Magnetisation in pulsed magnetic fields

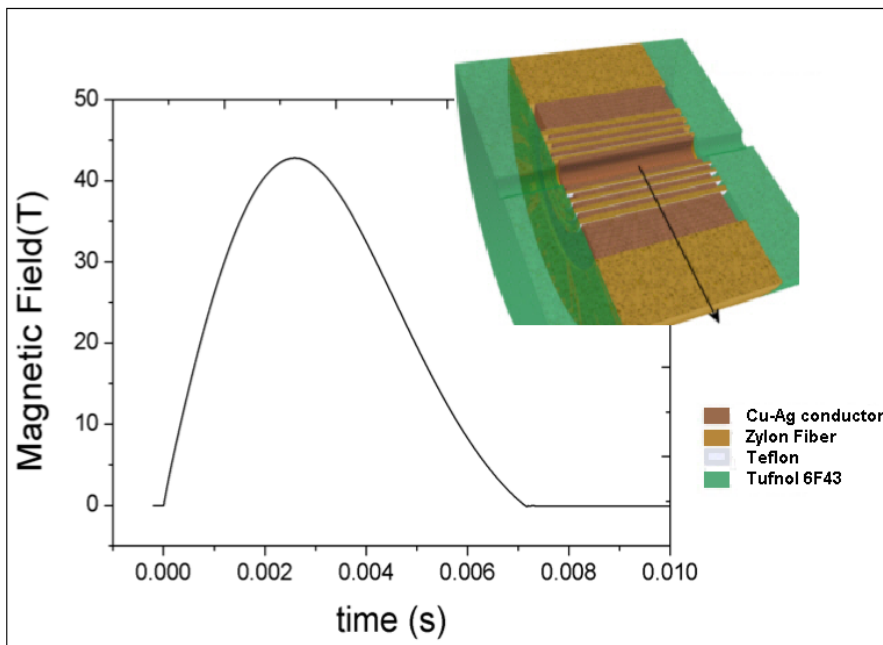


Figure 2.7: Typical pulse shape for measurements in the Nicholas Kurti Magnetic Field Laboratory (NKMFL), Oxford. The inset shows the cross-section of a typical magnet built by the magnet laboratory in Oxford [32].

on studies of the magnetisation in pulsed fields. Magnetisation M is defined as the magnetic moment of a material per unit volume and can be expressed by relating it to induction B and magnetic field H :

$$B = \mu_0(H + M). \quad (2.11)$$

When all the magnetic moments are aligned in the direction of the external field the magnetisation saturates and is labelled M_{sat} . The value and evolution of magnetisation with field and temperature changes, depending on the type of material [2], and studying the shape and magnitude of magnetisation makes it possible to extract information on the nature of the magnetic interactions present in the sample.

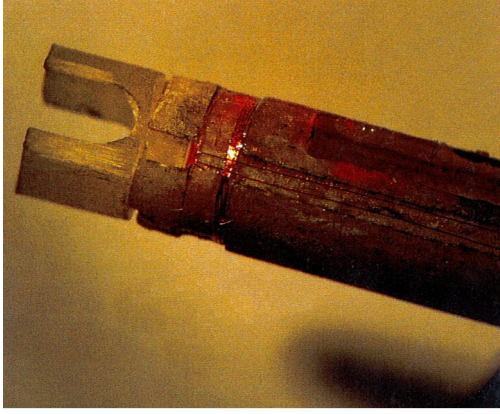


Figure 2.8: View of the magnetisation probe. The B-dot and compensation coil are wrapped around the outside.

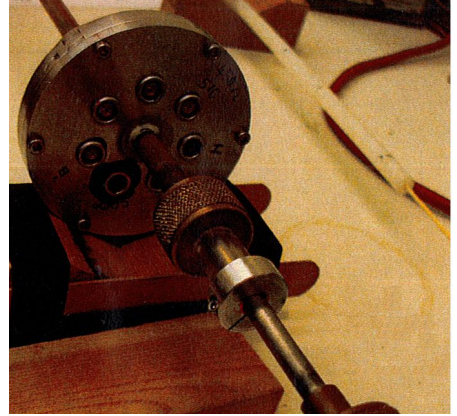


Figure 2.9: Top-view of the magnetisation probe. The sample position is controlled from here.

The experiment

For the experiments included in this thesis, magnetisation was measured with a compensated coil magnetometer shown in Figure 2.8. In such a system the rate of change of magnetic field is measured via the voltage induced in a simple coil and integrated to obtain the field profile. The instrument takes advantage of the high rate at which the field changes in pulsed magnets.

The magnetic field induces a magnetisation in the sample. This is picked up as an induced voltage by a coil that surrounds the sample, which is given by

$$V = \frac{dM}{dB} \times \frac{dB}{dt}. \quad (2.12)$$

In order to obtain accurate values of the sample magnetisation the additional voltage from the self-induction of the measurement coil must be minimised. For this reason the coil is made out of two counter-wound coils that are connected in series and have a total of ~ 1500 turns. The areas of the two coils have to be as similar as possible in order for the pick-up voltage of the empty coil to be close

2.3 Magnetisation in pulsed magnetic fields

to zero.

The remaining signal induced in the coil by external field change is then accounted for by a single-turn “compensation” coil. The voltage of the measurement coil and the voltage of the compensation coil are balanced out to give zero in a 10 T pulse signal when the sample is not located in the pick-up coil.

The sample is mounted inside a small ampule (Figure 2.10 and Figure 2.11), which is then attached to a probe that makes it possible to insert and extract the sample while the magnetometer is in place from the top of the probe (see Figure 2.9).

The experiment is executed by taking a background measurement in which the sample is removed from the coils. This background signal contains an in phase component due to the difference in area of pick up and compensation coil, which can be removed by a circuit for fine compensation. The remaining out of phase component, resulting from for example eddy currents, is subtracted from the measurement with the inserted sample at the same compensation and same peak field.

The field is measured by a so-called “B-dot” coil, which is attached to the probe in proximity to the sample. A voltage $V \propto \frac{dB}{dt}$ is induced in the “B-dot”. The voltage change is recorded and by integrating $\frac{dB}{dt}$ a time profile of the field is obtained. Combining the $\frac{dM}{dt}$ data (Eqn. 2.12) and the signal from the B-dot coil and integrating, results in data of the form of M vs B . These can then be calibrated using low-field susceptibility data to obtain absolute values of magnetisation at high fields. As the measured signal is proportional to $\frac{dM}{dB}$ it is very sensitive to steep changes in magnetisation and is most effective for measurements that exhibit such features as for example metamagnetic transitions [64].

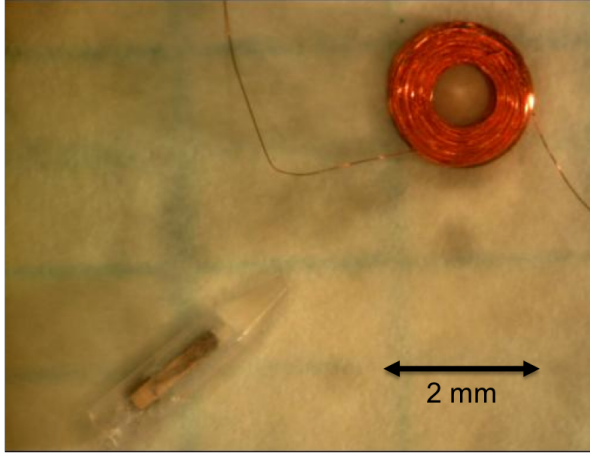


Figure 2.10: A typical sample mounted inside an ampoule and the pick-up coil before it is attached and connected to the probe.

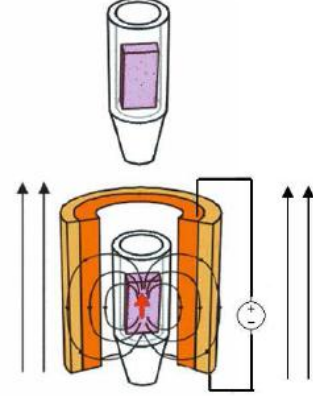


Figure 2.11: Schematic of the sample at the two different measurement positions, inside and outside the coil.

2.4 Low-field magnetic susceptibility, heat capacity and steady-field magnetisation

Magnetic susceptibility and magnetisation up to 7 T

Low-field magnetic susceptibility is measured to obtain a basic characterization of the magnetic properties of a sample in advance of pulsed field measurements. It is a bulk measurement that provides information such as the size of the average magnetic moment, the temperature and nature of the magnetic transitions and can potentially shed light on type and strength of coupling. Magnetic susceptibility measurements were performed using a Quantum Design Magnetic Property System (MPMS). The instrument is an automated, computer-controlled system that enables temperature control over a range of 1.8 K to 400 K and magnet control up to 7 T (produced by a superconducting magnet), as well as measurement and sample-handling control. It provides the means to measure the magnetic

2.4 Low-field magnetic susceptibility, heat capacity and steady-field magnetisation

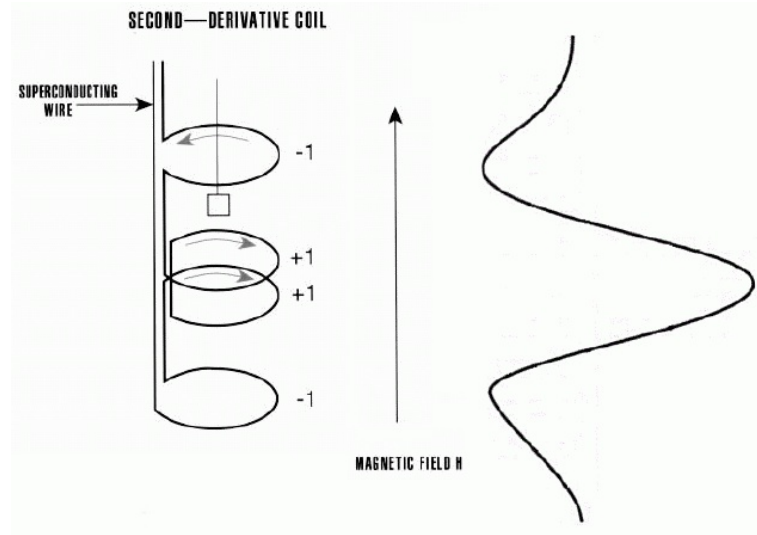


Figure 2.12: SQUID detection coils and the typical signal shape from which the magnetisation is extracted. The detection coils consist of a superconducting wire which forms three sets of coils: 1 - single turn, clockwise; 2 - two turns, counter-clockwise; 3 - single turn, clockwise. This system is used to reduce the noise caused by the fluctuations in the large magnetic field of the superconducting magnet.

moment of a sample in function of temperature and field.

The core of this instrument is a Superconducting QUantum Interference Device (SQUID), which acts as a very sensitive magnetometer and consists of a superconducting current loop with a pair of Josephson junctions. The SQUID is connected to a set of superconducting detection coils and they form a closed superconducting loop. The technique is based on the effect created by a sample being moved through the detection coils. The change in sample position leads to a change in the flux of the coils and this leads to a change in the persistent current in the circuit. Since the SQUID output voltage is proportional to the current in the loop, a measurement of this voltage can be used to infer the magnetic moment in the sample.

The sample is mounted in a gel capsule held inside a plastic drinking straw.

2.4 Low-field magnetic susceptibility, heat capacity and steady-field magnetisation

This is then inserted coaxially inside the detection coils and the sample position adjusted to obtain the ideal signal in function of position, which is of the form $\frac{\sin x}{x}$. Both the coil configuration and the sample response are shown in Figure 2.12. To achieve satisfactory results the sample has to be much smaller than the detection coils, but big enough to create a good signal. For the measurement, the sample is then moved to different positions where several readings of the SQUID voltage are taken and averaged. Fitting the data to one of three different models that are included in the instrument software (“full scan”, “linear regression”, “itinerant regression”) makes it possible to extract the magnetic moment at different temperatures and field strengths and thus give a measure of magnetic susceptibility.

Heat capacity

The Physical Property Measurement System (PPMS) is an automated instrument similar to the MPMS. A multifunctional probe with a series of different sample platforms makes it very versatile. It can perform a variety of material property measurements as a function of field (up to 14 T) and temperature (0.4 K – 400 K). These include heat capacity, thermal transport, DC and AC magnetometry, resistivity and AC transport. For the experiments presented here the heat capacity option was used.

Heat capacity measurements give information on the entropy change of a sample as a function of temperature and thus make it possible to extract information on the lattice, electronic and magnetic properties. The results obtained from heat capacity allow a direct comparison between experiment and theory, making them a valuable tool in condensed matter physics. The heat capacity is measured as a

2.4 Low-field magnetic susceptibility, heat capacity and steady-field magnetisation

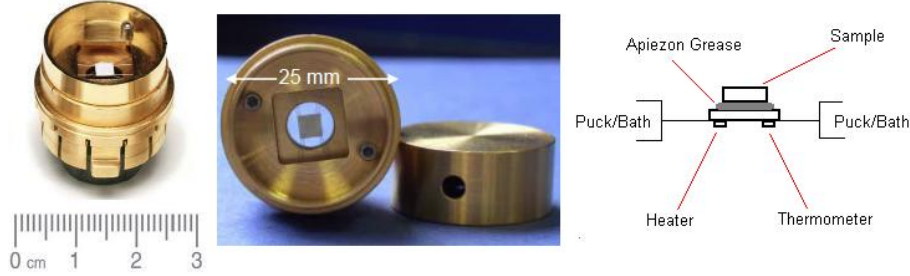


Figure 2.13: Heat capacity puck and schematic of sample platform with mounted sample.

function of temperature at constant pressure:

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_P, \quad (2.13)$$

where dQ is the change in heat energy in the system. To realise the experiment the sample goes through heating and cooling periods of a fixed time duration. The temperature profile of the sample is monitored to extract the thermal response and thus the heat capacity. The sample is mounted on a quartz platform with a thin layer of apiezon grease. A thermometer and heater are attached to the platform and two small wires provide electrical contact as well as a well-defined thermal link. Samples between 1 mg – 200 mg are measured with this system. The sample has to be relatively flat to allow good thermal contact and ensure that the time to reach thermal equilibrium is relatively small.

The “addenda” is produced for calibration, by measuring the response of the puck and grease without a sample. After each measurement, the provided software fits the whole temperature range to model the relaxation of the sample, sample platform and bath:

$$C_{total} \frac{dT}{dt} = -K_W(T - T_B) + P(t). \quad (2.14)$$

C_{total} in this expression describes the heat capacity of sample and platform, K_W represents the thermal conduction of the wires, T_B is the temperature of the bath and $P(t)$ is the heater power.

2.5 Participants involved in experiments

The results in this thesis stem from collaborative work with institutions and facilities across the world.

- The electron spin resonance (ESR) described in Chapter 5 was performed by Ross McDonald and Oscar Ayala-Valenzuela both at the NHMFL, Los Alamos National Laboratory.
- Quantum Monte Carlo Simulations used in Chapter 5 were done by Pinaki Sengputa, at the School of Physical and Mathematical Sciences, Nanyang Technical University, Singapore.
- Crystal synthesis and related crystal structure measurements were performed by three different research groups: the Solid State Chemistry Research group at the Inorganic Chemistry department, Oxford University, produced the pnictide compounds described in Chapter 3; the iridates analysed in Chapter 4 were grown by Prof. Gang Cao at the Center for Advanced Materials at the University of Kentucky;

2.5 Participants involved in experiments

the organic chemists Jamie Manson at the Eastern Washington University and John Schlueter at Argonne National laboratory synthesised the various coordination polymers described in Chapter 5.

- Magnetic susceptibility measurements, pulsed field magnetisation experiments and muon spin rotation were performed by myself, the principle researcher, in collaboration with the following people: Stephen Blundell, Paul Goddard, Tom Lancaster, Andrew Steele, Jack Wright and Saman Ghannadzadeh in the Correlated Electrons Group, Oxford University; Peter Baker and Francis Pratt at ISIS, Rutherford Appleton Laboratory; John Singleton at the NHMFL, Los Alamos National Laboratory.

3

Fe-based superconductors

3.1 Introduction

Since the observation of high-temperature superconductivity in the cuprates in 1986 scientists have been trying to understand the mechanism at work in these systems. Until recently, high-temperature superconducting behaviour was confined to systems containing copper oxygen planes, so that it seemed that the presence of copper atoms was of key importance.

In 2008 Hosono *et al.* observed superconductivity in fluorine doped LaFeAsO [80]. LaFeAsO_{1-x}F_x with $x = -0.11$ reached a T_c of 26 K. It is composed of FeAs layers, in which the Fe is arranged in a square planar lattice. These alternate with LaO layers along the c-axis. Nobody had foreseen that a T_c so high could be reached in a material containing a ferromagnetic element such as Fe. This surprising discovery has led to a frenzy of research activity in the condensed matter community. A range of new materials containing Fe-As layers has been found and T_c is now as high as 56 K [38]. The fascination with these compounds lies in the fact that, like the cuprates, they are unconventional, non-BCS superconduc-

3.2 Overview of Fe - based superconductors

tors. Two decades after the discovery of high-temperature superconductivity in the cuprates, this new class of superconductors could bring new insights into the mechanism of high-temperature superconductivity [67].

In this chapter I first introduce Fe-based superconductors, describing general properties and characteristics and their importance in the context of condensed matter research. I then present a study of the magnetism in the pnictide parent compound SrFeAsF . I go on to describe the interplay and coexistence of magnetism and superconductivity in the superconductor NaFeAs and will present the phase diagram of Co-doped NaFeAs .

3.2 Overview of Fe - based superconductors

Similar to the cuprate superconductors, all pnictide superconductors have a layered structure. Where the cuprates are built of Cu-O planes the central building block in the pnictides is layers of FeAs, in which the Fe finds itself in a square planar lattice arrangement, tetrahedrally coordinated by As or Te as shown in Figure 3.1. Superconductivity is thought to be associated with these layers [69, 80], which alternate with spacer layers along the c-axis.

To date, five different structure types have been identified. The simplest one, the 11 system, FeSe or FeTe , contains no spacer layers, whereas the other groups all have one or more. The other four systems are: the 111 system, $A\text{FeAs}$, with $A = \text{Li}$ or Na , the 1111 system, $M\text{FeAsO}$, with $M = \text{rare earth}$ and $M'\text{FeAsF}$, with $M' = \text{Ca, Sr}$, the 122 system, $R\text{Fe}_2\text{As}_2$, with $R = \text{Ca, Sr, Ba or Eu}$ and the more complicated $\text{Sr}_3\text{Sc}_2\text{O}_5\text{Fe}_2\text{As}_2$.

The generic phase diagrams of both cuprates and pnictides are shown in Fig-

3.2 Overview of Fe - based superconductors

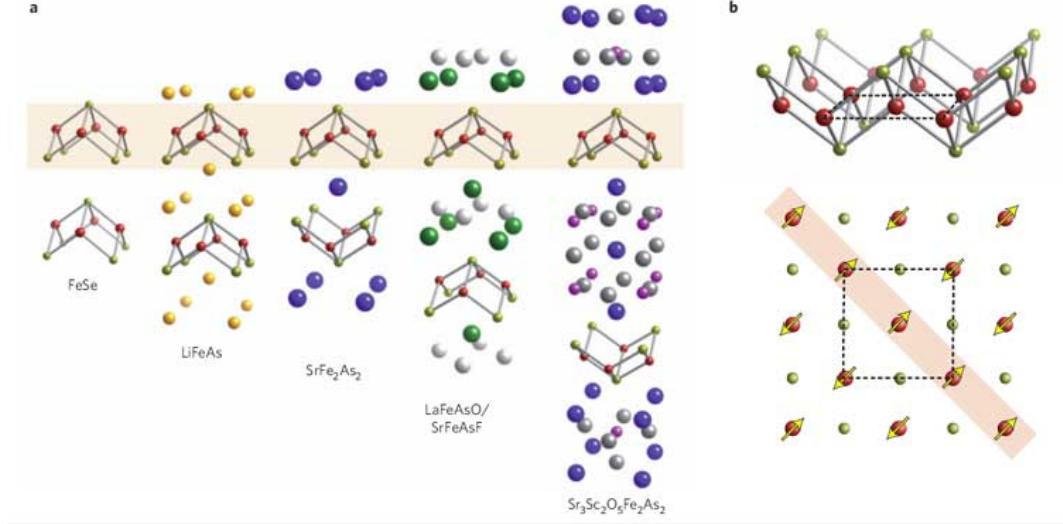


Figure 3.1: (a) The five different structure types of the pnictide superconductors. The common FeAs/Se layer, found in all groups, is highlighted by the shaded region. (b) View of one single FeAs block showing its tetragonal unit cell and the same block viewed from above showing the spins of the Fe-atoms forming the antiferromagnetic phase [69].

ure 3.2. The parent compounds are non-superconducting and optimal, bulk phase superconductivity is induced by changing the electron count [16], applying an external hydrostatic pressure [70], or making an isoelectronic chemical substitution which adjusts the structure (essentially applying a “chemical pressure”) [57] leading to a dome-like superconducting region in the phase diagram.

In contrast to the antiferromagnetic Mott insulating cuprates, the pnictides are bad metals at low temperatures. The formation of the Cooper pairs in both systems is of unconventional nature and spin fluctuations are thought to be the origin for d-wave pairing in the cuprates and s-wave pairing in the pnictides [60]. The difference in the pairing symmetries can be related back to the complicated nature of the multiple Fermi Surfaces in the Fe-based superconductors [6].

Both the cuprates as well as the pnictides undergo a magnetic transition at

3.2 Overview of Fe - based superconductors

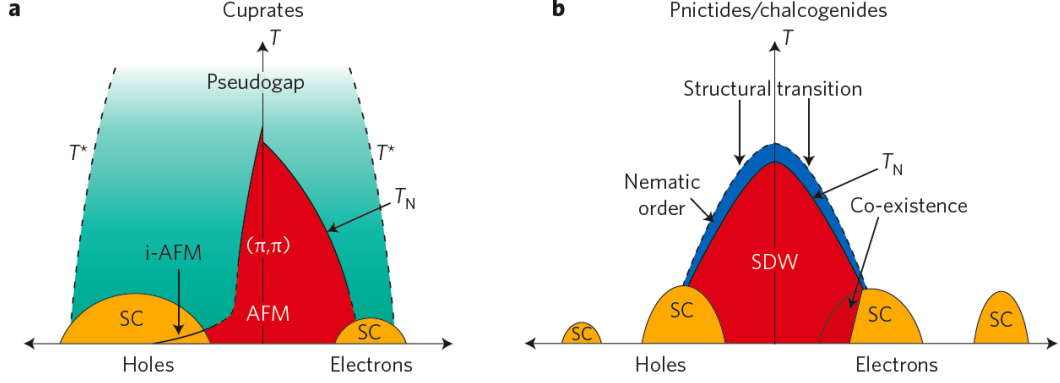


Figure 3.2: Every compound has its own particular phase diagram, but they show similarities that can be summarized in a generic phase diagram that only has to be slightly altered to adapt to the various compounds. These are the generic phase diagrams for the cuprates (a), and the Fe-based superconductors (b). Both the cuprates and the pnictides exhibit the typical superconducting dome on electron or hole doping. In some types of Fe-based compounds superconductivity emerges at very high doping levels. Antiferromagnetic order at stoichiometric phase is also observed in both types of high- T_c s, although the order does not seem to be driven by the same mechanism. The phases corresponding to the pseudogap in the cuprates and the nematic order in the pnictides are specific differences between the systems. [6]

low temperatures (in the range of 100 - 200 K). In the Fe-based superconductors this is accompanied by a structural transition, from tetragonal to orthorhombic, which is either simultaneous or precedes the magnetic transition, depending on the compound. The magnetic order is found to be a stripe-like antiferromagnetic order and coexistence between magnetic and superconducting phases is found in certain families [26, 34, 59].

Whether the magnetic transition is driven by the structural transition and what is driving the latter is an important issue for the understanding of the magnetic order in these materials. As in the case of the cuprates the interplay between magnetism and superconductivity seems to be of importance in the Fe-based superconductors. In addition the magnetic order arises from the Fe d-band

3.3 Two-dimensional magnetism in SrFeAsF

electrons, which are the same electrons that seem to form the superconductivity [60].

Magnetism has been thought to be antagonistic to superconductivity in BCS-type superconductors. But since the discovery of high-temperature superconductivity in cuprates, magnetism seems to be playing an important role in unconventional superconductors, not only in high- T_c systems but also in heavy fermions, ruthenates and organic and molecular superconductors. Trying to find answers to the questions of how magnetism and superconductivity interact, and to what extent magnetism is a crucial ingredient for unconventional superconductivity could give us important insights into the mechanism of high-temperature superconductivity.

3.3 Two-dimensional magnetism in SrFeAsF

Introduction

SrFeAsF was discovered in 2008 as a new parent compound of pnictide superconductors. It is part of the 1111 family of fluoroarsenide systems, which are isostructural with the oxopnictides, $M\text{FeAsO}$. These were the first Fe-based systems in which superconductivity was observed. In the fluoroarsenides the oxygen is replaced by fluorine and the rare earths are replaced by either Sr, Ca or Eu to achieve charge neutrality.

Superconductivity can be induced by doping in two different ways. You can either dope on the Sr site with a rare earth such as Pr, Nd or Sm; or on the Fe site with Co. The highest T_c achieved so far is 56 K in SrFeAsF doped with Sm, a value comparable to the transition temperatures observed in the $M\text{FeAsO}$

family [4] .

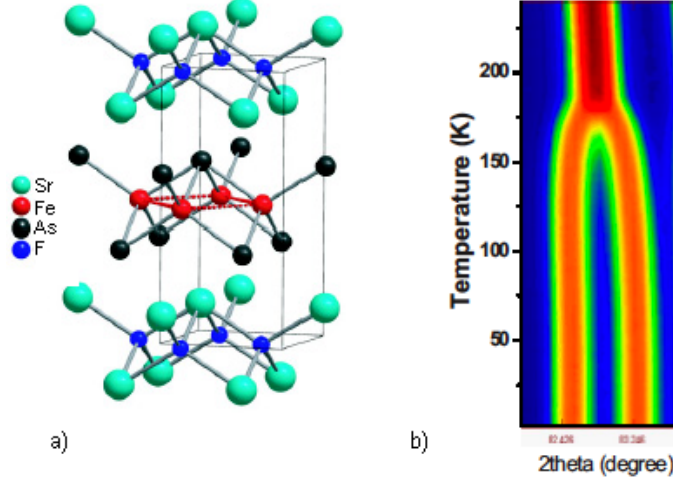


Figure 3.3: (a) Crystal structure of SrFeAsF [82]. (b) Evolution of $(220)_T$ reflections with temperature as shown in Ref. [93]. The structural phase transition is clearly revealed by the splitting of tetragonal $(220)_T$ into orthorhombic $(400)_O$ and $(040)_O$ reflections.

At 300 K the parent compound SrFeAsF has the tetragonal space group $P4/nmm$ and crystallizes in the ZrCuSiAs-type structure. It is made of tetragonally arranged FeAs layers that are separated by divalent metal fluoride layers, as shown in Figure 3.3. At 2 K the system has an orthorhombic structure with the $Cmma$ space group.

Measurements of resistivity and magnetisation exhibit an anomaly at $T_{\text{an}} = 173$ K, which has been attributed to a smooth structural phase transition from tetragonal to orthorhombic. As explained above in a large number of pnictide parent compounds such a transition has been found to be linked to a certain extent to the antiferromagnetic ordering transition of the material. Furthermore band-structure calculations suggest an onset of spin density wave antiferromagnetism at low temperatures in SrFeAsF, driven by nesting between electron and hole

3.3 Two-dimensional magnetism in SrFeAsF

pockets or by magnetic exchange coupling between the local moments [93].

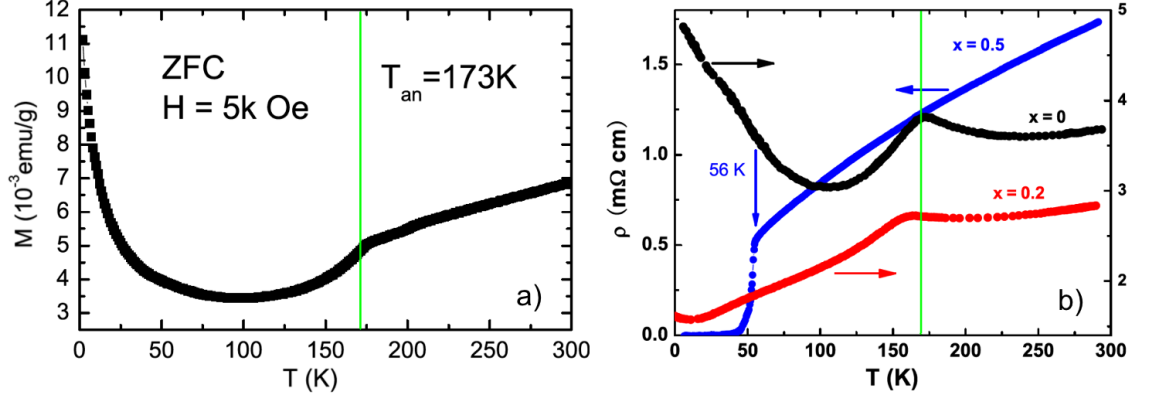


Figure 3.4: (a) Magnetisation vs temperature in the parent compounds SrFeAsF shows an anomaly at $T_{\text{an}} \sim 173$ K and a linear temperature dependence above that temperature, which is attributed to short range correlations; graph adapted from [39]. (b) Resistivity vs temperature for $\text{Sr}_{1-x}\text{Sm}_x\text{FeAsF}$ at $x = 0$, $x = 0.2$ and $x = 0.5$; Graph adapted from [91].

On doping with either Sm [91] or Nd [23] superconductivity is induced. Resistivity data obtained by Wu *et al.* for $\text{Sr}_{1-x}\text{Sm}_x\text{FeAsF}$ is shown in Figure 3.4. At a doping of $x = 0.2$ the anomaly that is seen in the parent compound is slightly suppressed but still existent. At the same time the low temperature resistivity changes behaviour from an upturn, semiconducting type behaviour in the parent compound to a decreasing resistivity in the doped material. Further doping to $x = 0.5$ leads to the onset of superconductivity at 56 K and the disappearance of the anomaly. There is a clear link between the suppression of T_{an} and the onset of superconductivity.

This type of behaviour has been studied intensely in the 1111-type $M\text{FeAsO}$ compounds, LaFeAsO , NdFeAsO , PrFeAsO and CeFeAsO . All these materials exhibit a structural transition at $T_{\text{S}} \sim 150$ K and a transition to long range anti-ferromagnetic order at about 20 K below T_{S} , with a very small magnetic moment

3.3 Two-dimensional magnetism in SrFeAsF

on the Fe-site. These features are suppressed by doping and eventually disappear with the onset of superconductivity, apart from a phase in which magnetism and superconductivity seem to coincide in $\text{SmFeAsO}_{1-x}\text{F}_x$.

In contrast the 122-type compounds generally have coincidental structural and magnetic transitions, for example SrFe_2As_2 with $T_{\text{S,N}} = 205$ K, and the magnetism has a more three-dimensional nature in these materials compared to the single-layer FeAs compounds.

The identification of the nature of this transition and the coincidence of T_{N} and T_{S} in this compound gives valuable information on the type of magnetism, on the effect doping has on structure, magnetism and superconductivity and on their interdependence. In this section I present the results of DC susceptibility, heat capacity and μ -SR measurements on the parent compound SrFeAsF.

Susceptibility and μ SR of SrFeAsF

The SrFeAsF sample was synthesized by Lee Kerslake and Dr. Simon Clarke at the Chemistry department in Oxford. It is a two-step process similar to that described in Ref [82]. The samples that were produced for this project were studied with X-ray diffraction and were found to be made of 97 % SrFeAsF with an impurity of SrF_2 . The lattice parameters agreed with other publications with $a = 4.00059$ Å, $c = 8.9647$ Å and $V = 143.478$ Å³ [82].

The DC susceptibility measurements were executed on a SQUID magnetometer. Initially the magnetic moment of a sample was measured as a function of magnetic field at 300 K and it was established that there were no significant ferromagnetic impurities in the sample. The distinct shape of a ferromagnetic material in a magnetic field means that the presence of ferromagnetic impurities

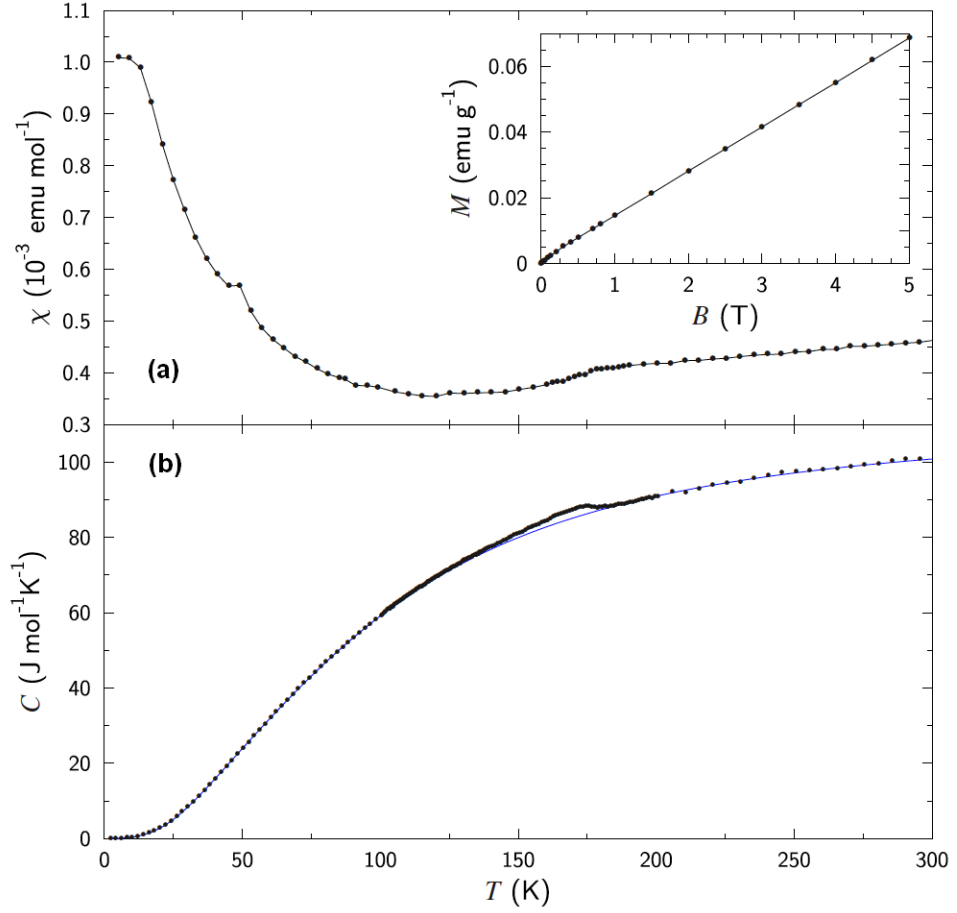


Figure 3.5: (a) Susceptibility vs temperature of SrFeAsF at a field of 0.1 T. Possible features can be made out at $T = 175$ K, at 125 K, 75 K and 50 K, but none of them are sufficiently clear to identify a transition. The first of these coincides with the structural transition temperature. The inset shows magnetisation vs field at 300 K. (b) Heat capacity vs temperature with a small peak at T_S and a fit to the heat capacity [4].

3.3 Two-dimensional magnetism in SrFeAsF

would result in a deviation from the linear behaviour, due to the saturation of the ferromagnetic contribution at a critical field, which is not observed here. We proceeded to measure the susceptibility against temperature in a field of 1000 Oe, which enabled us to identify a broad feature at 175 K, that can be identified as the anomaly that was observed in previous publications and has been attributed to the structural and magnetic transitions. Other possible features are at 125 K, 75 K and 50 K, but none of them are sufficiently clear to identify a transition. The feature at about 50 K is probably due to a small amount of adsorbed O₂ apparent because of the small sample moment.

The heat capacity was measured in the PPMS using the relaxation-time approach described in Section 2.4. We observe a monotonically increasing heat capacity as expected from the electronic and phonon contributions, with the total amplitude of the lattice modes close to that expected from the Dulong-Petit law. A feature is observed at $T = 175$ K. To have a closer look at this feature the background is subtracted, so that only the contributions from the magnetic and structural transitions remain.

The lattice background is estimated by fitting the following function to the data:

$$C(T) = \gamma T + A_D C_D(T, \theta_D) + A_E C_E(T, \theta_E). \quad (3.1)$$

The first term describes the electronic contribution, where γ is the Sommerfeld coefficient. The second and third terms describe the lattice contributions, where D and E denote the Debye and Einstein contributions respectively. Including the Einstein as well as the Debye term was shown to give a better fit compared to fitting only with the Debye term [5, 83]. The resulting fit is comparable to

3.3 Two-dimensional magnetism in SrFeAsF

other oxypnictide compounds without rare earth magnetic moments [61] and we were able to extract the following components $\gamma = 3.44(7) \text{ mJ mol}^{-1} \text{ K}^{-2}$, $A_D = 56.6(5) \text{ J mol}^{-1} \text{ K}^{-1}$, $\theta_D = 237(1) \text{ K}$, $A_E = 52.2(4) \text{ J mol}^{-1} \text{ K}^{-1}$, and $\theta_E = 407(3) \text{ K}$. Both the original data and the fit are depicted in Figure 3.5.

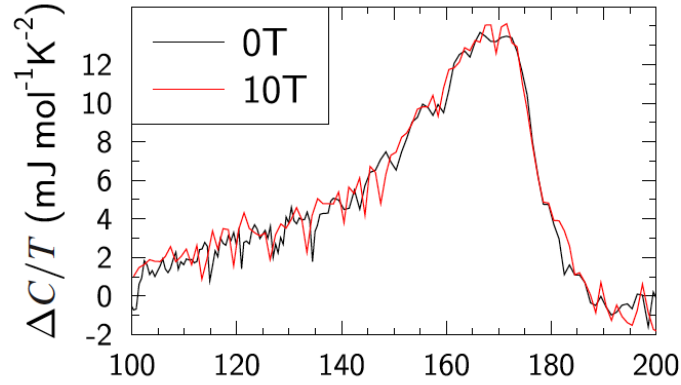


Figure 3.6: Contribution to heat capacity from the transitions after subtraction of the background due to electronic and lattice terms.

Figure 3.6 shows the contribution that has been attributed to the magnetic and structural transition after the subtraction of the background fit. Note that the 0 T and the 10 T data are almost identical with an entropy change between 100 K and 185 K of $0.5 \text{ J mol}^{-1} \text{ K}^{-1}$. No distinct feature that would point to the transitions being at different temperatures such as was observed in LaFeAsO [61] is visible. But the overall entropy change is at a similar value, whereas it is a lot smaller than the entropy change at the coinciding transition temperatures of SrFe₂As₂ [44].

Although no clear feature can be observed for the magnetic transition it is possible that the peak associated with T_N is masked by the built-up of 2D correlations, which would lead to a large “hump” at temperature above T_N , such as described in more detail in Chapter 5 [75]. Whether a peak is visible depends

3.3 Two-dimensional magnetism in SrFeAsF

on the ratio $\alpha = J_{\perp}/J$ where J stands for the exchange interaction within the layers and $J_{\perp}$ for the exchange interaction between the layers. α can be used as a measure of the two-dimensionality of a material. The lower the value of α the more two-dimensional the magnetism. Simulations of localized spin-1/2 Heisenberg models as a function of α show no anomaly at T_N for $\alpha \leq 0.05$, giving an approximate upper bound for this ratio in SrFeAsF.

The magnetism was then further investigated with μ SR. The experiments were performed in GPS at the Paul Scherrer Institute (See Chapter 2.2 for more details). The sample in this case was a pressed powder pellet of 1 cm diameter inside a silver packet on a silver backing plate. This arrangement makes it possible to easily subtract the time and temperature independent background of the silver. The measurement was taken from 300 K down to 10 K. At high temperatures an exponentially relaxing signal is observed, which is typical for the paramagnetic phase of a material. Significantly, no change in the signal is observed between the data above and below T_{an} which shows that there is no magnetic transition coincidental with the structural transition.

In addition at temperatures above the transition a so-called ‘F- μ -F’ signal is typically observed in compounds that contain fluorine. This signal is associated with the muon forming ‘hydrogen’-type bonds with neighbouring fluorine atoms. No ‘F- μ -F’ signal was seen in SrFeAsF, which is probably because the magnetic transition temperature is too high for the muon to be sufficiently bonded to the fluorines.

On cooling the signal becomes oscillatory a clear sign of magnetic order. Figure 2.8 shows the asymmetry data for $T = 10$ K, 116 K and 140 K. The observation of two precession frequencies in the magnetically ordered phase in-

3.3 Two-dimensional magnetism in SrFeAsF

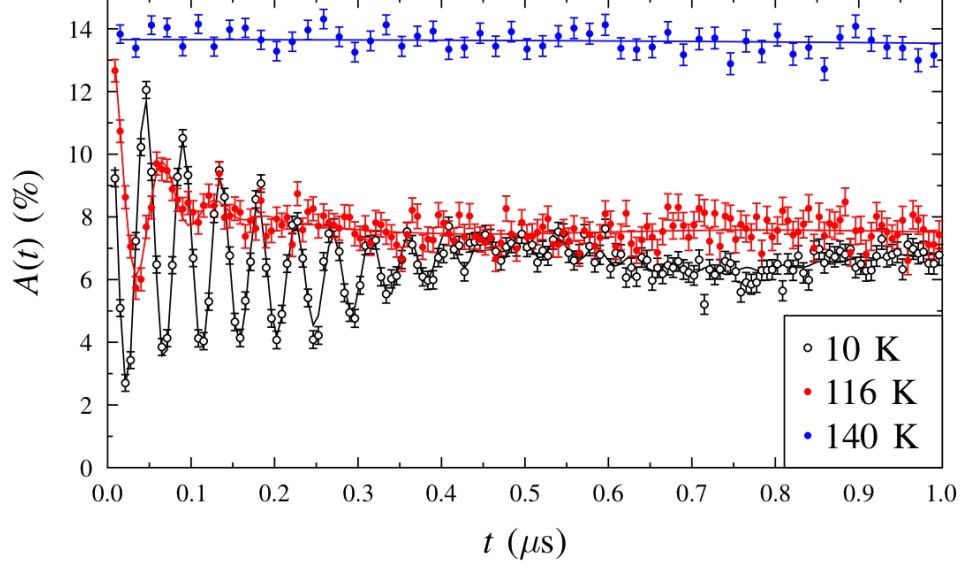


Figure 3.7: Asymmetry in muon polarisation at 10 K, 116 K and 140 K for SrFeAsF [4]

indicates that there are two muon stopping sites. We were able to describe the asymmetry data using the fitting function:

$$A(t) = A_{\text{bg}}e^{-\Lambda t} + A_3e^{-\lambda_3 t} + \sum_{i=1,2} A_i e^{-\lambda_i t} \cos(2\pi\nu_i t). \quad (3.2)$$

The first term describes the background depolarisation of the muons that stop outside the sample, the second is the exponential relaxation of the muon spins aligned with the local field direction at the stopping sites and the two damped frequencies are described by the last term. This function was used to fit all data from 10 K up to 120 K. The oscillatory components disappear above that temperature. After preliminary fits showed that the frequencies stayed proportional to each other through all temperatures up to T_N , the fits were repeated with the setting of $\nu_2 = 0.09 \nu_1$, resulting in the graph shown in Figure 3.8.

The muon precession frequencies are proportional to the internal field at the

3.3 Two-dimensional magnetism in SrFeAsF

muon site and scale with the ordered moment, so can be considered to be an effective order parameter for the system. Therefore fitting extracted frequencies as a function of temperature to the phenomenological function

$$\nu(T) = \nu(0)[1 - (T/T_N)^\alpha]^\beta, \quad (3.3)$$

makes it possible to estimate the transition temperature and the critical parameters α and β , leading to $T_N = 122$ K, $\alpha = 3.0(3)$, $\beta = 0.22(3)$.

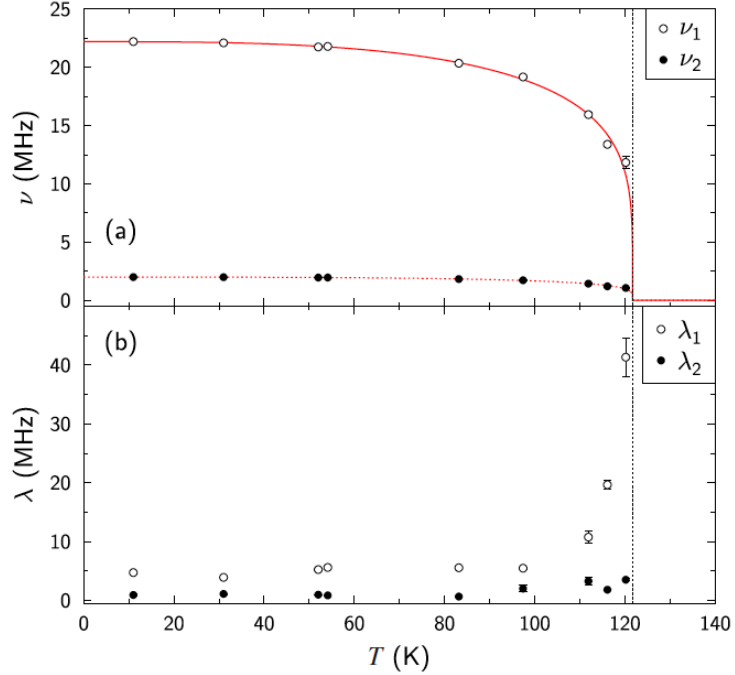


Figure 3.8: The two precession frequencies of and their relaxation components observed in SrFeAs below 120 K. ν_1 and ν_2 were fitted in proportion with $\nu_2 = 0.09 \nu_1$. The red line represents the fit to Eqn. 3.3 [4]

The values have been confirmed in a recent publication by Xiao *et al.* [93], with a similar fit to the temperature dependence of integrated intensity of (103) magnetic Bragg reflection.

These results show that the magnetic transition clearly occurs at a much lower

3.3 Two-dimensional magnetism in SrFeAsF

temperature than the structural phase transition. The separation of T_N and T_S in SrFeAsF is of the order of 50 K, which is greater than any that has been observed in the oxypnictides. There are evident similarities with previous measurements in LaFeAsO. In both compounds the transition is very sharp and the lower frequency persists all the way to T_N and becomes over-damped when it is approaching the transition. In addition ν_1 takes about 85% of the signal in SrFeAsF which is a similar value to the one found in LaFeAsO [61].

The value of β is also interesting as it is close to the number 0.23 [81], which suggests a 2D XY ordering parameter. This combined with the fact that T_N is not detected in heat capacity measurements adds weight to the suggestion that the interactions in this compounds are of 2D nature [4].

In summary, I have shown that the structural and magnetic transitions for SrFeAsF do not coincide, but are 50 K apart. While the μ SR measurements show that the magnetic environment within the FeAs planes is very similar to that in oxypnictide compounds, I note that the magnetic ordering transition is not as clear in the magnetisation and heat-capacity measurements. The heat-capacity and μ SR measurements, in particular the lack of a heat-capacity anomaly at T_N and the low value of $\beta = 0.22$, both suggest far more two-dimensional magnetic interactions. This is consistent with the expectation that the interplanar exchange mediated by a fluoride layer will be weaker than that mediated by an oxide layer.

3.4 NaFeAs and its phase diagram

Introduction

NaFeAs is a pnictide superconductor of the 111-class. It is isostructural with LiFeAs, which was shown to be a bulk superconductor in its undoped, stoichiometric form with a T_c of 18 K. It is a general feature of many of the iron-based superconductors that, when the compounds are stoichiometric, the compounds are itinerant antiferromagnets with a structural distortion at T_S (where $T_S \geq T_N$). When these compounds are doped either on the iron site, or on the sites in the intervening layers, or when a hydrostatic pressure is applied, the magnetic ground state is suppressed and superconductivity emerges as described above. Apart from LiFeAs there are only a few more exceptions, such as FeSe which have superconducting ground states when stoichiometric, which makes the 111 compounds very interesting for the investigation of the interplay between magnetism and superconductivity.

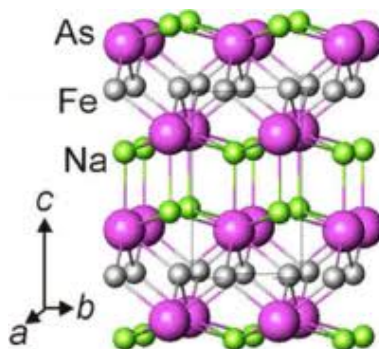


Figure 3.9: Structure of NaFeAs [71]. Fe is tetrahedrally coordinated by four As ions; Na lies in a five coordinate square-based pyramidal site between the FeAs layers.

Both LiFeAs and NaFeAs have the PbFCl-structure type. They are made of anti-PbO type FeAs layers, with Na located between the layers.

The As in NaFeAs forms a distorted tetrahedral arrangement around the Fe-ions as can be seen in Figure 3.9 [71]. At low temperatures NaFeAs goes through a structural transition from the tetragonal $P4/nmm$ space group to the orthorhombic $Cnmm$ (~ 60 K in the stoichiometric phase). Figure 3.10 shows data that have been taken with high resolution neutron scattering as described in Ref. [72].

Superconductivity and magnetism in NaFeAs

Stoichiometric NaFeAs was produced by Dinah A. Parker in the inorganic chemistry department of Oxford University by the reaction of stoichiometric quantities of elemental reagents. The lattice parameters of $a = 3.9494(2)$ Å and $c = 7.0396(8)$ Å were determined by X-ray diffraction. The diffraction data did not indicate more than 1% - 2% Na deficiency, with the Fe-content fixed, which confirms that this material is not doped.

DC susceptibility measurements on NaFeAs taken in fields of 50 Oe show evidence for superconducting behaviour with an onset of diamagnetism, below 9 K. Similar results were obtained by Chu *et al.*, confirming our observation [25]. Zero-field cooled and field-cooled measurements were taken to estimate the superconducting volume fraction and the results are shown in Figure 3.11. We observe a broad transition in temperature and, surprisingly, the value of susceptibility at the base temperature of 2 K is 10% of the value expected for a sample with 100% superconducting volume fraction.

In order to ascertain to what extent the result was modified by the addition of signal coming from a possible iron impurity, the magnetisation of the sample was measured at 300 K. The deviation from the linearity can be used to extrap-

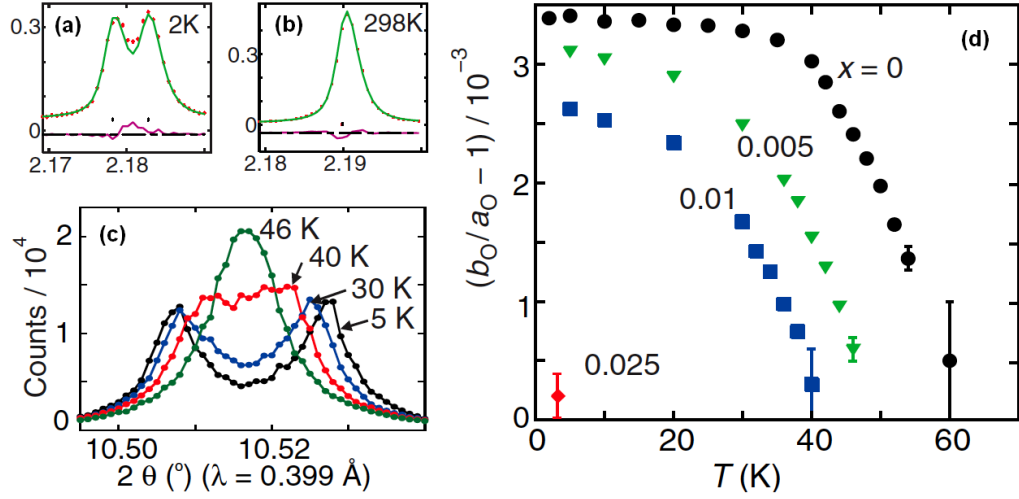


Figure 3.10: Structure distortion in NaFeAs: (a) and (b) show the splitting of the tetragonal 112 reflection into the orthorhombic 022 and 202 reflections. (c) Evolution of the orthorhombic 022/202 reflections in NaFe_{0.995}Co_{0.005}As at high resolution. At 46 K the orthorhombic and tetragonal models give fits of comparable quality. (d) Temperature dependence of the distortion for NaFe_{1-x}Co_xAs. The error bars lie within the points except when the presence of the distortion is marginal (adapted from Ref. [72]).

3.4 NaFeAs and its phase diagram

olate the amount of metallic Fe contained in the sample, which was found to be 0.08 % by mass of metallic Fe. But correcting the susceptibility data using this information still could not explain the small value of the diamagnetism in NaFeAs.

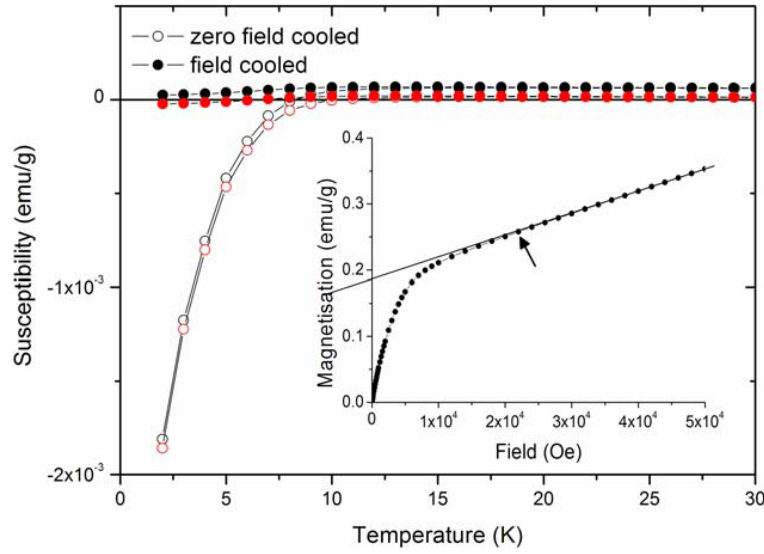


Figure 3.11: Field-cooled and zero-field-cooled susceptibility of NaFeAs. The inset shows the magnetisation of the same sample at 300 K. The two colours represent the results for two different samples. The deviation from the linear behaviour gives an estimate of the Fe-impurity in the sample

At the time at which these measurements were first taken, magnetism had not been observed in NaFeAs. LiFeAs does not exhibit magnetic order [13]. Hence it was important to determine whether there was any sign of magnetism in the isostructural NaFeAs. Since macroscopic techniques such as transport and susceptibility were not able to detect any anomaly in the properties that could be related to magnetic or structural phase transition, it made NaFeAs an ideal candidate for the investigation with μ SR.

3.4 NaFeAs and its phase diagram

μ SR measurements were performed using the GPS spectrometer at the Paul Scherrer Institute, Switzerland. The powder was tightly sealed in an Ag foil packet which was sealed under argon for transport to the spectrometer. The outside of the Ag foil packet was exposed to air for less than two minutes during loading into the He atmosphere of the cryostat. Above 45 K the muon decay asymmetry has an exponentially-relaxing form typical for a paramagnet. Oscillations in the muon decay asymmetry were observed at all temperatures below 40 K and indicate that the sample is antiferromagnetically ordered throughout at least 90% of its volume. Repeating the experiment on a second sample from the same batch gave the same behaviour. Figure 3.12 shows the results of these measurements.

The oscillations below the transition could be fitted using two components, corresponding to two magnetically equivalent muon stopping sites. The following function was used for the fit:

$$A(t) = \sum_{i=1,2} A_i e^{-\lambda_i t} \cos(2\pi\nu_i t). \quad (3.4)$$

The fitted frequencies were plotted as a function of temperature and using Eqn.3.3 the transition temperature $T_N = 45.0(2)$ K and critical exponent $\beta = 0.20(2)$ were extracted. These results are consistent with AFM order with a primarily two-dimensional character.

The higher of the two frequencies makes up 80% of the signal, similar to what has been observed in LaFeAsO and SrFeAsF (see Section 3.3). This suggests that the ordering moment of the Fe atom is of the order of 0.1–0.2 μ_B , which explains why it is difficult for other techniques to pick up the magnetism in NaFeAs. The

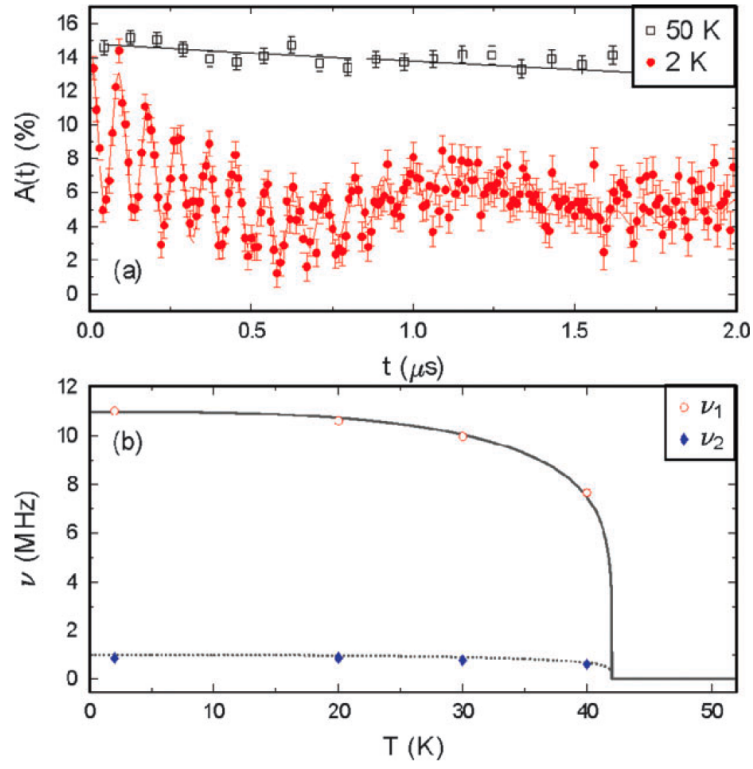


Figure 3.12: (a) Muon decay asymmetry spectra below (2 K) and above (50 K) the magnetic ordering transition (45 K). (b) Precession frequencies as a function of temperature, along with a fit to Eqn.3.3.

3.4 NaFeAs and its phase diagram

measurements reported here were the first clear evidence of magnetism in NaFeAs

Transverse field μ SR was then used to probe the superconducting region. A magnetic field applied perpendicular to the initial muon-spin direction produces a vortex lattice in the superconducting phase of type-II superconductors. This vortex lattice will produce a broadening in the oscillation signal picked up by the muons. In this un-doped NaFeAs sample transverse field measurements did not show any broadening of the spectra that could be caused by superconductivity. This shows that the superconducting volume fraction is limited to 20% [71], which agrees with our susceptibility measurements and the results obtained by Chu *et al.* [25].

The results show that NaFeAs, which is stoichiometric within the uncertainty of the neutron diffraction measurements, is not a bulk superconductor, in apparent contrast to LiFeAs. The μ SR experiment probes the bulk of the sample, demonstrating that magnetic order occurs throughout most of its volume below 42 K, and places an upper limit of about 20% on the superconducting volume fraction. The magnetic phase has since been observed with neutron diffraction [58] and in magnetometry measurements [21]. The moment on the iron site was found to be $\mu_B = 0.09(4)$ by de la Cruz *et al.* and $\mu_B = 0.075(15)$ by Wright *et al.* [90]. The magnetometry measurements reported here and by others show, however, that there is a portion of the sample (about 10%) which is superconducting at low temperatures. This demonstrates the microscopic coexistence between magnetic and superconducting states within the stoichiometric NaFeAs system, analogous to the behaviour observed in $\text{SmFeAsO}_{1-x}\text{F}_x$.

The phase diagram of Co-doped NaFeAs

The evolution from magnetic order to superconductivity and the interplay and competition between both states is one of the important issues that we are trying to resolve when studying pnictide compounds. The coexistence of superconductivity and magnetism in NaFeAs makes it particularly interesting for the investigation of the evolution of structural, magnetic and superconducting transition, with doping. Phase diagrams for $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}$ [26], $\text{CaFe}_{1-x}\text{Co}_x\text{AsF}$ [59], $\text{CaFeAsO}_{1-x}\text{F}_x$ [95] and $\text{SmFeAsO}_{1-x}\text{F}_x$ [34] have been found in previous publications and are shown in Figure 3.13.

In this section I present the effect of doping with Co and Ni on the Fe-site of NaFeAs and by combining diffraction, susceptibility and μSR results a phase diagram for this particular compound is obtained ¹. The doped samples were prepared with the same technique as before, with ground transition metal added into the procedure. Magnetometry measurements were carried out using 30 mg samples on a SQUID magnetometer under zero-field cooled and field cooled conditions in a measuring field of 5 mT. The evolution of the low temperature magnetic susceptibility with composition is shown in Figure 3.14 and it is clear that small doping away from the stoichiometric compound leads to a fast increase in the superconducting volume fraction, up to 100 %, as well as an increase in T_c to a maximum of $T_c = 21$ K.

The comparison of the effect of Co and Ni doping can give us valuable information on the parameters that control the superconductivity in this compound. Co-doping will add one additional electron per atom, whereas Ni at the same doping level will give double the number of added electrons. As can be seen in

¹The work in this section is also part of the DPhil of Jack Wright. [90]

3.4 NaFeAs and its phase diagram

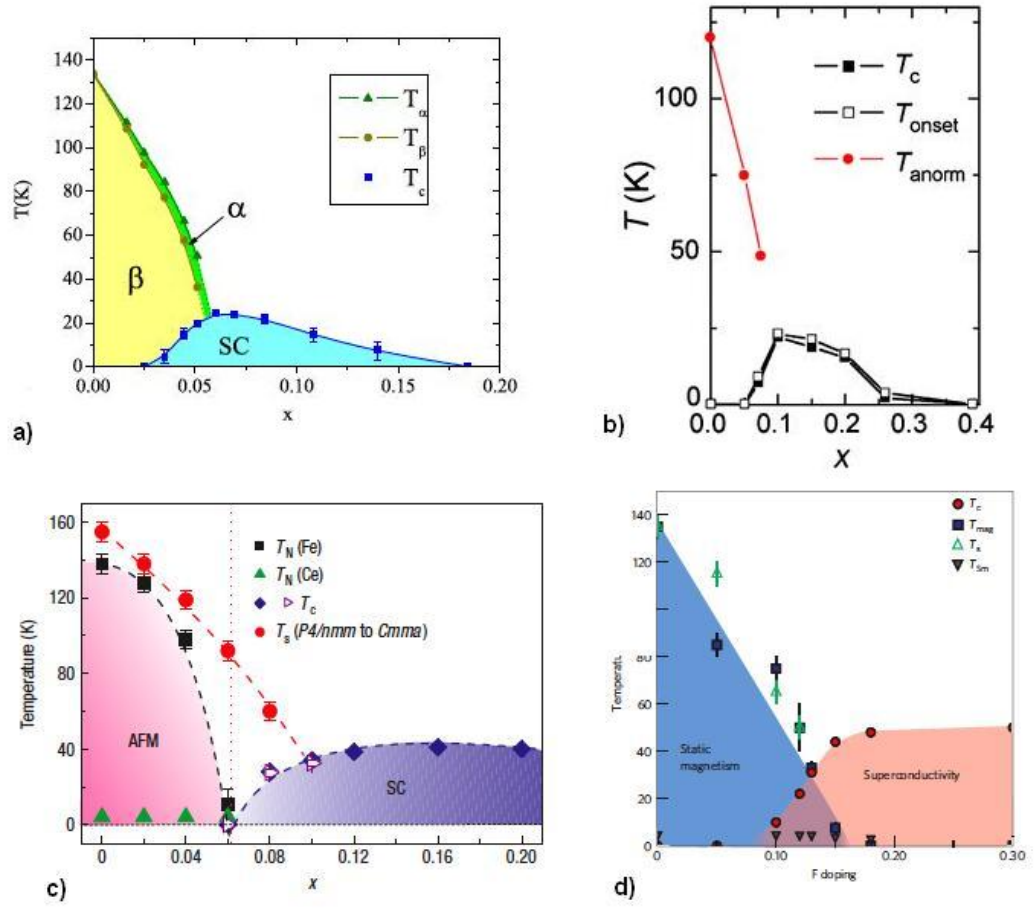


Figure 3.13: Phase diagrams of (a) $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}$ [26], (b) $\text{CaFe}_{1-x}\text{Co}_x\text{AsF}$ [59], (c) $\text{CaFeAsO}_{1-x}\text{F}_x$ [95] and (d) $\text{SmFeAsO}_{1-x}\text{F}_x$ [34]. They all have a similar superconducting dome and magnetic order at low doping levels.

Figure 3.14 similar behaviour and T_c dependence is observed for doping levels with similar amounts of electrons.

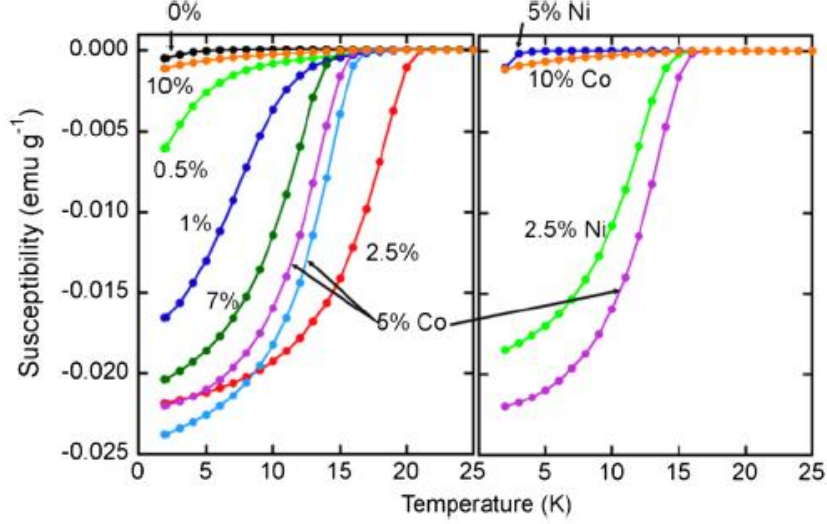


Figure 3.14: Effect of doping NaFeAs with Co and Ni. The data at 5 % Co-doping is plotted on both graphs, showing that the critical temperatures for samples for 5 % Co-doping and 2.5 % Ni-doping are practically the same [72].

The isoelectronic compounds $\text{NaFe}_{0.95}\text{Co}_{0.05}\text{As}$ and $\text{NaFe}_{0.975}\text{Ni}_{0.025}\text{As}$ as well as $\text{NaFe}_{0.9}\text{Co}_{0.1}\text{As}$ and $\text{NaFe}_{0.95}\text{Ni}_{0.05}\text{As}$ are almost identical. This is a clear indication that electron count and band filling are key parameters, controlling superconductivity.

To probe the magnetism in Co-doped NaFeAs, the samples were measured in the GPS instrument at the Paul Scherrer Institute. Asymmetry spectra of a series of doped compounds at 1.5 K are shown in Figure 3.15. Similar results as before were observed for all samples with doping $x \leq 0.0125$, evidence for long-range magnetic order at these doping levels. The asymmetry was fitted using the two-component function 3.4. With increasing x the oscillations become less distinct and are heavily damped until they vanish at $x \geq 0.0125$. This shows that doping

leads to smaller internal fields and a more inhomogeneous field distribution.

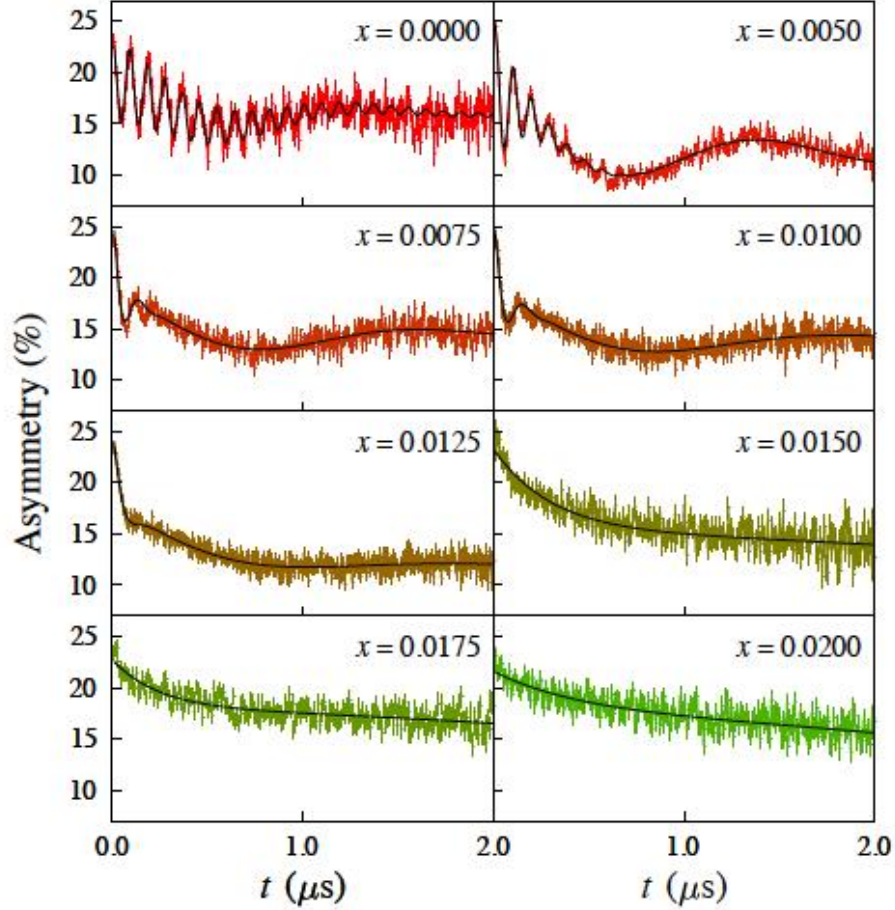


Figure 3.15: Comparison of the zero-field μ SR asymmetry spectra for $\text{NaFe}_{1-x}\text{Co}_x\text{As}$, measured at 1.5 K. With increasing x the frequencies decrease until only a fast relaxing component remains as an indication of magnetic order, which eventually also dies away. At $x = 0.02$ the signs of order have completely disappeared [90].

Doping levels between $x = 0.015$ and $x = 0.02$ lead to a fast-relaxing component at early times that dies away as x increases. These data are best fitted to a relaxation function:

3.4 NaFeAs and its phase diagram

$$A(t) = A_{\text{slow}}e^{-\sigma^2 t^2} + A_{\text{fast}}e^{-\lambda_f t}. \quad (3.5)$$

The first term fits a slowly-relaxing Gaussian function that can be attributed to the magnetism of statically disordered moments, probably of nuclear origin, and the second term is a fast exponential relaxation component. This fast relaxing component is most likely associated with magnetic fluctuations of electron spins, which quickly dephase muons. The fact that these two contributions are summed suggests that only a fraction of the muons are dephased by the electronic fluctuations. This could be explained by the occurrence of regions within the sample with some degree of inhomogeneous magnetism, for $x \geq 0.0125$. The fast relaxation component decreases with increasing x in this region, which implies that the extent of the magnetically fluctuating regions decreases as x increases.

Using Eqn. 3.4 to fit the frequencies and then Eqn. 3.3 makes it possible to extract critical parameters and the magnetic transition temperatures for a range of doping levels. The fits obtained in this way are shown in Figure 3.16.

Combining all the results obtained from synchrotron X-ray diffraction, SQUID magnetometry and μ SR makes it possible to compile the phase diagram for Co doped NaFeAs as shown in Figure 3.17. T_c increases with doping, reaching an optimal value of $T_c = 21$ K, whereas T_S and T_N decrease with doping and eventually disappear. The structural transition, which occurs before the magnetic transition, persists to higher doping levels than the antiferromagnetic transition. The coexistence of magnetism and superconductivity persists up to doping levels of $x = 0.0125$ and then evolves into a phase in which superconductivity exists in parallel with inhomogeneous magnetism.

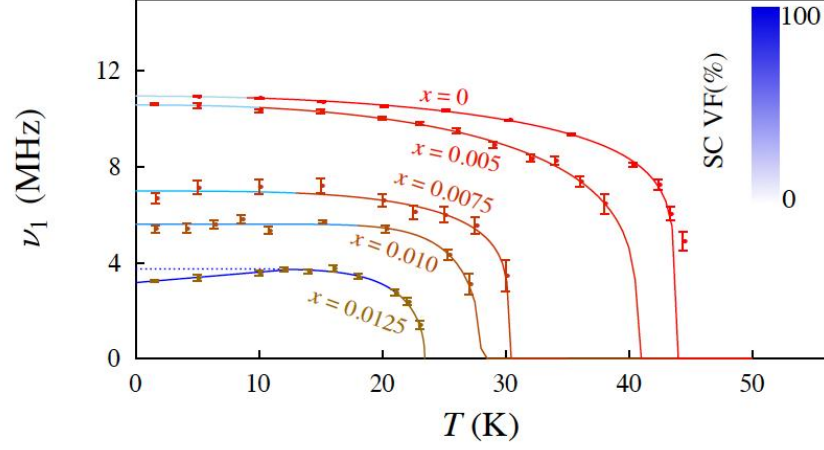


Figure 3.16: High frequency vs temperature for a range of doping levels. The blue line sections show where the sample superconducts and the shade of blue indicates the volume fraction obtained from SQUID magnetometry [90].

This evolution is linked to the increase of the superconducting volume fraction from 10% for stoichiometric NaFeAs to 100%. Compared to phase diagrams of other pnictide compounds the phase diagram of Co-doped NaFeAs is compressed along the x-axis, with optimal doping at $x = 0.015$ (for example in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2$ the optimal doping is $x = 0.065$). Therefore there will be smaller structural and electronic changes made to the stoichiometric system upon doping and this will reduce the effect of inhomogeneous doping in this system.

In conclusion, the parent compound NaFeAs lies just within a superconducting dome that can be traversed by the addition of 0.1 electrons per Fe atom and shows coexistence of antiferromagnetism and superconductivity over a region less than 0.025 electrons per Fe wide. Since the structural effects of Co and Ni doping are very similar I am able to demonstrate the determinative role of electron count in controlling the physics of iron-arsenide layers. While there are similarities with the phase diagrams of more complex iron-arsenide systems, the position of

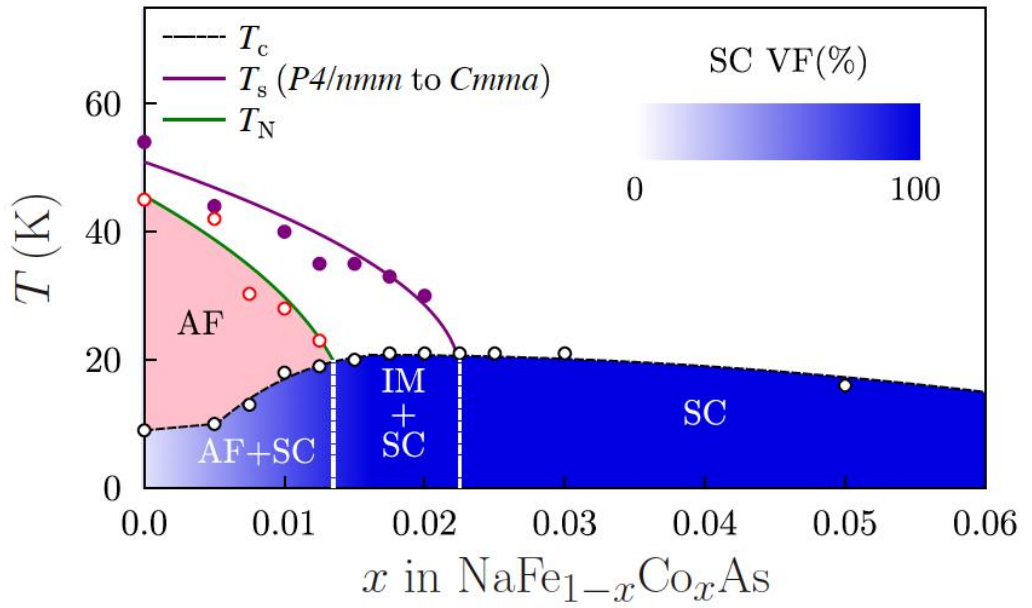


Figure 3.17: Phase diagram of Co-doped NaFeAs. Undoped NaFeAs shows a coexistence of antiferromagnetism and superconductivity. A structural transition precedes the magnetic transition and it persists to doping levels at which the antiferromagnetism has disappeared and has turned into inhomogeneous magnetism. The superconducting fraction increases with decreasing magnetism as well as the superconducting transition temperature, with optimal doping of $x = 0.015$ and a $T_c = 21$ K. [90]

3.4 NaFeAs and its phase diagram

the parent compound is special in this case as coexistent superconductivity and magnetism is found without extrinsic doping. It is clear that there is a direct competition of magnetism and superconductivity in this compound where the strengthening of the superconducting order parameter and the increasing volume fraction is seen directly to depress the magnetic and structural order parameters at low temperature.

4

Complex iridates

4.1 Introduction

Transition metal oxides are an important class of materials because they have a wide variety of optical, electrical, dielectric, magnetic, and thermal properties. They have attracted widespread interest in recent years, driven partly by the observation of high temperature superconductivity in cuprates, colossal magnetoresistance in manganites and p-wave superconductivity in ruthenates [29, 42].

A wide variety of behavior can be expected since the transition metal ion can be any one of the 3d, 4d or 5d series and the possible crystal architectures that can be synthesized include chains, ladders, square layers, triangular layers, kagome layers, pyrochlore lattices and many more. The 5d series has received the least attention but the spatially extended nature of the 5d orbitals makes them rich in novel physical phenomena.

The particular extension of the orbitals means that the electrons behave more like free electrons, which reduces the effect of electron correlations (Coulomb interaction U) significantly. It also leads to the hybridization of the 5d-2p orbitals

of the transition metal and the oxygen octahedron that surrounds it, resulting in large crystal field splitting [18]. The strong electron-lattice coupling can lead to a distortion of the bonding lengths and angles between the transition metal and the oxygen.

Spin-orbit coupling is also strong, due to the large atomic number Z . Spin-orbit coupling is proportional to Z^4 , which means that in heavier elements it becomes more and more important. In these materials it reaches energies in the order of 0.1-1 eV, approaching that of the Coulomb interaction ($U \sim 1 - 3$ eV), which is significantly reduced due to the extension of the orbitals. These competing energy scales are at the heart of the novel physical phenomena that often deviate from conventional expectations.

The iridium ion is a particularly attractive candidate for study because Ir^{4+} ($5d^5$) is an $S = \frac{1}{2}$ species and iridates display a wide variety of unusual characteristics. $\text{Na}_4\text{Ir}_3\text{O}_8$ [96] is an insulating quantum spin liquid, Na_2IrO_3 , a $J_{eff} = 1/2$ frustrated AF Mott insulator on honeycomb lattice [78] and the pyrochlore iridates $A_2\text{IrO}_3$ ($A = \text{Na}$ or Li), possibly exhibit a quantum spin Hall effect [77] and are thought to be the realization of the Kitaev spin liquid [43].

Like the ruthenates (4d electrons), many of the iridates also defy the notion that 5d transition-metal oxides should be much more conducting than their 3d counterparts because of the reduced electron correlations. Many of the iridates known to date have an insulating ground state, on the verge of a metallic state, and display exotic magnetism with high magnetic ordering temperatures, but small magnetic moments, such as BaIrO_3 , which is weakly ferromagnetic at high temperatures with a moment of $\mu = 0.03 \mu_B/\text{Ir}$.

This is one of the reasons why it is difficult to gain information on the micro-

scopic ordering in these compounds. In addition, Ir is a strong neutron absorber, which makes neutron scattering virtually impossible. A further difficulty is the extremely small size of the crystals that can be grown. Muon spin rotation is therefore an invaluable tool for the investigation of iridates.

In this chapter I present μ SR results for the compounds Ca_4IrO_6 , $\text{Ca}_5\text{Ir}_3\text{O}_{12}$, $\text{Sr}_3\text{Ir}_2\text{O}_7$, Sr_2IrO_4 . The basic characteristics of these compounds are shown on Table 4.1. Sr_2IrO_4 is particularly interesting as it is a $J_{\text{eff}} = 1/2$ spin-orbit entangled Mott insulator and has been suggested as a possible high temperature superconductor [86].

Ca_4IrO_6 and $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ are antiferromagnetically ordered at low temperature but exhibit weak ferromagnetism due to spin canting [18, 85]. $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ exhibits a more complex partial spin ordering due to the presence of both Ir^{4+} and Ir^{5+} ions [18]. These two compounds have a large value of the ratio θ/T_N where θ is the Curie-Weiss temperature, demonstrating the presence of competing interactions.

	space group	μ_{eff} ($\mu_B/\text{f.u.}$)	θ (K)	T_N (K)	$ \theta/T_N $
Ca_4IrO_6	$\text{R}\bar{3}\text{c}$	1.76	-54	13.95(6)*	3.8(2)*
$\text{Ca}_5\text{Ir}_3\text{O}_{12}$	$\text{P}\bar{6}2\text{m}$	1.5	-280	7.84(7)*	35.7(1)*
$\text{Sr}_3\text{Ir}_2\text{O}_7$	$\text{I}4/\text{mmm}$	0.69	-17	285	0.06
Sr_2IrO_4	$\text{I}4_1/\text{acd}$	0.33	251	230.4(3)*	1.08(2)*

Table 4.1: Principle characteristic of the four compounds. The values annotated with (*) are results from the μ SR study presented here.

$\text{Sr}_3\text{Ir}_2\text{O}_7$ is a weak ferromagnet showing complicated crossovers in its magnetic behaviour that have not yet been explained at the microscopic level [19]. Sr_2IrO_4 is a Mott insulator driven from the metallic state by the spin-orbit coupling to a $J_{\text{eff}} = \frac{1}{2}$ state [49, 50]. It is also a weak ferromagnet, shows a novel magnetoelectric

state with a thus far unexplained magnetic transition [22, 53] and has even been suggested as a candidate for high-temperature superconductivity if doped [86].

In order to study systematically the dependence of local magnetic properties on crystal architecture we have used muon spin rotation (μ SR) to investigate the microscopic magnetism and the critical behavior of each of these compounds. The nature of the muon spin rotation technique makes it very sensitive to the local magnetic environment, and especially to short-range magnetic order.

The results presented in this chapter find a comparatively conventional development of the internal magnetic field in Ca_4IrO_6 with some more complex features in $\text{Ca}_5\text{Ir}_3\text{O}_{12}$. Compared to these, the results for $\text{Sr}_3\text{Ir}_2\text{O}_7$ and Sr_2IrO_4 reveal very different behavior. Two magnetic transitions are evident in the data for $\text{Sr}_3\text{Ir}_2\text{O}_7$, while in the Mott insulator Sr_2IrO_4 we observe the development of spin reorientation at low temperature.

4.2 Experimental methods

Small crystallites of the materials were made by Prof. Gang Cao at the Center for Advanced Materials at the University of Kentucky.

Zero-field μ SR measurements [7] were made using the General Purpose Surface-muon spectrometer at the Swiss muon source. Each sample was wrapped in 25 μm silver foil and mounted on a silver backing plate. As described in Chapter 2.2 the observed property in the experiment is the time evolution of the muon-spin polarisation, which is proportional to the positron asymmetry function $A(t)$ and depends on the local magnetic field B at the muon stopping site.

In these polycrystalline samples the internal magnetic field will be randomly

orientated with respect to the initial muon polarisation. Because of this we can expect that in a fully ordered magnet $\frac{2}{3}$ of the signal will be due to oscillations about the magnetic field perpendicular to the muon spin and $\frac{1}{3}$ will be relaxations due to the magnetic fluctuations parallel to the muon spin direction [7].

4.3 Ca_4IrO_6 and $\text{Ca}_5\text{Ir}_3\text{O}_{12}$

The structure of Ca_4IrO_6 is depicted in Figure.4.1. It has a rhombohedral structure, in which 1D chains of IrO_6 octahedra alternate with CaO_6 trigonal prisms [18, 74]. In contrast, $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ has a triangular lattice and a hexagonal structure [33, 85] and, unusually amongst iridates, in addition to Ir^{4+} ($S = \frac{1}{2}$) it also includes Ir^{5+} ($S = 0$) [30, 40] ions. In spite of these differences both structures lead to the formation of spin chains perpendicular to a triangular lattice promoting the occurrence of frustration.

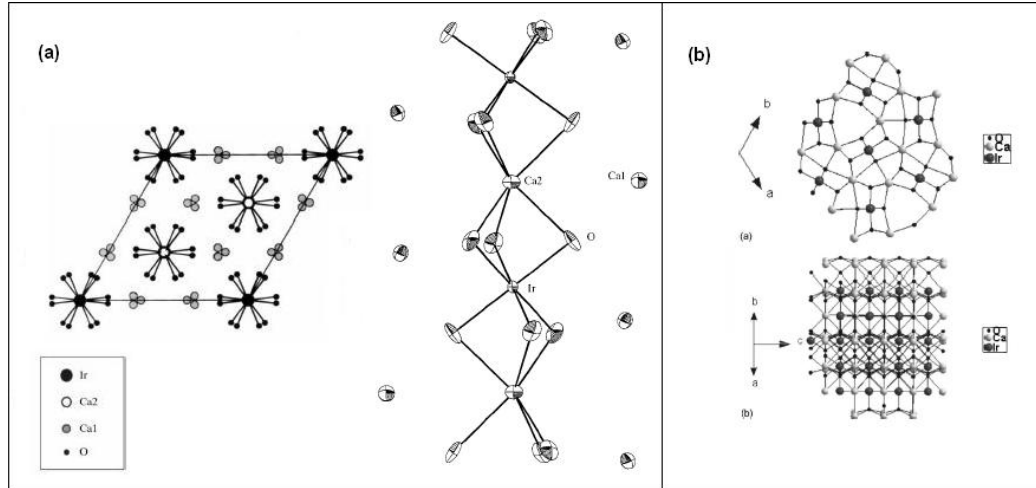


Figure 4.1: Crystal structure of (a) Ca_4IrO_6 , showing the rhombohedral structure and the 1D chains of IrO_6 octahedra. [31]; and (b) $\text{Ca}_5\text{Ir}_3\text{O}_{12}$, projected on the ab plane and its chain arrays along the c axis. [18]

Both compounds are insulators (below 300K for $\text{Ca}_5\text{Ir}_3\text{O}_{12}$) and exhibit antiferromagnetic order. The transition temperature for Ca_4IrO_6 was reported [18, 74] to be in the range of 12–16 K. $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ is found to order into an antiferromagnetic state below 7.8 K [18, 85].

Example data for Ca_4IrO_6 above and below the transition are shown in Figure 4.2(a). The measurements were taken over the whole range of temperature in order to identify the transition temperature and study the magnetic order in the compound. Ca_4IrO_6 shows conventional behaviour. In the paramagnetic phase, the signal is described by a single exponential relaxation and below T_N we observe two well-defined precession frequencies along with a fast relaxing component at early times. The data in this regime may be parameterised using the equation:

$$\begin{aligned}
 A(t) = & A_1 \exp(-\lambda_1 t) \cos(2\pi\nu_1 t) \\
 & + A_2 \exp(-\lambda_2 t) \cos(2\pi\nu_2 t) \\
 & + A_3 \exp(-\Lambda t) + A_{\text{bg}}
 \end{aligned} \tag{4.1}$$

where A_i are the amplitudes of the components, λ_i are the corresponding relaxation rates, ν_i are the precession frequencies, and Λ is the relaxation rate of the fast-relaxing component. The constant A_{bg} accounts for muons stopped outside the sample as well as the expected one-third contributions arising from muon-spin components directed parallel to the local magnetic field.

Preliminary fits showed little change with temperature of A_1 , A_2 , A_3 , λ_1 and λ_2 below the transition and it was possible to obtain satisfactory fit to the data by fixing these parameters to temperature-independent values (4.02%, 1.37%, 11.2%, 5.03 MHz and 1.55 MHz respectively) and allowing ν_1 and ν_2 to vary in

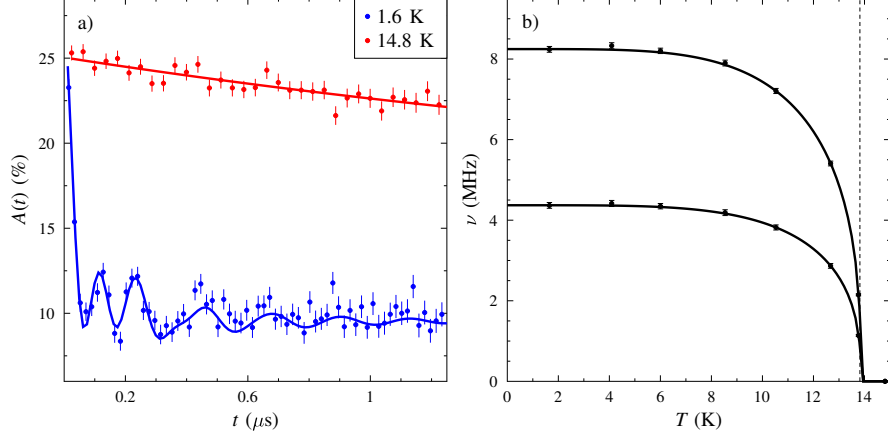


Figure 4.2: (a) Raw data for Ca_4IrO_6 above and below the magnetic phase transition. The low temperature data are fitted with two oscillating components as described by Eqn. (4.1). (b) Precession frequencies for the ordered state. [35]

a fixed proportion $\nu_2/\nu_1 = 0.53$ (a ratio determined to better than 4% accuracy by first allowing them to vary independently). In addition, the large relaxation rate Λ was found to scale with ν_1^2 and reaches 22 MHz at 1.5 K. We deduce that there are two independent muon sites which experience a quasistatic local field (leading to the oscillatory components) and a further site at which the muon spin relaxes in a manner dominated by the magnitude of the local field (leading to the fast-relaxing component). The fast-relaxing component observed below the magnetic ordering temperature probably reflects a class of muon site at which the local field is large but where some degree of spatial or temporal disorder exists. The results of fitting the frequencies ν_1 and ν_1 in fixed proportion are illustrated in Figure 4.2 (b).

The fitting extracted frequencies as a function of temperature to the phenomenological function:

$$\nu_1(T) = \nu_1(0)[1 - (T/T_N)^\alpha]^\beta, \quad (4.2)$$

yields values for the the following parameters: $T_N = 13.85(6)$ K, $\nu_1(0) = 8.29(3)$ MHz, $\alpha = 4.2(3)$, and $\beta = 0.37(1)$, and this value of β is consistent with a typical three-dimensional magnetic order parameter as it is close to the number 0.36 [8].

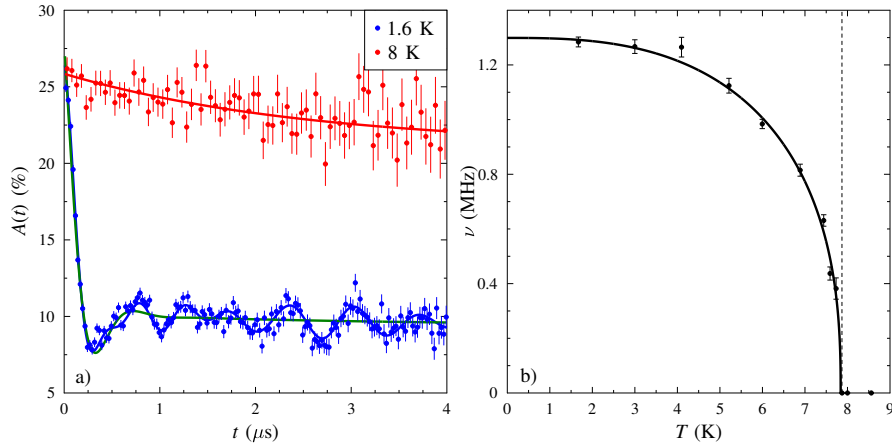


Figure 4.3: (a) Raw data for $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ above and below the magnetic phase transition. The data below the transition is fitted shown with a single frequency (green) and a five frequency (blue) fit. (b) Precession frequency extracted from a single frequency fit to the $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ data. [35]

The form of the raw data in $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ is more complicated. It still shows a typical paramagnetic trace at high temperatures and oscillations below the transition, but data obtained from the precession of the muons at low temperatures combines a larger number of components.

Though dominated by a single primary oscillation frequency, fitting with additional frequency components with smaller amplitudes (and frequencies ranging from 0.8–4 MHz) improved the quality of the fit using up to four or five frequencies. Figure 4.3 shows the data above and below the transition together with a fit to the low temperature data using one and five frequencies for comparison. While the five frequency fit clearly succeeds in describing the data over a significantly longer time, the parameters of the smaller amplitude oscillations

are not well defined and the frequencies could not be followed through to higher temperatures.

The single frequency fit achieves a satisfactory and consistent parametrisation of the largest amplitude oscillating component across the temperature range measured. These results indicate the existence of several magnetically inequivalent muon stopping sites, which suggest a more complicated magnetic structure in $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ compared to Ca_4IrO_6 . This could stem from the inclusion of both Ir^{4+} and Ir^{5+} ions in $\text{Ca}_5\text{Ir}_3\text{O}_{12}$.

The data set was analysed by fitting just to the frequency component with the largest amplitude, the precession frequency of which is shown in Figure 4.3 and reaches ≈ 1.3 MHz as $T \rightarrow 0$. This precession frequency was fitted to Eqn. (4.2), yielding $T_N = 7.84(7)$ K, $\nu(0) = 1.30(2)$ MHz, $\alpha = 2.8(5)$ and $\beta = 0.40(6)$ and, similarly to Ca_4IrO_6 , these parameters are also consistent with three-dimensional behavior.

4.4 Sr_2IrO_4 and $\text{Sr}_3\text{Ir}_2\text{O}_7$

$\text{Sr}_3\text{Ir}_2\text{O}_7$ and Sr_2IrO_4 are of particular interest, since their crystal structure are close to the ruthenates $\text{Sr}_3\text{Ru}_2\text{O}_7$ and Sr_2RuO_4 . The latter has been studied in great detail since superconductivity has been observed in Sr_2RuO_4 , but not in $\text{Sr}_3\text{Ru}_2\text{O}_7$. In addition, the single layer iridium perovskite Sr_2IrO_4 is the analogue of the high T_C cuprate La_2CuO_4 . They are structurally identical, but with stronger spin orbit coupling in the Ir(5d) compared to the Cu(3d). It has been suggested that doping could induce superconductivity in Sr_2RuO_4 , similar to the cuprates. $\text{Sr}_3\text{Ir}_2\text{O}_7$ and Sr_2IrO_4 are both antiferromagnetic with transition tem-

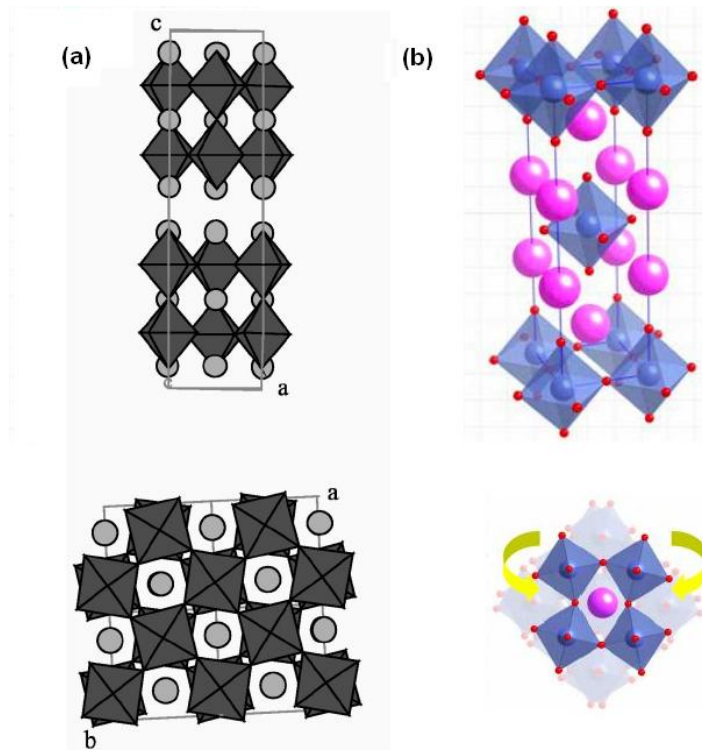


Figure 4.4: Crystal structures of (a) $\text{Sr}_3\text{Ir}_2\text{O}_7$ with the Ir-O bilayers [19]; and (b) Sr_2IrO_4 with single Ir-O layers [28]. Both have Sr-O interlayers and the rotated octahedra are shown for both compounds.

peratures T_N at 285 K Ref. [19] and 240 K [17], respectively. Both compounds contain Ir^{4+} ($S = \frac{1}{2}$) ions. In both compounds, a weak ferromagnetic moment is observed suggesting that they are canted antiferromagnets [49, 51, 65].

$\text{Sr}_3\text{Ir}_2\text{O}_7$ belongs to the Ruddlesden-Popper series $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$ with $n = 2$ and is constructed out of Ir-O bilayers with Sr-O interlayers [19], as shown in Figure 4.4. Field cooled magnetization data picked up three anomalies, a kink at $T^* = 260$ K, a steep downturn at $T_D = 50$ K and the magnetization becoming negative below about 20 K [19]. These features were not observed in the zero-field-cooled magnetization data, implying a strong spin disordering or a random orientation of magnetic domains that persists through T_N . The transitions at T^* and T_D could also be identified in resistivity data, but so far there is no explanation for the comprehensive magnetization and transport behavior [19].

The results of our μSR experiments on $\text{Sr}_3\text{Ir}_2\text{O}_7$ are summarised in Figure 4.5 where the muon decay asymmetry for 1.5 K, 150 K and 260 K are presented. The presence of a fast relaxing component observed at short times can be taken to be a signature of magnetic order, but oscillations with a single precession frequency are only observed between 20 K and 160 K. In this temperature interval we fitted the data using

$$A(t) = A_1 \exp(-\lambda_1 t) \cos(2\pi\nu_1 t) + A_2 \exp(-\Lambda t). \quad (4.3)$$

The disappearance of the precession signal below 20 K is unusual and corresponds to the temperature at which the magnetization was observed to become negative [19]. We note that it was not possible to fit the frequency to Eqn. (4.2) since the oscillations are only observed outside the critical region.

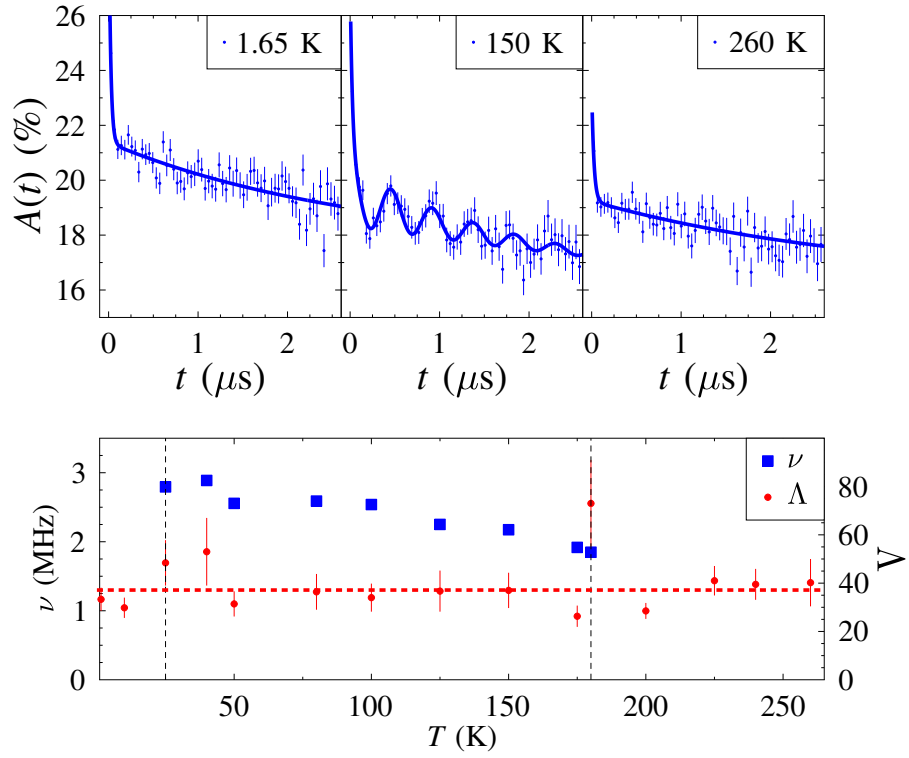


Figure 4.5: Data for $\text{Sr}_3\text{Ir}_2\text{O}_7$ in the three different phases of the material. The data in the intermediate phase was fitted with an oscillating component ν (blue squares) and a relaxing component Λ (red circles) [Eqn. (4.3)]. The relaxation Λ (red circles) can be observed over the whole range of temperatures [35].

Sr_2IrO_4 is the $n = 1$ member of the Ruddlesden-Popper series (i.e. it has the K_2NiF_4 structure) and is therefore constructed out of single Ir-O layers with Sr-O interlayers [28] shown in Figure 4.4. The balance of energies plays a very important role for the properties of this material. The extended orbitals that lead to large crystal field energies result in the splitting of the $5d^5$ states into a lower t_{2g} and higher e_g orbital state separated by $10Dq$.

The broad $5d^5$ that is created that way is expected to lead to a more metallic and less magnetic state than can be observed in 3d, 4d and 4f compounds. since the electronic correlations (parameterised by U) are weak. Surprisingly Sr_2IrO_4 is found to be an insulator (see Figure 4.7), which seems to suggest unrealistically high coulomb interaction.

This is where the strong spin-orbit coupling comes in. It acts on the t_{2g} configuration resulting in a filled $J_{eff} = \frac{3}{2}$ quadruplet band and a half-filled $J_{eff} = \frac{1}{2}$ doublet band. The large crystal field also results in the $J_{eff} = \frac{1}{2}$ being higher than the $J_{eff} = \frac{3}{2}$ since the $J_{eff} = \frac{1}{2}$ is branched off from the $J_{\frac{5}{2}}$ manifold.

The narrow bandwidth of the upper $J_{eff} = \frac{1}{2}$ band that is created this way then leads to a Mott insulating state, even though the electronic correlations (parameterised by U) are weaker than in more familiar Mott insulators, such as the underdoped cuprates. Sr_2IrO_4 can therefore be thought of as a spin-orbit induced Mott insulator [45, 49, 63, 87]. Figure 4.6 illustrates this model.

In addition, a metamagnetic transition occurs at 0.2 T, well below 240 K [50]. Figure 4.8 shows magnetization and heat capacity data by Chikara *et al.* [22] who have recently discovered another magnetic transition at 100 K, which is thought to be a reorientation transition of the spins.

The data obtained for Sr_2IrO_4 show much richer behavior than the data for

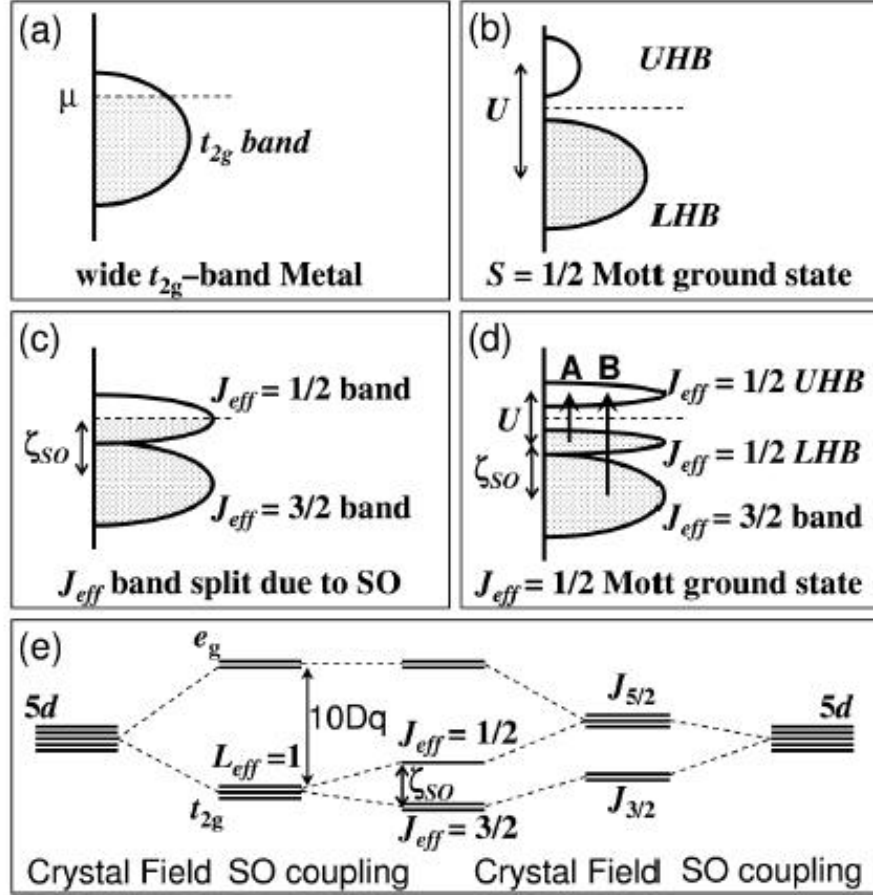


Figure 4.6: Combined effect of crystal field splitting and spin orbit coupling on Sr_2IrO_4 and the resulting $J_{eff} = \frac{1}{2}$ Mott insulating ground state: The extended orbitals lead to crystal field splitting. The energy diagrams for the $5d^5$ lower t_{2g} configuration (a) without spin-orbit coupling and Coulomb interaction; (b) with an unrealistically large Coulomb interaction but no spin-orbit coupling; (c) with spin-orbit coupling but no Coulomb interaction; and (d) with spin-orbit coupling and coulomb interaction. (e) level splittings of $5d^5$ by the crystal field and spin orbit coupling, [49]

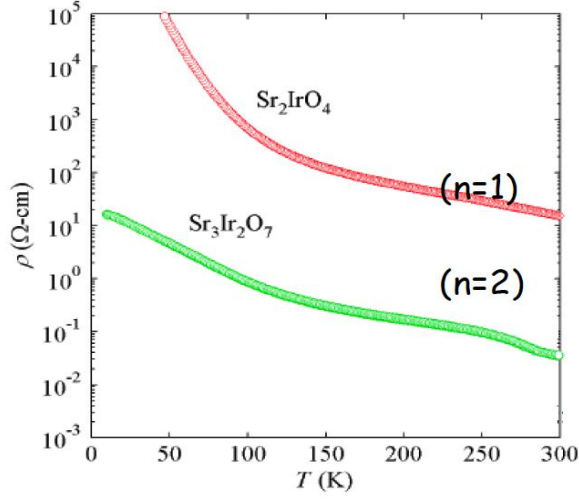


Figure 4.7: Resistivity vs temperature of $\text{Sr}_3\text{Ir}_2\text{O}_7$ and Sr_2IrO_4 adapted from [76].

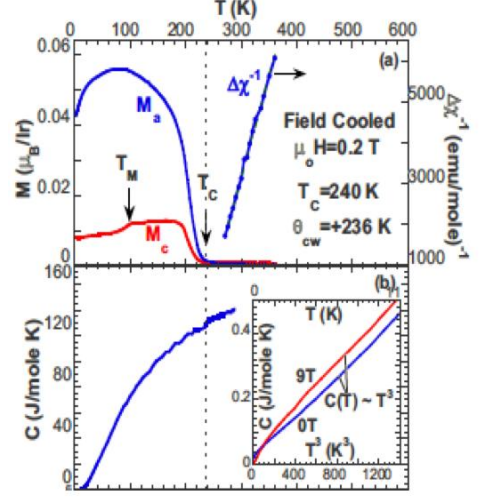


Figure 4.8: Magnetization (field applied along a-axis and c-axis) and heat capacity of Sr_2IrO_4 [22].

$\text{Sr}_3\text{Ir}_2\text{O}_7$. The μSR spectra at three different temperatures are shown in Figure 4.9. Above the magnetic ordering transition there is no oscillatory signal and, as is generally the case in paramagnets, the data are well described by an exponential relaxation. Between T_N and 20 K the data could be parameterised using one oscillation component and one exponentially relaxing component. Below 100 K, the relaxation rates Λ and λ_1 both increase, the former quite sharply, and below 20 K a second frequency needs to be included for a satisfactory fit.

The values obtained with this fitting procedure are plotted in Figure 4.10. The higher of the two frequencies has a smaller amplitude and also has the smaller linewidth while the lower frequency is rather similar in magnitude to that observed in $\text{Sr}_3\text{Ir}_2\text{O}_7$, suggesting a rather similar muon site within the perovskite block in both compounds. As the temperature decreases in Sr_2IrO_4 the precession signal appears to evolve continuously in frequency, amplitude and relaxation rate,

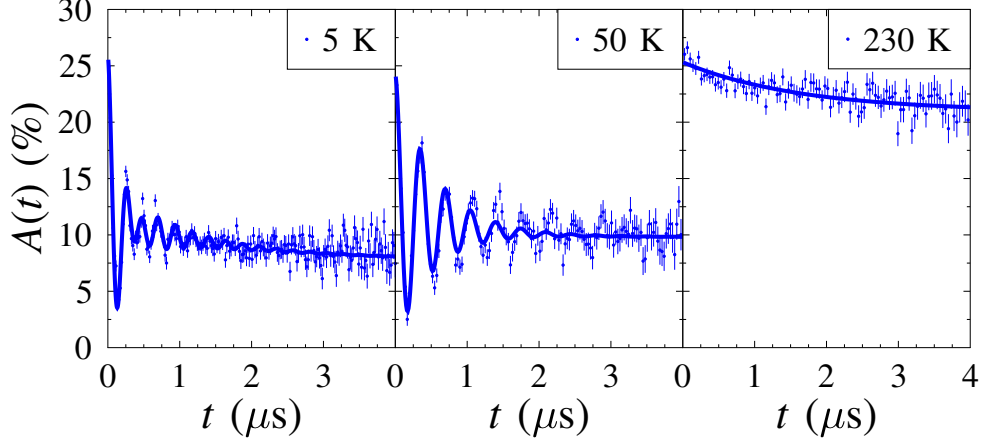


Figure 4.9: Raw data for Sr_2IrO_4 above and below the magnetic phase transition. The low temperature data was fitted with one relaxation component and two oscillating components [Eqn. (4.1)], whereas for the data above 20 K we used a relaxing component and only one oscillating component [Eqn. (4.3)] [35].

transforming into the lower frequency component seen in Figure 4.10. The new component which appears below 20 K represents additional amplitude.

The temperature interval in which the relaxation rates are growing upon cooling, just before the second frequency appears, is shown as a shaded region in Figure 4.10. Using the procedure that was described before, the single precession frequency was fitted with Eqn. (4.2) in the temperature region from 20 K up to T_N and yields $T_N = 230.4(3)$ K, $\nu(0) = 2.93(1)$ MHz, $\alpha = 0.98(4)$ and $\beta = 0.21(1)$. Fitting just the data points close to T_N to the form $\nu(T) / (1 - T/T_N)$ yields $T_N = 228.2(1)$ K and $\beta = 0.19(1)$ (see Figure 4.11) and inset). Both these estimates of β are consistent with a two-dimensional magnetic order parameter [8].

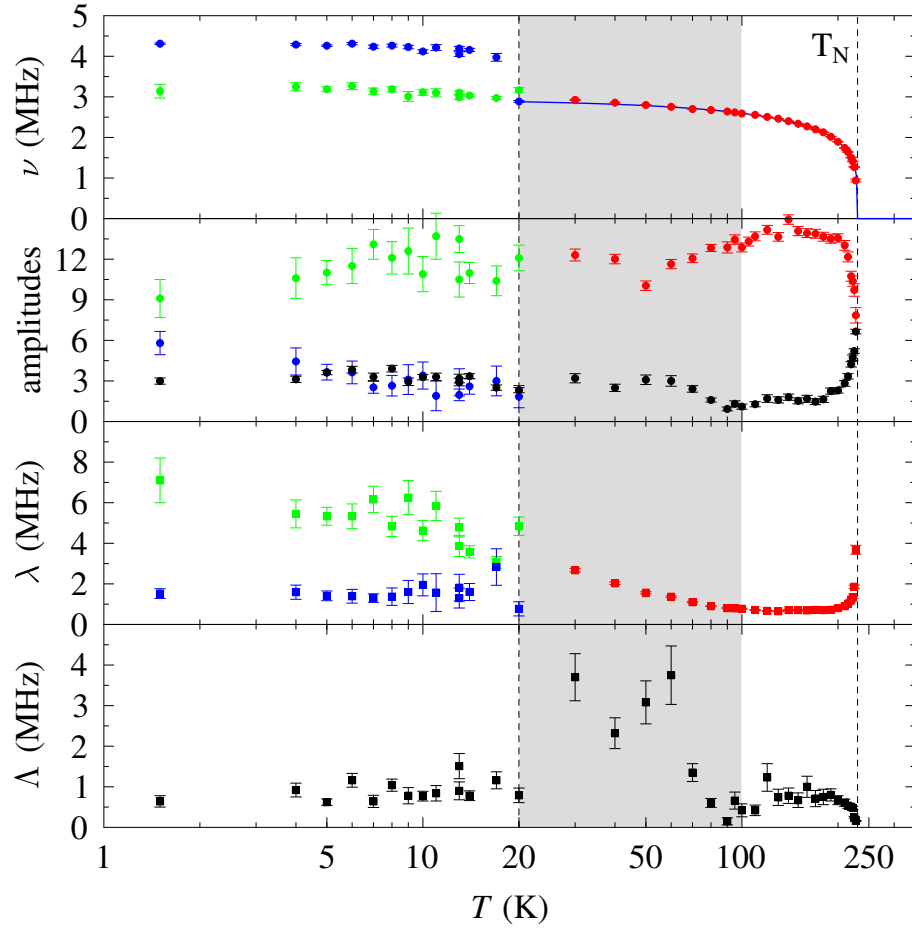


Figure 4.10: Fitted frequencies, amplitudes, linewidths and relaxation of Sr_2IrO_4 . The amplitudes and linewidths corresponding to the different components have been differentiated by color. The shaded region marks the temperature interval in which the relaxation rates increase on cooling, before the single precession frequency splits into two.

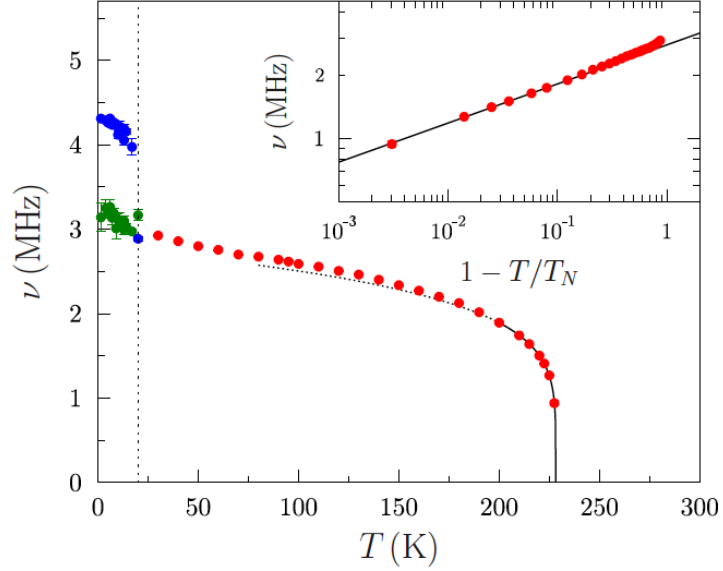


Figure 4.11: Temperature dependence of the fitted frequencies observed in Sr_2IrO_4 . Inset: a fit of these data near T_N .

4.5 Conclusion

The results are summarised in Figure 4.12 and Table 4.2, where the asymmetry spectra at the base temperatures are shown for the four samples as well as the evolution of frequencies with temperature. The results of these experiments confirm the occurrence of antiferromagnetic order in Ca_4IrO_6 and $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ and provide very accurate measurements of the Néel temperature in each case. The more complex nature of the muon signal in $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ as compared with that in Ca_4IrO_6 can be attributed to the larger number of magnetically inequivalent muon stopping sites. The presence of both Ir^{4+} and Ir^{5+} in $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ means that the electronic moments are more dilute and this is consistent with the smaller magnitude of the internal field measured by the muons, almost half that found for Ca_4IrO_6 .

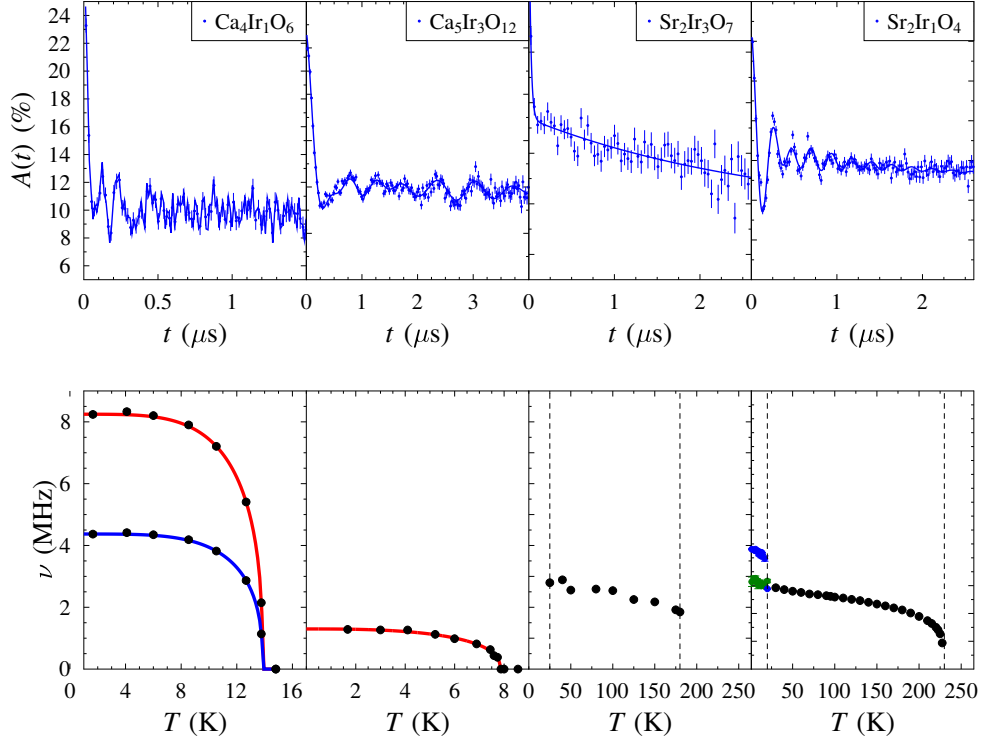


Figure 4.12: Muon spin precession spectra at base temperature for the four compounds, as well as the evolution of the frequencies with temperature. There are very obvious differences between the compounds, can be seen at a first glance. Ca_4IrO_6 shows very conventional behaviour with two frequencies appearing below the ordering transition temperature. $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ is more complex: the data is fitted ideally with 5 different frequencies, but only a single frequency can be followed through to higher temperature and its magnitude is lower than both the frequencies of Ca_4IrO_6 . $\text{Sr}_3\text{Ir}_2\text{O}_7$ is very different with a frequency below 200 K and then increasing slightly until disappearing below 20 K. The most interesting behaviour is observed in Sr_2IrO_4 , where a single frequency below the transition splits into two frequencies at 20 K.

	T_N (K)	α	β	$\nu_1(0)$ (MHz)	$\nu_2(0)$ (MHz)
Ca_4IrO_6	13.95(6)	4.2(3)	0.37(1)	8.29(3)	4.39(4)
$\text{Ca}_5\text{Ir}_3\text{O}_{12}$	7.84(7)	2.8(5)	0.40(6)	1.30(2)	—
$\text{Sr}_3\text{Ir}_2\text{O}_7$	285	—	—	—	—
Sr_2IrO_4	230.4(3)	0.98(4)	0.21(1)	2.93(1)	—

Table 4.2: The critical parameters extracted from μSR for all four compounds.

$\text{Sr}_3\text{Ir}_2\text{O}_7$ and Sr_2IrO_4 exhibit much more surprising and complicated behaviour. In $\text{Sr}_3\text{Ir}_2\text{O}_7$ a single frequency was observed between 20 K and 160 K. The disappearance of precession below 20 K and above 160 K cannot be explained. The change below 20 K does not correlate with any previously identified magnetic transition but corresponds to the temperature at which the field-cooled magnetization becomes negative.

Although the high temperature behavior of Sr_2IrO_4 is conventional, with the appearance of one frequency below the transition temperature at 260 K, the low temperature behavior is very unusual. Cooling below around 100 K induces a marked change in behavior resulting in the development of a second precession signal which fully establishes below 20 K. It has previously been suggested [22] that a reorientation transition occurs at 100 K in this material, and this is compatible with our data and correlates with a change in the Ir–O–Ir bond-angle. In this model, the magnetic structure changes due to a temperature-induced change in couplings, and this causes two structurally equivalent muon sites to experience increasingly distinct local fields which lock in below 20 K. This development of a reoriented phase may be gradual (occurring over the shaded region of Figure 4.10) which could result from the balance of competing energies and could be at the root of the magnetoelectric behavior [22].

5

Low-dimensional coordination polymers

5.1 Introduction

A purely 1D or 2D system will not show long-range magnetic order at any temperatures above $T = 0$ K. But experimental realisations of these systems, only approximate the purely 2D and 1D models and will invariably possess some degree of 3D (interlayer or interchain) coupling, which leads to order at finite temperatures. The short range correlations that build up above the ordering transition will have a reducing effect both on the ordered moment and the entropy change that is associated with the magnetic transition, making it difficult to measure these systems with conventional methods [37].

Many inorganic low-dimensional materials have exchange energy scales of order $J = 1000$ K thus requiring magnetic fields of up to 1000 T in order to successfully perturb the system. The molecular materials that are introduced in this chapter have exchange energies of $J \sim 10$ K, so that the phase diagram is accessible with typical laboratory magnetic fields of 10 T - 60 T. We can also take

advantage of the fact that the shape of the magnetisation $M(B)$ curve at low temperatures is determined by the precise dimensionality as well as the anisotropy of the systems and can thus be used to extract information on the exchange anisotropies.

In this chapter, I present how the coupling strengths and the type of magnetism in low-dimensional materials can be determined using a combination of magnetic susceptibility at low fields, magnetisation in pulsed magnetic fields, muon spin rotation and theoretical models. I introduce coordination polymers, which are molecular materials that enable the targeted design of magnetic system and are utilised as testing grounds to experimentally test fundamental theories of magnetism.

These materials are self-organizing systems, in which a magnetic ion is linked by molecular groups or ligands, forming chains and layers. They are produced by Jamie Manson at the Eastern Washington University and John Schluter at Argonne National laboratory. The synthesis consists of mixing the ingredients together in a water or ethanol solution with only a small amount of intervention required for the rest of the process. A high level of control over the molecular architecture can be achieved through the adjustments of initial synthesis ingredients and conditions. These adjustments can consist of a change of magnetic anion centres, of bridging ligands or of coordinated molecular groups that will have an effect on the magnetic behaviour.

In this chapter I consider materials based on $\text{Cu}^{2+} 3d^9$, which exhibit the Jahn-Teller effect. In a regular octahedral environment, the tetragonal distortion lifts the degeneracy between the $d_{x^2-y^2}$ and d_{z^2} orbitals, with the d_{z^2} orbital lower or higher in energy depending on the tetragonal elongation or compression respec-

5.2 Overview of low-dimensional magnetism

tively. In most cases octahedra containing copper ions are tetragonally elongated and are found to have a $d_{x^2-y^2}$ ground state, through which the magnetism is mediated.

I will first give an introduction to the magnetism in Q1D and Q2D spin- $\frac{1}{2}$ Heisenberg antiferromagnetic systems and the method utilised to study them. The next part of this chapter will introduce the family of Q2D molecular magnets $[\text{Cu}(\text{Y}_2)(\text{pyz})_2]X$ to show how slight changes to the molecular architecture lead to a change of the exchange interactions. I will then proceed to show how by changing the chemical composition the dimensionality of these materials can be switched from Q2D to Q1D whilst maintaining a similar value of the largest exchange constant. I conclude by describing a series of different Q1D systems.

5.2 Overview of low-dimensional magnetism

The magnetism of a system is determined by the interaction between the spins, which in the case of these low-dimensional, spin- $\frac{1}{2}$ materials is assumed to be purely Heisenberg-like. Therefore they can be described using the following Q2D (or Q1D) antiferromagnetic Hamiltonian:

$$H = J \sum_{\langle i,j \rangle_{\parallel}} S_i \cdot S_j + J_{\perp} \sum_{\langle i,j \rangle_{\perp}} S_i \cdot S_j - h \sum_i S_i^z \quad (5.1)$$

where J represents the strength of the intra-layer (chain) coupling and $J_{\perp}$ the coupling between layers (chains). The terms $\sum_{\langle i,j \rangle_{\parallel}} S_i \cdot S_j$ and $\sum_{\langle i,j \rangle_{\perp}} S_i \cdot S_j$ describe the summations over the nearest neighbours parallel and perpendicular to the planes (chains), respectively. The last term is associated with the Zeeman energy in a uniform magnetic field B with $h = g\mu_B B$.

Compound	B_c (T)	g	J (K)	T_N (K)	$\alpha = J_\perp/J$	D
[Cu(HF ₂)(pyz) ₂][BF ₄] [*]	18.0	2.13(1)	6.3	1.54	9×10^{-4}	2D
[Cu(HF ₂)(pyz) ₂][PF ₆] [*]	35.5	2.11(1)	12.4	4.31	1×10^{-2}	2D
[Cu(HF ₂)(pyz) ₂][SbF ₆] [*]	37.6	2.11(1)	13.3	4.31	9×10^{-3}	2D
[Cu(HF ₂)(pyz) ₂][AsF ₆] [*]	36.8	-	12.36	4.34	1×10^{-2}	2D
[Cu(HF ₂)(pyz) ₂][TaF ₆]	36.8(5)	~ 2.1	12.36(7)	4.22(1)	1×10^{-2}	2D
[Cu(HF ₂)(pyz) ₂](ClO ₄) ₂	20.9(4)	1.98(2)	6.8(1)	1.91(1)	4×10^{-3}	2D
[Cu(4-pppy-O) ₂ (pyz) ₂](ClO ₄) ₂	20.8(3)	2.1(1)	6.8(4)	1.63(1)	6×10^{-4}	2D
[Cu(pyo) ₂ (pyz) ₂](ClO ₄) ₂	20.7(4)	2.03(1)	6.9(6)	-	-	2D
Cu(pyz) ₂ (ClO ₄) ₂	51.8(3)	2.0(2)	17.1(4)	4.2(1)	8×10^{-4}	2D
[Cu(pyz) ₂ (pyO) ₂](PF ₆) ₂	23.7(1)	2.04(1)	8.1(3)	1.71(2)	1×10^{-4}	2D
[Cu(pyz)(pyO) ₂ (H ₂ O) ₂](PF ₆) ₂	12.8(4)	2.06(1)	8.8(2)	0.27(1)	1×10^{-2}	1D
CuCl ₂ (pyO)(H ₂) ₂	16.1(3)	2.1(1)	11.5(2)	1.0(1)	0.04(1)	1D
CuCl ₂ (pyz)	52.0(5)	28.2(5)	45.9(1)	3.2	-	1D
CuBr ₂ (pyO)(H ₂) ₂	66.7(5)	2.1(1)	44.3(6)	≤ 1	$\leq 0.009(1)$	1D
CuBr ₂ (pyz)	77.2(4)	2.21(2)	46(1)	3.6	-	1D
[Cu(2.3-me ₂ pyz)(CH ₃ O ₃ O ₃)(H ₂ O) ₂](CH ₃ SO ₃)	11.4(3)	2.2(1)	7.9(2)	≤ 2	$\leq 0.21(3)$	1D
Cu(2.5-me ₂ pyz)(CH ₃ SO ₃)(NO ₃)(H ₂ O)	9.5(3)	1.99(1)	6.2(2)	≤ 2	$\leq 0.21(3)$	1D

Table 5.1: List of compounds that are referred to in this thesis and their main characteristics. The critical field B_c was extracted from pulsed-field magnetisation, g was evaluated from single-crystal electron paramagnetic resonance (EPR) and when that was not available from high-temperature magnetic susceptibility. The in-plane exchange energy J is calculated using Eqn. 5.2; Néel temperatures T_N were measured using μ SR. The exchange anisotropy α was estimated using Eqn. 5.3 and Eqn. 5.4. The last column indicates the dimensionality of the system. The compounds annotated with (*) have been taken from a previous study [37].

5.2 Overview of low-dimensional magnetism

At the critical field the following expression is valid for spin- $\frac{1}{2}$ systems:

$$g\mu_B B_c = nJ + n_\perp J_\perp. \quad (5.2)$$

In this case n is the number of exchange bonds linked to the coupling J and $n_\perp$ is the number of exchange bonds linked to the coupling $J_\perp$. Thus for a quasi-two dimensional magnet $n = 4$ and $n_\perp = 2$ and for a quasi-one dimensional system $n = 2$ and $n_\perp = 4$.

In the highly anisotropic systems described here, we can assume that the exchange anisotropy $\alpha = J_\perp/J \ll 1$ and so using the value for the critical field obtained with magnetisation experiments, and given a value for g it is possible to deduce the exchange energy J . In addition, as described above, the shape of the magnetisation depends on the nature of the anisotropy. Low-temperature quantum Monte-Carlo simulations for the Q1D and Q2D cases for different anisotropies that were calculated by Pinaki Sengupta [37] are shown in Figure 5.1.

It is also possible to estimate the magnetic dimensionality, exchange anisotropy as-well as the g -factor from the temperature dependence of the low-field magnetic susceptibility. In quasi-low-dimensional systems spin correlations begin to build up above the transition temperature and thereby affect the thermodynamic properties of the system. This results in a broad maximum (a “hump”) in the susceptibility and the heat capacity.

These correlations also reduce the entropy of the system, so that when the weak interchain or interplane interactions force the system to long range order, the resulting entropy change is rather small because the spins have already become correlated. The peak with which the ordered transition can be identified is masked

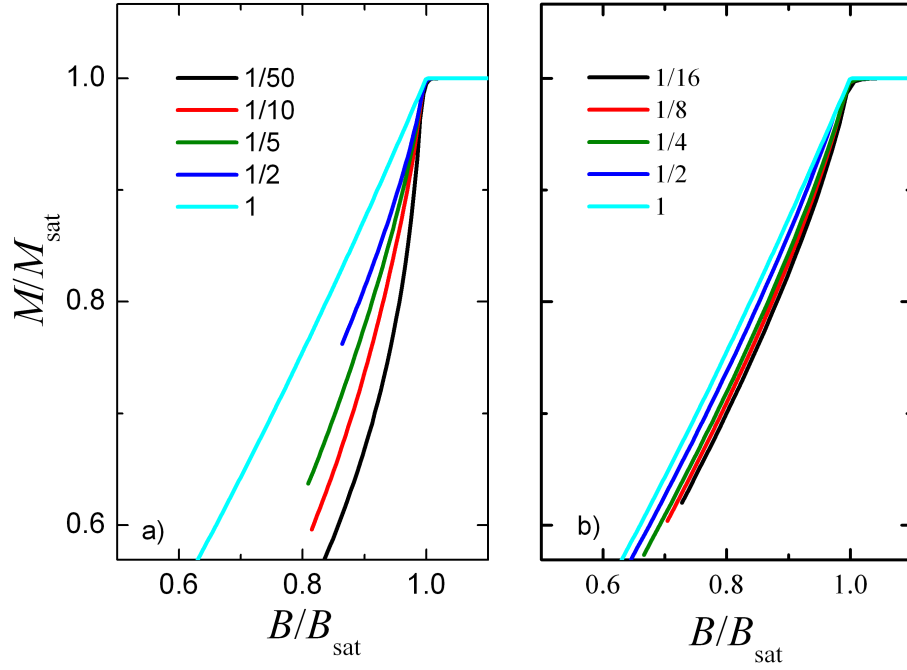


Figure 5.1: Monte-carlo simulations calculator by Pinaki Sengputa for the (a) Q1D and (b) Q2D case. The technique used for the calculations is described in more detail in Ref [37]. The graphs are plots of M/M_{sat} vs B/B_C for a range of different anisotropies $\alpha = J_{\perp}/J$. The $\alpha = 1$ line is identical in both graphs.

5.2 Overview of low-dimensional magnetism

in many of these systems by the much larger “hump” resulting from the spin correlations above T_N . Local probes, such as μ SR, do not suffer from the same drawbacks as thermodynamic techniques because they directly sense the static ordered field which only occurs once 3D long range order sets in. Thus μ SR can be used to determine the critical temperature in highly anisotropic materials.

Combining the transition temperature from μ SR, the primary exchange energy extracted from pulsed magnetic fields, the results of quantum Monte-Carlo simulations allows us to determine the exchange anisotropy $J_\perp/J$. For quasi-one-dimensional Heisenberg antiferromagnets the following expression holds [94]:

$$\alpha = J_\perp/J = \frac{T_N}{4c\sqrt{\ln(\frac{J\lambda}{T_N}) + \frac{1}{2}\ln\ln(\frac{J\lambda}{T_N})}} \times \frac{1}{J}. \quad (5.3)$$

The parameters c and λ are constants, $c = 0.233$ and $\lambda = 2.6$. And for quasi-two-dimensional Heisenberg antiferromagnets in the limit of $0.001 \leq J_\perp/J \leq 1$ the relationship is better described by [94]:

$$\alpha = J_\perp/J = e^{(2.43 - 2.29J/T_N)}. \quad (5.4)$$

It is important to note that since Eqn. 5.4 is a function that will rapidly vary with J/T_N , so that only slight changes in any of these parameters will lead to a large change in $J_\perp/J$.

The different results presented here combine these techniques to paint a complete picture of the low dimensional molecular polymers that are under investigation.

5.3 Exchange interaction and anisotropy of the coordination polymers $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{X}$

In this section we consider a series of coordination polymers of the form of $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{X}$. Figure 5.2 shows the crystal structure of these systems. They are made of four-fold symmetric $[\text{Cu}(\text{pyz})_2]^{2+}$ planes that are connected along the c -axis by weak HF_2 links, resulting in a pseudo-cubic structure. The X -counterions are placed at the body-centred positions of each cube. The strong super-exchange interaction between the neighbouring Cu^{2+} ions is mediated through the pyrazine ligands and thus Q2D magnetism is created in these systems.

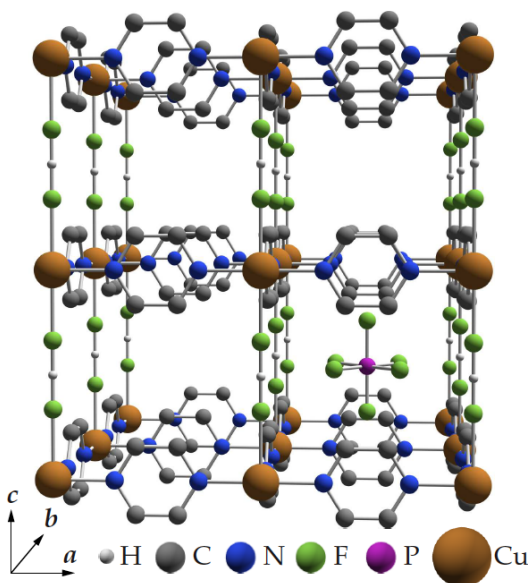


Figure 5.2: Crystal structure of the $[\text{Cu}(\text{H}_2)(\text{pyz})_2]\text{X}$ - family. X represents the non-coordinated counterion which can be any of the following: PF_6 , SbF_6 , AsF_6 , BF_4 , ClO_4 and TaF_4 . The Cu -ions are bridged by pyrazine ligands and form a layers that are interconnected by HF_2 links. The strong magnetic exchange J lies within the planes, a small exchange interaction $J_\perp$ between the layers leads to ordering at low temperatures.

In a previous study by Goddard et al [37], a range of samples was studied with

5.3 Exchange interaction and anisotropy of the coordination polymers [Cu(HF₂)(pyz)₂]X

two classes of counterion: the octahedral PF₆, SbF₆, AsF₆ and tetrahedral BF₄ and ClO₄. They showed that the exchange interaction J , transition temperature T_N and anisotropy $J_{\perp}/J = \alpha$ are almost identical for systems that have the same type of counterion; $J = 13$ K, $T_N = 4.3$ K, $\alpha = 10^{-3}$, and $J = 7$ K, $T_N = 1.9$ K, $\alpha = 10^{-2}$ for the octahedral and tetrahedral class respectively.

In this section, I present the results for the sample [Cu(HF₂)(pyz)₂]TaF₆ in the same series of coordination polymers. This data is included in a detailed μ SR study of these Q2D materials by Steele et al [79]. The magnetic ordering transitions were extracted with μ SR. The results of zero-field μ SR experiments, at 2.3 K, on the GPS system at PSI, are shown in Figure ??.

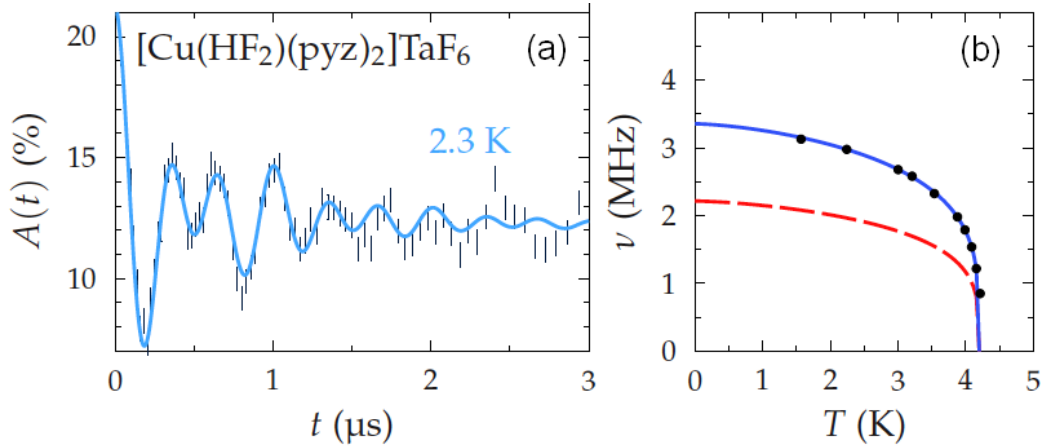


Figure 5.3: (a) Muon Spin Rotation asymmetry spectra of [Cu(HF₂)(pyz)₂]TaF₆ for T_N , along with the fit to Eqn. 5.5; (b) frequencies as a function of temperature. There are no data points for the second frequency because it was held in fixed proportion to the first. [79]

The sample exhibits oscillations at temperatures below 5 K, which are strongly indicative of long-range order throughout the bulk of the material. The data is fitted with the following expression:

5.3 Exchange interaction and anisotropy of the coordination polymers [Cu(HF₂)(pyz)₂]X

$$\begin{aligned}
A(t) &= A_1 \exp(-\lambda_1 t) \cos(2\pi\nu_1 t) \\
&+ A_2 \exp(-\lambda_2 t) \cos(2\pi P\nu_1 t) \\
&+ A_3 \exp(-\Lambda t).
\end{aligned} \tag{5.5}$$

In Eq. 5.5 A_i represents the amplitudes of each of the components, the first two terms describe the frequency components from the muons that stop inside the sample and the third describes the contribution from the muons that either stop in the silver sample holder and cryostat tails or have a spin that lies parallel to the local field. There are two muon stopping sites in the sample, resulting in the two frequencies, which vary in proportion, $\nu_2 = P\nu_1$ at all temperatures to achieve the most satisfactory fit. The parameter P was identified by fitting the asymmetry at the lowest temperature, where Eqn. 5.5 fits the data most accurately.

The evolution of the precession frequencies is shown in Figure 5.3 b) and fitting these results to the phenomenological function Eqn. 3.3 yields a transition temperature of $T_N = 4.22(1)$ K and $\beta = 0.25(1)$. This is in agreement with the previous results, which found the ordering temperature of the [Cu(HF₂)(pyz)₂]X systems with an octahedral X counterion to be of the order of $T_N \approx 4.3$ K [37, 79].

The magnetic behaviour of the material was studied via low-temperature pulsed-field magnetisation measurements up to 60 T, using the system described in Section 2.3. Single crystals were available for this particular sample, which made it possible to perform the measurement with the field applied perpendicular as well as parallel, to the layers. The results of magnetisation measurements

5.3 Exchange interaction and anisotropy of the coordination polymers [Cu(HF₂)(pyz)₂]X

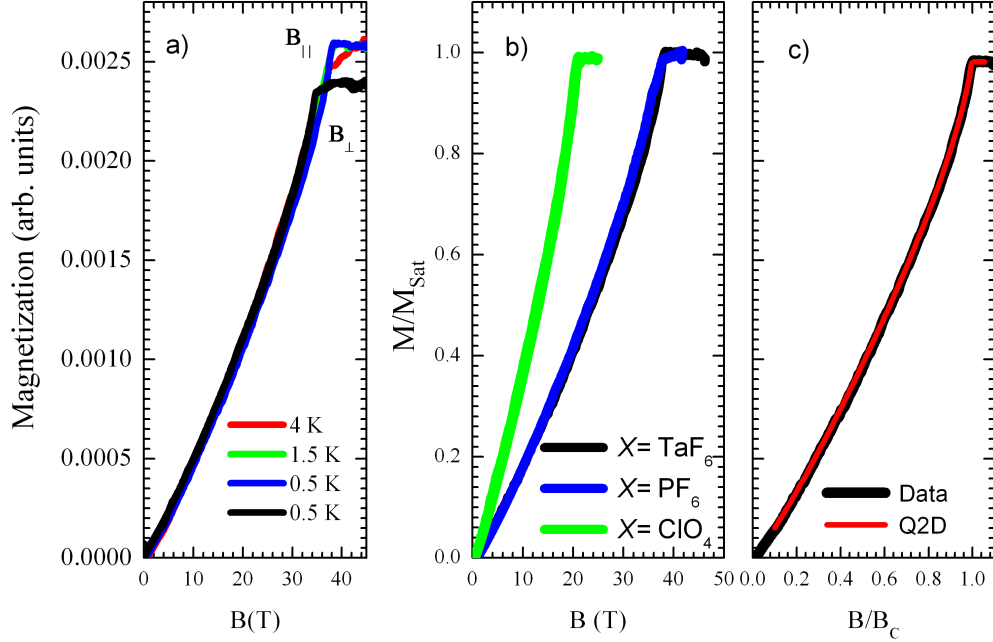


Figure 5.4: a) Magnetisation $M(B)$ at 0.5 K, 1.5 K and 4 K for the field applied parallel to the layers and $M(B)$ at 0.5 K for the field applied perpendicular to the layers. The shift of B_c is due to the g-factor dependence. b) Normalized magnetisation M/M_{sat} versus field B for [Cu(HF₂)(pyz)₂]TaF₆, [Cu(HF₂)(pyz)₂]PF₆ and [Cu(HF₂)(pyz)₂]ClO₄. The critical fields of the $X = \text{TaF}_6$, PF₆ compounds are almost identical, whereas the $X = \text{ClO}_4$ compounds has a much lower B_c . c) Data for [Cu(HF₂)(pyz)₂]TaF₆ as well Quantum Monte Carlo simulations for $\alpha = J_{\perp}/J$ 1/16 are plotted in reduced units M/M_{sat} and B/B_c .

for [Cu(HF₂)(pyz)₂]TaF₆ are shown in Figure 5.4. When $T \ll T_N$, the magnetisation is concave at low fields with a sharp change at a critical field B_c , at which the magnetisation saturates and takes the constant value M_{sat} .

At different field orientations, the value of B_c changes. When the field is applied parallel to the layers, B_c is higher than when the field is applied perpendicular to the layers. This agrees with previous results on this family of compounds [37] and has been shown to be a result of the g-factor anisotropy. The nor-

5.3 Exchange interaction and anisotropy of the coordination polymers [Cu(HF₂)(pyz)₂]X

malized magnetisation (M/M_{sat}) is plotted against field B for [Cu(HF₂)(pyz)₂]TaF₆, [Cu(HF₂)(pyz)₂]PF₆ and [Cu(HF₂)(pyz)₂]ClO₄ in Figure 5.4 b). Both octahedral types show identical behaviour whilst the critical field is much smaller in ClO₄ and confirms that this material fits in with the previous study by Goddard et al [37].

The shape of the magnetisation conforms with one expected for a Q2D Heisenberg antiferromagnet. In Figure 5.4 c) the data is compared to the results of the low-temperature quantum Monte-Carlo simulations based on the Hamiltonian described by Eqn.5.1 for the Q2D case. The data agrees well with Q2D model with $\alpha \sim 1/16$. The model is based on the assumption that $T = 0$. Since the data was taken at finite temperatures there will be slight deviations particularly around the critical field.

The critical field B_c (taken to be the mid-point of the transition in dM/dB) can be extracted from the data, and was found to be 34.29(1) T for the field applied perpendicular to the layers and 38.20(4) T for the field applied parallel to the layers. Eqn. 5.2 becomes $g\mu_B B_C = 4J + 2J_\perp$ in the case of Q2D materials. Since we do not have electron spin resonance or susceptibility data to determine the value of g , we use an average critical field B_{cAv} to calculate the value of J , which is defined as $B_{cAv} = (2B_{c||} + B_{c\perp})/3$, since there are two different directions for which the field is applied parallel to the planes and one field direction in which it is applied perpendicular to the planes. This results in $B_{cAv} = 36.8(5)$ T

Assuming that $\alpha = J_\perp/J \ll 1$ and that the g -factor is $g \sim 2.1$ from similar compounds [37], enables us to extract $J = 12.36(7)$ K. The results of magnetisation and μ SR data can be combined [94] using Eqn. 5.4 to give an additional estimate of exchange anisotropy α in [Cu(HF₂)(pyz)₂]TaF₆: evaluating $J_\perp/J$ yields

5.3 Exchange interaction and anisotropy of the coordination polymers [Cu(HF₂)(pyz)₂]X

$J_{\perp}/J=0.01(4)$. This is a result which is very close to the other compounds with octahedral counterions (Table 5.1).

In summary, it is possible to show that [Cu(HF₂)(pyz)₂]TaF₆ fits in with the trend observed in the [Cu(HF₂)(pyz)₂]X-family. [Cu(HF₂)(pyz)₂]TaF₆ has a transition temperature of $T_N=4.22(1)$ K comparable to the other systems with octahedral counterions, in which $T_N=4.3$ K. $J=13$ K, $\alpha=1\times 10^{-3}$. In addition the primary exchange interaction is roughly double the value found in the tetrahedral compounds, in keeping with observed previous observations. A more complete picture could be obtained with electron spin resonance and susceptibility measurements, which would enable us to estimate the g -factor and confirm the value of J .

The doubling of the exchange interaction as well as the change in anisotropy is a puzzling observation in these materials since there is little variation in the Cu-Cu distance within the layers across the family of compounds and the counterions sit in body centered positions and thus might not be expected to have a direct effect on the layers from which the magnetism originates. It has been suggested that the effect observed here is correlated with the configuration of the pyrazine ligands, through which the strong exchange is mediated. The geometry of the larger octahedral counterion such as TaF₆ lets the pyrazine rings stand upwards almost perpendicular to the layers, whereas the ligands are tilted at an angle of $\sim 30^\circ$ in the compounds with the smaller tetrahedral counterions.

It is plausible to think that both the change in exchange interaction strength and the angle of the pyrazine ligands result from the same effect. One possible way of understanding the effect is by taking into account the exchange interactions from the next-nearest-neighbours within the Cu-pyz-planes. In such a model the

next-nearest-neighbour antiferromagnetic interactions reduce the effective inter-layer exchange extracted from magnetic measurements to $J_{eff} = J_1 - J_2$, where J_1 is the nearest-neighbour exchange and J_2 the next-nearest-neighbour exchange. Whereas J_1 is affected only by the pyrazine ligands, J_2 will be mediating superexchange through the coordinated counterions, which explains why a change in the class of counterion will result in a similar change of effective exchange interaction strength.

5.4 Magnetism of $[\text{Cu}(Y)_2(\text{pyz})_2](\text{ClO}_4)_n$

In the previous section I have presented how the type of counterion placed at the body-centred site in the pseudo-cubic system of the $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]X$ family, will have a determining effect on the magnetism and particularly on the strength of the primary exchange interaction. In this section I will further investigate this family of compounds by concentrating on the $X=\text{ClO}_4$ class. Figure 5.5 shows the crystal structure of $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$, $[\text{Cu}(\text{py-O})_2(\text{pyz})_2](\text{ClO}_4)_2$, $[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ and $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$.

The four systems have similar structures, based on 2D square lattices of Cu-pyz-Cu. Strong exchange interaction between the Cu-ions is mediated through the pyrazine bridges. In the original system [Figure 5.5(a)], $\text{F} \cdots \text{H} \cdots \text{F}$ form bridging ligands via the strong H-bond and lead to a pseudo-cubic structure with the ClO_4 counter-ions places at the axial sites.

The structure is significantly altered when the ligands between the layers are replaced by non-bridging py-O [Figure 5.5 (b)] and 4-phpy-O [Figure 5.5 (c)]. Although the magnetic layers stay intact the substitution with py-O, leads to

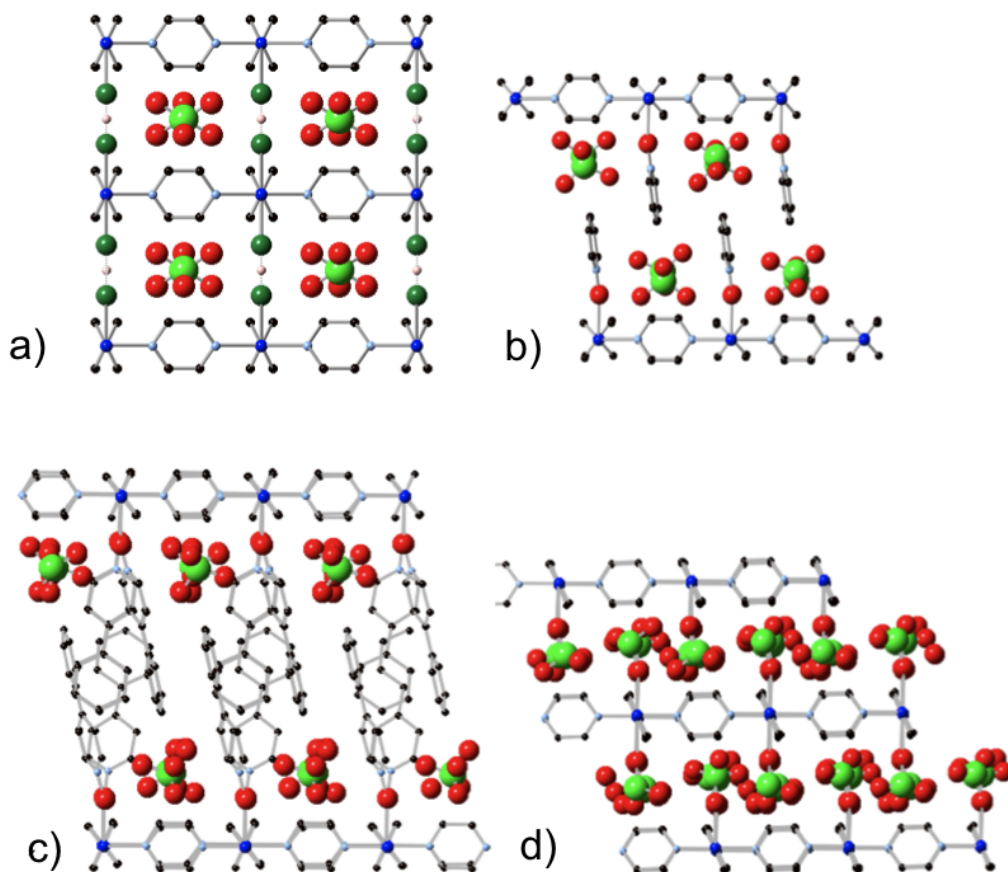


Figure 5.5: Crystal structures of (a) $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$, (b) $[\text{Cu}(\text{py-O})_2(\text{pyz})_2](\text{ClO}_4)_2$, (c) $[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ (d) $\text{Cu}(\text{py-O})_2(\text{pyz})_2(\text{ClO}_4)_2$. Cu=blue; C=black; N=light-blue; Cl=green; O=red; F=dark-green; H=pink. All four systems are based on Cu-pyz layers that mediate the dominant exchange interaction. In (a) $\text{F} \cdots \text{H} \cdots \text{F}$ hydrogen bonds form bridging ligands. The layers of the three other systems are separated by non-bridging ligands that lead to staggering. Whereas the ClO_4 molecules are placed at the axial sites in (a), (b) and (c), they bond to the Cu-pyz planes in (d) through an O-Cu bond.

5.4 Magnetism of $[\text{Cu}(\text{Y})_2(\text{pyz})_2](\text{ClO}_4)_n$

a larger separation between the layers and staggering. In addition, the amount of non-coordinated ClO_4 molecules in between the layers doubles. These effects become even more pronounced in the system in which the non-bridging ligand is 4-phpy-O.

In $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$ (Figure 5.5d) the ClO_4 molecules are non-bridging ligands with Cu-O bonds. It has layers that are much closer to each other and staggering is also observed. A comparison of the crystal structure details for all the $[\text{Cu}(\text{Y})_2(\text{pyz})_2](\text{ClO}_4)_n$ compounds studies is given in Table 5.3.

To get an understanding of the magnetism in these systems, the magnetisation at high fields was examined. Magnetisation was measured up to 60 T and the normalized magnetisation M/M_{sat} for $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$, $[\text{Cu}(\text{py-O})_2(\text{pyz})_2](\text{ClO}_4)_2$, $[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ and $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$ is plotted in Figure 5.6.

The shape of the magnetisation of all four systems is indicative of Q2D antiferromagnetic interactions. The results of M/M_{sat} versus B for $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$, $[\text{Cu}(\text{py-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ and $[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ are almost identical. $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$ saturates at a much larger field. The critical field, which is again defined as the midpoint of the transition in dM/dB can be extracted and is found to be 20.9(4) T for $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$, 20.7(4) T for $[\text{Cu}(\text{py-O})_2(\text{pyz})_2](\text{ClO}_4)_2$, 20.8(3) T for $[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ and 51.8(3) T for $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$.

The magnitude of the coupling constants J can be deduced by assuming $J_{\perp} \ll J$ and using the g-values from a Curie-Weiss fit to high temperature susceptibility data (see below) and the quasi-two-dimensional form of Eqn. 5.2: $g\mu_B B = 4J + 2J_{\perp}$.

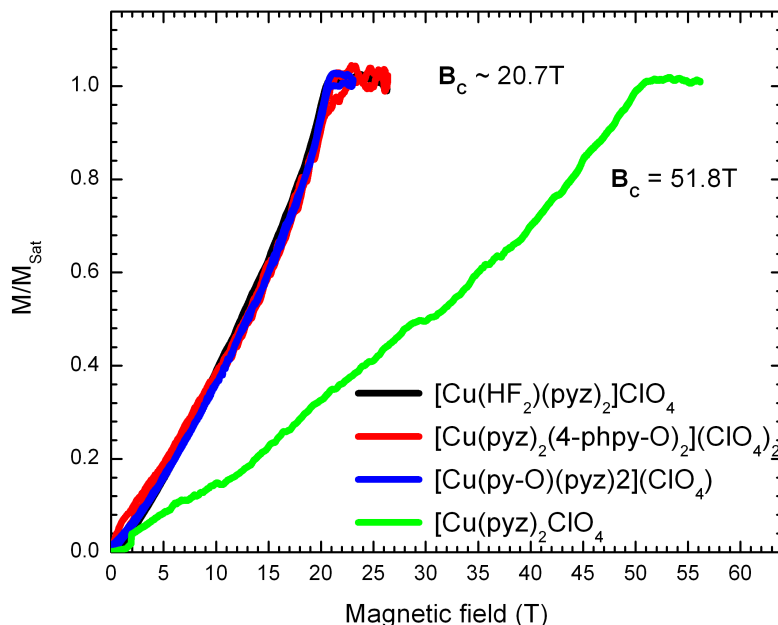


Figure 5.6: Magnetisation data for $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$, $[\text{Cu}(\text{py-O})_2(\text{pyz})_2](\text{ClO}_4)_2$, $[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$, $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$. The first three samples have very similar critical fields, while the fourth sample saturates at a much higher field.

This yields exchange energies $J = 6.8(1)$ K, $J = 6.8(4)$ K, $J = 6.9(6)$ K and $J = 17.1(4)$ K for $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$, $[\text{Cu}(\text{py-O})_2(\text{pyz})_2](\text{ClO}_4)_2$, $[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ and $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$ respectively.

The values for $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$, $[\text{Cu}(\text{py-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ and $[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ are within error of each other, which suggests that the primary exchange interaction J within the layers is unchanged by the substitution of the interlayer links and the resulting changes in crystal structures. In contrast the critical field of $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$ is a lot larger, indicating a much larger coupling within layers of this system compared to the others.

5.4 Magnetism of $[\text{Cu}(\text{Y})_2(\text{pyz})_2](\text{ClO}_4)_n$

The magnetic susceptibility was measured for $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$, $[\text{Cu}(\text{py-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ and $[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$. The data were obtained with SQUID magnetometer, described in Chapter 2.4. The data were measured from 2 K to 300 K in a field of 0.1 T. The g -factor of these materials can be estimated by fitting the reciprocal magnetic susceptibility, $\frac{1}{\chi}(\text{T})$, to the Curie-Weiss law:

$$\frac{1}{\chi} = \frac{(T - \theta)}{C} \quad (5.6)$$

$$C = \frac{N\mu_0\mu_B^2}{3k_b} g^2 S(S + 1) \quad (5.7)$$

The resulting g -factors are listed in Table 5.4. The data was taken on powder samples and these usually give higher g -factors than the free electron values of 2.0032 but are typical of Cu^{2+} . Susceptibility data are plotted as function of temperature in Figure 5.7. The Inset shows the results of the Curie-Weiss fits.

The data sets are different for the four samples, but all exhibit the hump at $T \sim J$, which is expected for an anisotropic antiferromagnet. The isolated two-dimensional model described in Woodward *et al.* [89], that is based on the low dimensional Heisenberg Hamiltonian of Eqn. 5.1 is in good agreement with the data. The Woodward model describes the susceptibility accurately for a range of $T \geq 0.15 J$. At lower temperatures the data will diverge from the model as the transition to 3D order is approached. The model predictions can be expressed in the following way:

$$\chi = C/T \left[1 + \sum_{n=1}^5 a_n (-J/T)^n \right] / \left(1 + \sum_{n=1}^5 b_n (-J/T)^n \right) \quad (5.8)$$

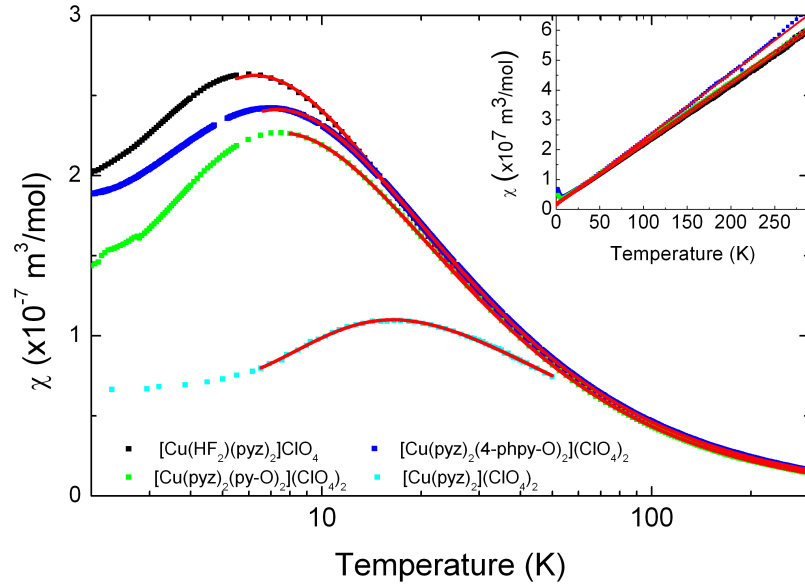


Figure 5.7: Results of temperature-dependent susceptibility measurements data for $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$, $[\text{Cu}(\text{py-O})_2(\text{pyz})_2](\text{ClO}_4)_2$, $[\text{Cu}(4\text{-ppy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$, $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$. The red lines represent the susceptibility fits to the quasi-two-dimensional antiferromagnetic model according to Woodward *et al.* [89]. The data for $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$ are taken from Ref [92].

5.4 Magnetism of $[\text{Cu}(\text{Y})_2(\text{pyz})_2](\text{ClO}_4)_n$

n	a_n	b_n
1	0.998586	-1.84279
2	-1.28534	1.14141
3	0.656313	-0.704192
4	0.235862	-0.189044
5	0.277527	-0.277545

Table 5.2: Parameters a_n and b_n as listed in Ref [88]. They were determined using a standard nonlinear, least-squares-fitting algorithm.

The parameters a_n and b_n are listed in Table 5.2 have been determined by Woodward *et al.* [88] using a standard nonlinear, leastsquares-fitting algorithm and C is defined as in Eqn. 5.7 .

Based on these expressions it is possible to estimate values of g and the intralayer exchange interaction J by fitting the susceptibility data from 300 K down to temperatures just below the hump. The red lines in Figure 5.7 represent the fits and the results for g and J are listed in Table 5.4. The primary exchange interactions J are similar (6.96(4) K, 7.61(3) K, 7.8(5) K) in the three first cases but substantially different (17.4(3) K) in the fourth sample. Note that there is a stronger similarity between the samples containing pyridine-N-oxides and that the J for the HF_2 -bonded sample is lower. These results suggest that J is sensitive to the axial ligand. $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$ where J is on the order of -17 K, seems to behave very differently to the other three.

Although the results do not fully agree with the values obtained from magnetisation measurements, the difference can be explained by the techniques used to determine the coupling strengths. In magnetisation data, it is more difficult to identify the slight difference in the critical field B_c , in the case where the magnitudes of the exchange interactions are very close. In addition the extraction of J from susceptibility data is based on a fit from a series of roughly 100 data-points,

whereas the exchange energy is determined from magnetisation data based on a single point.

Finally we examine the magnetic order in these systems. Previous data include a μSR study of $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$ by Lancaster *et al.* [55], in which they observe the existence of 3D long-range magnetic order throughout the bulk of the sample at temperatures below $T_N=4.21(1)$ K. Muon spin rotation measurements were performed on the Q2D magnets $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$ and $[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ at the MUSR and ARGUS instruments at ISIS. Powder samples were mounted on silver backing plates, wrapped in 12.5 μm silver foil and placed in a cryostat.

The asymmetry spectra $A(t)$ from the two compounds are shown in Figure 5.8. At temperatures below a critical T_N the asymmetry spectra can be described by two frequencies. This suggests that a significant number of muons are stopping at two sites with a constant internal field, giving rise to a coherent precessions of the ensemble of muon spins, which is indicative for long-range magnetic order.

It is possible to describe the asymmetry spectra of both $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$ and $[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ with the following expression:

$$\begin{aligned}
 A(t) &= A_1 \exp(-\lambda_1 t) \cos(2\pi\nu_1 t) \\
 &+ A_2 \exp(-\lambda_2 t) \cos(2\pi P\nu_1 t) \\
 &+ A_3 \exp(-\lambda_3 t) \\
 &+ A_{bg}.
 \end{aligned} \tag{5.9}$$

The three first terms in this equation are components resulting from muons stopped in the sample and the fourth term stems from the background of muons

Compound	Cu - Cu intra-layer (Å)	Cu - Cu inter-layer (Å)	tilt angle (°)	staggering angle (°)
$[\text{Cu}(\text{HF}_2)(\text{pyz})_2](\text{ClO}_4)_2$	6.863	6.689	64	0
$[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$	6.833	17.922	51.9, 66.1	3.45
$[\text{Cu}(\text{pyo})_2(\text{pyz})_2](\text{ClO}_4)_2$	6.88	13.1835	52.8, 47.8	12.3
$\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$	6.914	8.096	60.5	22.27

Table 5.3: Distances between atoms of interest for the magnetic exchange, as well as tilt and staggering angles of the four samples. The tilt angle is defined by how far the pyrazine tilts relative to the $|ab|$ -plane and the staggering angle describing the shift of the layers, the angle to which the Cu of the upper plane is moved away from being placed perpendicularly above the Cu of the lower plane.

Compound	B_c (T) (from $M(B)$)	g	J (K) (from $\chi(T)$)	J (K) (from $M(B)$)	$J_\perp$ (K)	T_N (K)	$ J_\perp/J $
$[\text{Cu}(\text{HF}_2)(\text{pyz})_2](\text{ClO}_4)_2$	20.9(5)	1.98(2)	6.96(4)	6.8(2)	0.024	1.91(1)	4×10^{-3}
$[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$	20.8(5)	2.1(1)	7.61(3)	6.8(4)	0.0046	1.63(1)	6×10^{-4}
$[\text{Cu}(\text{pyO})_2(\text{pyz})_2](\text{ClO}_4)_2$	20.7(5)	2.03(1)	7.8(5)	6.9(6)	-	-	-
$\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$	51.8(3)	2.0(2)	17.4(3)	17.1(4)	0.013	4.2	8×10^{-4}

Table 5.4: Values for the critical field B_c , g -factor, exchange energies J and $J_\perp$, magnetic transition temperatures and exchange anisotropy for $[\text{Cu}(\text{HF}_2)(\text{pyz})_2](\text{ClO}_4)_2$, $[\text{Cu}(\text{py-O})_2(\text{pyz})_2](\text{ClO}_4)_2$, $[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$, $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$, as presented in this thesis.

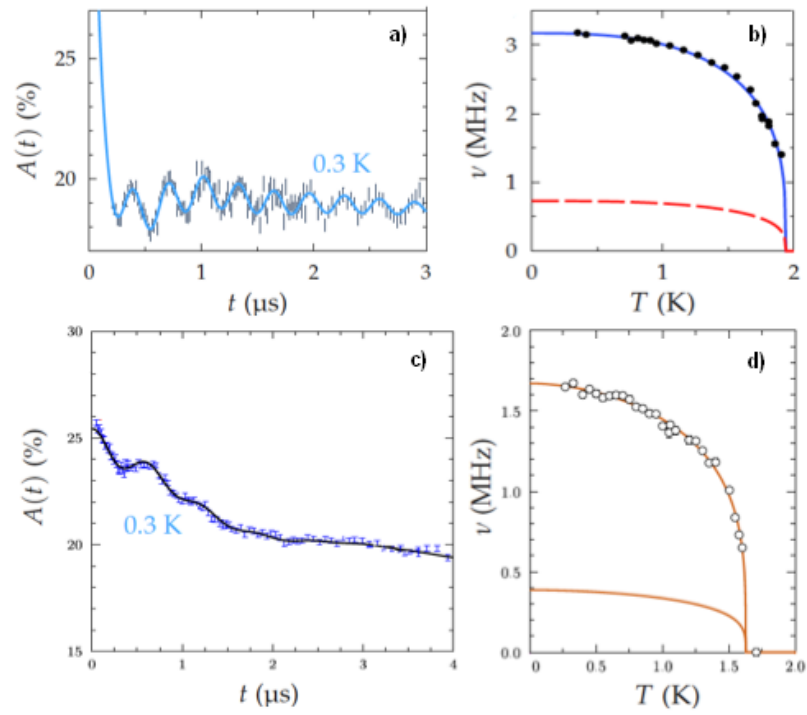


Figure 5.8: μSR Asymmetry spectra for (a) $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$ and (c) $[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ at 0.3 K. Both samples show oscillations at this temperature indicating that they are in the ordered state. The data of both samples was fitted with Eqn. 5.9. The results of the fitting as a function of temperature are plotted in panel (b) and (d).

5.4 Magnetism of $[\text{Cu}(\text{Y})_2(\text{pyz})_2](\text{ClO}_4)_n$

with spins parallel to the local field and spins stopping in the sample holder and cryostat tails. For $[\text{Cu}(\text{4-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ the background is constant. However in $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$ a better fit is achieved by letting the background slightly relax and thus setting it to $A_{bg} = A_0 \exp(-\Lambda t)$.

The two frequencies ν_1 were fitted in fixed proportion $\nu_2 = P\nu_1$ to one another. Both samples have a stopping site that gives rise to a relaxation. However the relaxation component is much smaller in $[\text{Cu}(\text{4-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$. This is most probably an artefact of a reduced time resolution from the muon pulse, which means the fast relaxation cannot be resolved in this material.

The magnitude of the oscillation is clearly lower in $[\text{Cu}(\text{4-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ compared to $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$. There are several reasons why this might be. We can exclude the possibility that only a small region of the sample undergoes a magnetic transition, due to an impurity phase, since this is not indicated in the susceptibility data. Most probably a range of similar muon sites may be present with a large distribution of frequencies and possibly the presence of dynamics washing out any clear oscillations in large fractions of the spectra and instead resulting in a relaxation.

The frequencies for both samples are extracted as a function of temperature and a fit to eqn 3.3, yields transition temperatures of $T_N = 1.91(1)$ K and $1.63(1)$ K and exponents $\beta = 0.27(2)$ and $0.25(2)$ for $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$ and $[\text{Cu}(\text{4-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ respectively. The values of β are typical of Q2D systems.

Using eqn 5.4 we evaluate the magnitude of $\alpha = J_\perp/J$. In the three materials that we have been able to identify transition temperatures for, the exchange energies are 4×10^{-3} K, 6×10^{-4} K and 8×10^{-4} K for $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$, $[\text{Cu}(\text{4-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ and $\text{Cu}(\text{pyz})_2(\text{ClO}_4)_2$ respectively, suggesting that the

5.4 Magnetism of $[\text{Cu}(Y)_2(\text{pyz})_2](\text{ClO}_4)_n$

interlayer exchange coupling is one order of magnitude larger in $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$ compared to the two other samples that were studied with μSR . This was to be expected since the layers are bridged by HF_2 and form a pseudo-cubic lattice.

In summary, I have presented the results of a series of measurements on $[\text{Cu}(Y)_2(\text{pyz})_2](\text{ClO}_4)_n$ systems, where Y is either HF_2 , pyO , 4- phpy-O , or omitted. The results of low field magnetic susceptibility, pulsed field magnetisation and μSR are summarized in Table 5.4.

From the crystal structure it might be expected that these system all have similar magnetic properties. They all contain two-dimensional square lattices of Cu-pyz-Cu . The magnetic behaviour of these materials results from the $3d_{x^2-y^2}$ orbital of the Cu which lies in the CuN_4 plane of the CuN_4F_2 octahedron, so that the spin exchange interactions between neighbouring Cu ions occur through the pyrazine ligands. These form magnetic planes that are stacked in layers to form the crystals. The interlayer exchange is assumed to be much weaker, since the interlayer links lie on the 4-fold rotational axis of the $3d_{x^2-y^2}$ and thus the orbital of the links can not overlap with it.

Assuming this is the case in these materials we would expect similar magnitudes of primary exchange interactions J , but a variation in the interlayer interactions $J_\perp$ and also different exchange anisotropies due to the change from bridging to non-bridging ligands and the variation of inter-layer distance and staggering of the layers. This is observed in $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$, $[\text{Cu}(\text{py-O})_2(\text{pyz})_2](\text{ClO}_4)_2$ and $[\text{Cu}(4\text{-phpy-O})_2(\text{pyz})_2](\text{ClO}_4)_2$. The three materials have very similar exchange couplings within their layers, but exhibit differing exchange anisotropies. $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{ClO}_4$ is found to be the least anisotropic of the systems, since its layers are bridged compared to the other compounds.

5.5 Tuning the dimensionality of coordination polymers

In the system where ClO_4 forms a non-bridging ligand instead of being a non-coordinated counterion, $[\text{Cu}(\text{pyz})_2]\text{ClO}_4$, a much larger primary exchange interaction is observed, and although the anisotropy is still low, the magnetic transition temperature is higher than in the other three systems.

One possible way this difference can be explained is by considering the reduced effective intralayer exchange $J_{eff} = J_1 - J_2$ as described in Section 5.3. This effect has been suggested as an explanation of the inelastic neutron scattering experiments in $[\text{Cu}(\text{pyz})_2]\text{ClO}_4$ [84]. By comparing data with series expansion calculations they estimate $J_1 = 17.61(2)$ K and $J_2 = 0.02 J_1$, which gives a J_{eff} that agrees with our susceptibility and magnetisation experiments. It is likely that J_1 will be the same in all systems presented in this chapter. However it is conceivable that in the systems in which the ClO_4 molecules are counterions placed in the interstitial sites J_2 is larger because, the ClO_4 molecules will mediate superexchange, in contrast to $[\text{Cu}(\text{pyz})_2]\text{ClO}_4$, where ClO_4 is a non-bridging ligand and is not placed in the interstitial sites. A larger J_2 would lead to a reduction of J_{eff} . In this model the value of J_2 would be of the order of $0.6J_1$.

5.5 Tuning the dimensionality of coordination polymers

In the previous sections I introduced coordination polymers as materials in which particular parameters can be changed whilst keeping others constant. This has been demonstrated in the systems based on Cu-pyz-Cu planes in which the exchange coupling is adjusted by adapting the crystal structure. It was shown that the coupling is affected by the substitution of both the non-coordinated anions

5.5 Tuning the dimensionality of coordination polymers

as well as the bridging ligands between the layers. In this section I will show how the dimensionality can be switched from Q2D to Q1D whilst maintaining the coupling strength. This is achieved by designing a specific Q2D material and then choosing to inhibit exchange along one crystal direction.

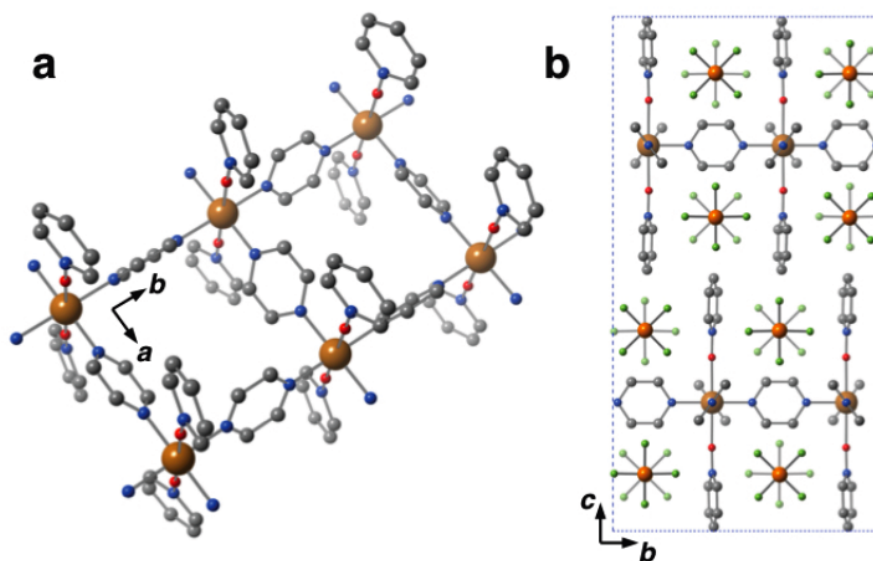


Figure 5.9: Crystal structure of the planar material $[\text{Cu}(\text{pyz})_2(\text{pyO})_2](\text{PF}_6)_2$. (a) 2D Cu- pyrazine network in the ab -plane. (b) View along the a -axis showing the staggering between adjacent Cu-pyrazine layers and the arrangement of the non-coordinated PF_6 counterions. Cu = brown, C = grey, N = blue, O = red, P = orange, F = green. Hydrogen ions have been omitted for clarity.

Figure 5.9 shows the crystal structure of the orthorhombic compound $[\text{Cu}(\text{pyz})_2(\text{pyO})_2](\text{PF}_6)_2$. This is a similar compound to $[\text{Cu}(\text{pyz})_2(\text{pyO})_2](\text{ClO}_4)_2$, which was described in the previous section. Similar to the other systems described in this chapter, it is made out of Cu ($s = \frac{1}{2}$) ions that are linked by pyrazine (pyz) molecules, forming 2D square layers. These layers are separated by non-bridging pyO molecules, which keeps the planes far apart and also leads to a staggering of the planes as shown in Figure 5.9 (b). These characteristics result in very small

5.5 Tuning the dimensionality of coordination polymers

exchange coupling between the layers and strong intralayer exchange through the Cu-pyz-Cu links.

To create a compound that is formed out of chains instead of layers the recipe on which they are based has to be changed. Instead of using a 3:1 pyz to pyO ratio for the procedure the ratio is changed to 2:1. The following steps in the synthesis are very similar for both compounds. The change in the initial ingredients results in the production of $[\text{Cu}(\text{pyz})(\text{pyO})_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$.

The structure of this new compound is shown in Figure 5.10. The pyz-links have only formed along one direction (b-axis), resulting in a system of chains to which non-bridging pyO are connected with water molecules in the interstitial sites.

In both these compounds the magnetism is based on the Cu^{2+} ions. In the material that is based on planes the ions have an octahedral symmetry with a tetragonal distortion along the c-axis. This means that the unpaired spin of the d^9 configuration occupies the $d_{x^2-y^2}$ orbital, leading to a higher electronic overlap in the Cu-pyz direction with strong superexchange mediated through the pyrazines. Electron Spin Resonance (ESR) performed by Ross D. MacDonald at the NHMFL provides values for the g-factor, which are listed in Table 5.14 alongside the other values resulting from this study. They confirm this model, by showing that the g-factor is lower parallel to the planes compared to perpendicular to the planes. The chain-like material is more complicated, but ESR was able to find that the highest electronic orbital overlap is along the Cu—pyz direction and along the Cu—pyO direction, implying that the involved orbital is also $d_{x^2-y^2}$. Since the Cu—pyO are not bridging it is likely that the exchange is mediated through the chains.

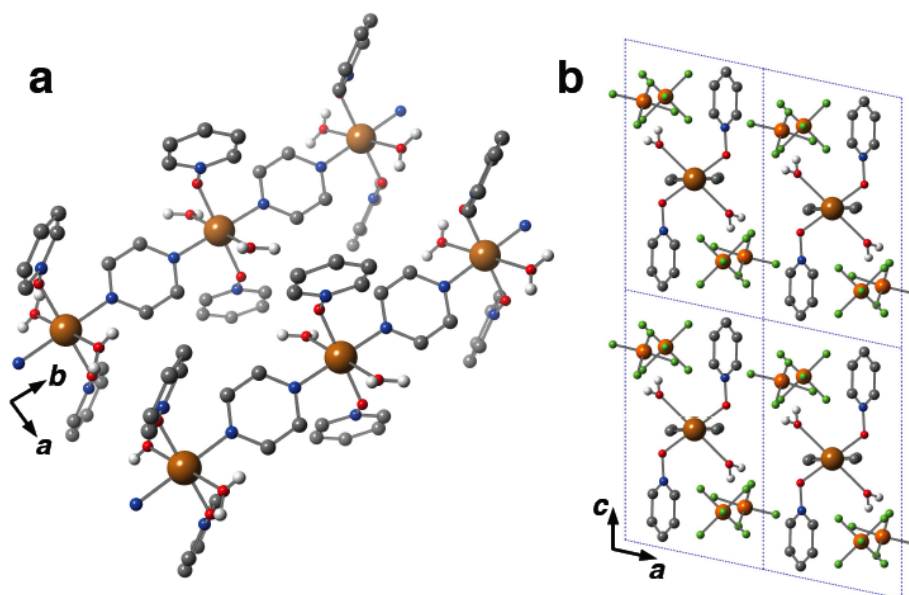


Figure 5.10: Crystal structure of the chain-like material $[\text{Cu}(\text{pyz})(\text{pyO})_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$. Compositionally this material is related to the planar material in Figure 5.9, but with one half of the pyrazine bridging ligands replaced by non-bridging water molecules. (a) 1D Cu-pyrazine chains in the ab -plane. (b) View along the chains showing the arrangement of the pyridine N-oxide and H_2O ligands as well as the non-coordinated PF_6 counterions. Cu = brown, C = grey, N = blue, O = red, P = orange, F = green, H = white. Hydrogen ions other than those in the water molecules have been omitted for clarity.

5.5 Tuning the dimensionality of coordination polymers

Previous heat capacity measurements have not been able to identify a magnetic transition [52]. As explained in Section 5.2, μ SR experiments are likely to be more sensitive and so such measurements were made on both samples on the LTF instrument at the Swiss Muon Source. Powder samples were mounted in vacuum grease on a silver plate and inserted into a dilution refrigerator. The asymmetry spectra $A(t)$ of both samples are shown in Figure 5.11. $[\text{Cu}(\text{pyz})_2(\text{pyO})_2](\text{PF}_6)_2$ exhibits oscillations below 1.7 K, which are indicative of long-range order. This sample shows similar results to $[\text{Cu}(\text{pyz})_2(\text{pyO})_2](\text{ClO}_4)_2$ (Section 5.4). However only one frequency is observed and, due to the resolution of the continuous muon source, a fast relaxing component is picked up in addition to the slow one that was also observed in the ClO_4 compound that had been measured at the pulsed muon source.

The asymmetry can be fitted with the following adapted function of Eqn. 5.9:

$$\begin{aligned}
 A(t) = & A_1 \exp(-\lambda_1 t) \cos(2\pi\nu_1 t) \\
 & + A_2 \exp(-\lambda_2 t) \\
 & + A_3 \exp(-\lambda_3 t) \\
 & + A_{bg}.
 \end{aligned} \tag{5.10}$$

The evolution of the frequency was extracted using this function and then fitted using eqn 3.3, giving $T_N=1.71(2)$ and $\beta=0.22(2)$.

The data for $[\text{Cu}(\text{pyz})(\text{pyO})_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$ do not exhibit any resolvable frequencies, but only a monotonic relaxation of the muon spin polarisation at all measured temperatures on top of a non-relaxing background, described by the

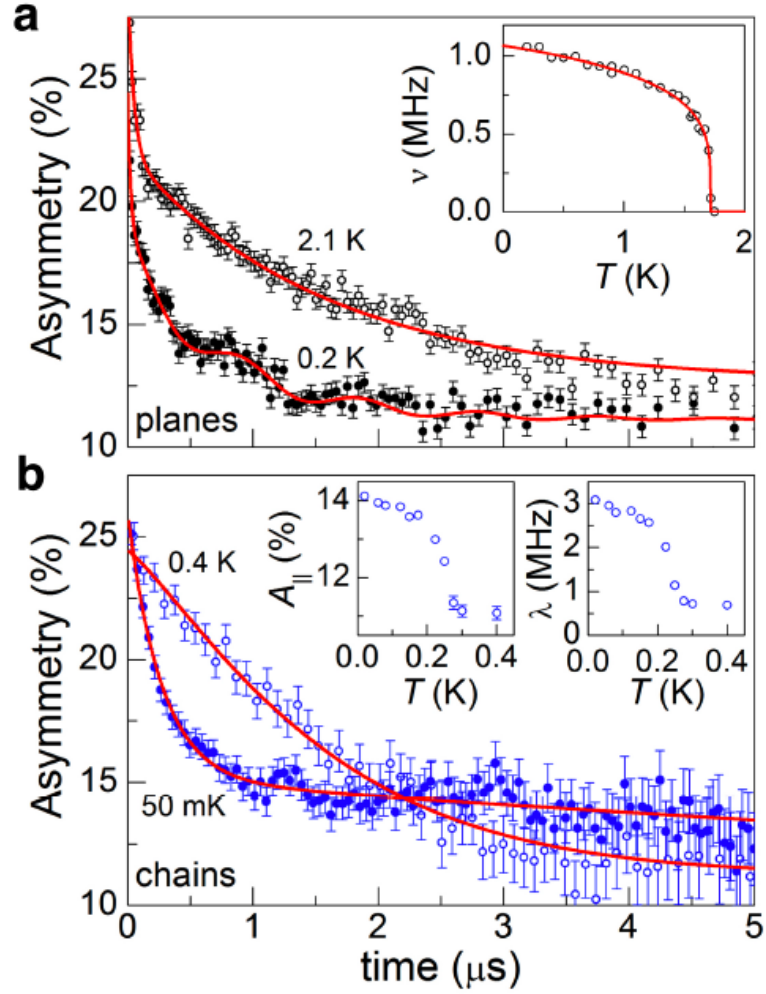


Figure 5.11: Example muon-spin relaxation (μ SR) spectra measured on planar $[\text{Cu}(\text{pyz})_2(\text{pyO})_2](\text{PF}_6)_2$ (a). Data at different temperatures are offset for clarity. Inset: Evolution of the precession frequency with temperature. Long-range magnetic order is observed below 1.71 K. μ SR spectra measured on chain-like $[\text{Cu}(\text{pyz})(\text{pyO})_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$ (b). Inset: The evolution of the amplitude $A_{\parallel}$ (left) and relaxation rate λ (right) with temperature indicates the onset of long-range magnetic order below about 0.27 K.

5.5 Tuning the dimensionality of coordination polymers

following expression:

$$A(t) = A_0 \exp(-\lambda t) + A_{||}. \quad (5.11)$$

Although no frequencies are observed a transition to magnetic order can still be identified. Both $A_{||}$ and λ suddenly increase below 0.27 K. This increase can be related to the transition from a system dominated by dynamic fluctuation to a state of quasi static magnetic order. The fluctuating field above the transition will contribute to the relaxing component and thus $A_{||}$ will be a relatively low component coming from muons stopping outside the sample. Below the transition 1/3 of the muon spins will be parallel to the local field and this additional constant contribution will be included in $A_{||}$, and so a sudden increase in $A_{||}$ is indicative of long-range order.

The increase of the relaxation, results from the fact that λ is expected to vary as a function of $\langle B^2 \rangle$. At the onset of magnetic order the ordered moment and thus $\langle B^2 \rangle$ will increase and this will be reflected in the relaxation. Based on the evolution in temperature of both of these components, the transition temperature was found at $T_N=0.27(1)$ K.

To identify the type of magnetism low-temperature magnetisation measurements up to 60 T were utilised. The data were taken, as described in Chapter 2.3. Figure 5.12 a) shows the results of magnetisation data measured with the field applied parallel to the ab-plane. The shape of both data sets suggest that they are low-dimensional antiferromagnets. The planar material has a similar concave curve as the materials described at in the previous sections, which is typical of a Q2D system. The curvature of the chain-like compound is much more pronounced, which as explained above, is a sign of Q1D order, where for an ideal

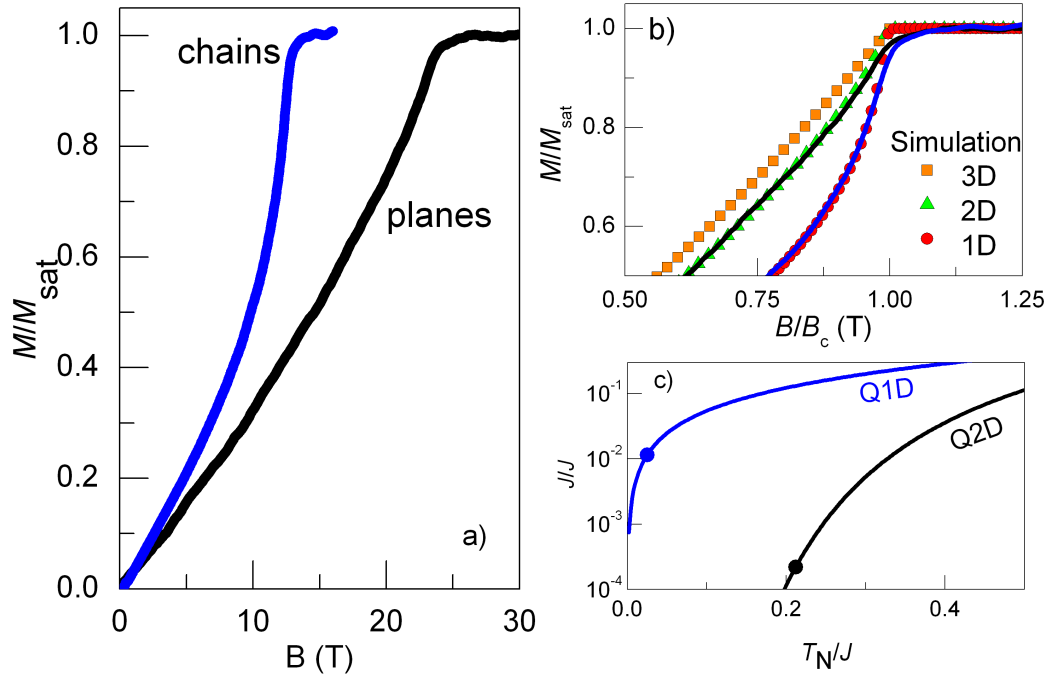


Figure 5.12: (a) Normalized pulsed field magnetisation of the planar $[\text{Cu}(\text{pyz})_2(\text{pyO})_2](\text{PF}_6)_2$ at $T = 1.5$ K, and chain-like $[\text{Cu}(\text{pyz})(\text{pyO})_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$ at $T = 0.5$ K. (b) The results of Quantum Monte Carlo simulations of the low temperature magnetisation for 3D, 2D, and 1D antiferromagnets. The lines are the pulsed field data scaled by the saturation field. (c) The relation between the exchange anisotropy and the ratio of critical temperature and primary exchange energy in Q1D and Q2D antiferromagnets deduced from QMC simulations.

5.5 Tuning the dimensionality of coordination polymers

system, dM/dB is known to diverge at the saturation field [12].

It is of interest to note that the chain-like material exhibits magnetisation data that resemble Q1D order although the data were taken at 0.5 K, which is above the magnetic transition temperature $T_N = 0.27$ K. This is due to the short range correlations that build up above the transition and give rise to the broad maximum in thermodynamic measurements at $T \sim J$. At 0.5 K the correlations have grown to such extent that a non-local probe, such as pulsed-field magnetisation, cannot distinguish between the two states.

In Figure 5.12 the data close to the critical field are shown alongside the quantum Monte-Carlo simulations for 3D, 2D and 1D antiferromagnets. The magnetisation data for the planar sample are in agreement with the 2D $J_{\perp}/J = 0$ model and the data for the chain-like sample agree with the 1D $J_{\perp}/J = 0.02$. A deviation from the model can be observed close to the saturation field due to the fact that the modeling is done for a system at $T = 0$ whereas the data are taken at finite temperatures.

The critical fields B_c can be extracted and are found to be 23.7(8) T for the planar sample and 12.8(4) T for the chain-like sample. We can then use Eqn. 5.2, $g\mu_B B_c = nJ + n_{\perp}J_{\perp}$, with $n = 4$ and $n_{\perp} = 2$ for the 2D case and $n = 2$ and $n_{\perp} = 4$ for the 1D case. So, assuming $J_{\perp} \ll 1$ eqn 5.2 becomes $g\mu_B B_c = nJ$.

By combining this information with the values of g provided by ESR, I estimate the primary exchange couplings to be $J = 8.10(3)$ K for the planar compound and $J = 8.8(2)$ K for the chain-like compound.

Susceptibility was measured to obtain another estimate of the primary exchange coupling, the g-factor and the dimensionality of the systems. Magnetic susceptibility measurements were taken on the PPMS over the whole tempera-

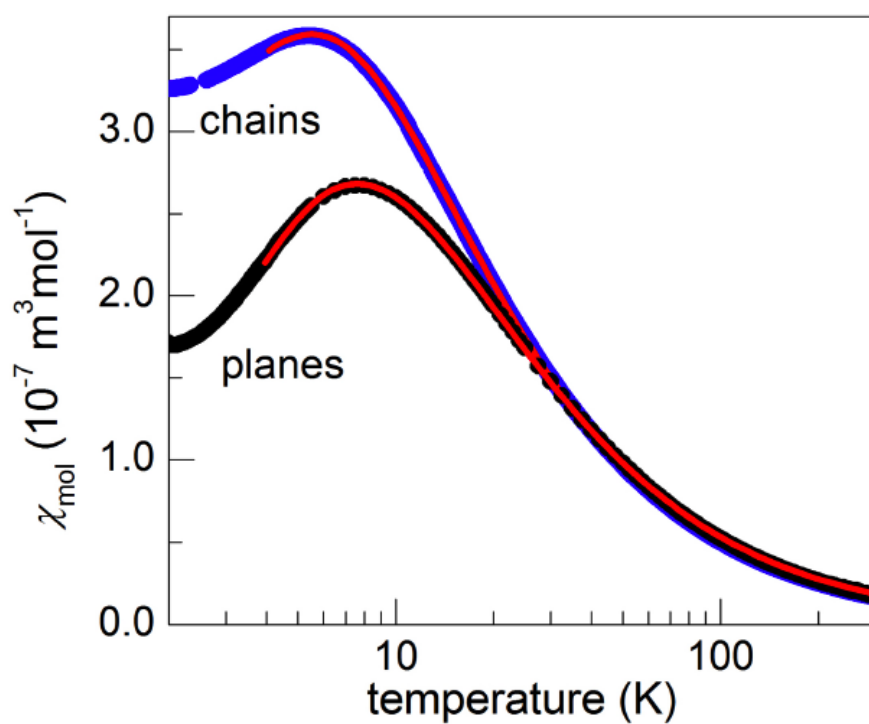


Figure 5.13: Results of temperature-dependent susceptibility measurements. Data points are the powder magnetic susceptibilities for both materials, red lines are fits to the low-dimensional models of Woodward and Johnston.

5.5 Tuning the dimensionality of coordination polymers

n	a_n	b_n
1	-0.053837836	0.44616216
2	0.097401365	0.32048245
3	0.014467437	0.13304199
4	0.0013925193	0.037184126
5	0.00011393434	0.00026467628
6	-	0.00026467628

Table 5.5: Parameters a_n and b_n as listed in Ref [88]. They were determined using a standard nonlinear, leastsquares-fitting algorithm.

ture range at a field of $B = 0.1$ T. Figure 5.13 shows the data for the planar and chain-like systems, which are very different but both exhibit the typical broad hump in $\chi_{mol}(T)$ at $T \sim J$ that is observed in highly anisotropic systems.

Fits from 300 K to temperatures just below the hump to low-dimensional models were in good agreement with the data. For the Q2D case the model according to Woodward *et al.* described in Section 5.4 using Eqn. 5.8 gave a satisfactory fit to the data with $g = 2.21$ and $J = 8.10(1)$. For the chain like compound the model by Johnston *et al.*[46] was used for the fitting, with a similar function:

$$\chi = C/T[1 + \sum_{n=1}^5 a_n(T/J)^n]/(1 + \sum_{n=1}^6 b_n(T/J)^n) \quad (5.12)$$

The parameters a_n and b_n are listed in Table 5.5 and C is defined in Eqn. 5.7. The fit with this expression gives values of $g = 2.11$ and $J = 8.58(1)$ K for the chain-like compound.

I have previously introduced how the size of the transition temperature T_N and the primary exchange interaction J can be related to the anisotropy in low-dimensional systems. Eqn. 5.4, describing this relationship for the 1D and 2D case was developed by Yasuda *et al.*[94] and is plotted in Figure 5.12 (c). The circles

5.5 Tuning the dimensionality of coordination polymers

in this graph represent the results for the samples presented in this section. The exchange anisotropy for the planar Q2D material is $J_{\perp}/J = 1 \times 10^{-4}$ and for the chain-like Q2D material $J_{\perp}/J = 1 \times 10^{-2}$. These values agree with the estimates made from the simulations of magnetisation shown in Figure 5.12 (b).

	Q2D	Q1D	technique
T_N (K)	1.71 ± 0.02	0.27 ± 0.01	μ^+ SR
B_c (T)	23.7 ± 0.8	12.8 ± 0.4	$M(B)$
J (K)	8.1 ± 0.3	8.8 ± 0.2	$M(B)$
J (K)	8.10 ± 0.01	8.58 ± 0.01	$\chi(T)$
g_{xy}	2.04 ± 0.01	2.06 ± 0.01	EPR
g_z	2.26 ± 0.01	2.32 ± 0.01	EPR
$J_{\perp}/J$	1×10^{-4}	1×10^{-2}	QMC

Figure 5.14: Magnetic properties of $[\text{Cu}(\text{pyz})_2(\text{pyO})_2](\text{PF}_6)_2$ (Q2D) and $[\text{Cu}(\text{pyz})(\text{pyO})_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$ (Q1D) determined using μ SR (muon-spin rotation), $M(B)$ (pulsed-field magnetisation), $\chi(T)$ (low-field magnetic susceptibility), ESR (electron-spin resonance), and QMC (quantum Monte Carlo calculations). For the Q2D (Q1D) material the g-factors g_{xy} and g_z are measured with the magnetic field within the planes (chains), and parallel to the c-axis (perpendicular to the Cu-pyO bond), respectively.

These results give a complete picture of the two closely related magnetic systems $[\text{Cu}(\text{pyz})_2(\text{pyO})_2](\text{PF}_6)_2$ and $[\text{Cu}(\text{pyz})(\text{pyO})_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$. The chains that form in the Q1D systems are very similar to the Cu-pyz chains that form the planes in the a and b directions in the Q2D system. Although they have different structures and compositions their primary nearest neighbour exchange is almost identical. The planar material has a critical field that is twice as large as the critical field of the chain-like material, resulting from the fact that there are twice as many nearest neighbours in the Q2D system.

In addition the Q2D system is very strongly anisotropic, comparable to the most 2D materials identified (23), some of which have been described above (See Table 5.1 for a comparison). The anisotropy is most probably a result of the

5.6 Halogen-halogen bonds in Spin- $\frac{1}{2}$ Heisenberg antiferromagnets

staggering and the large separation between the layers in the system.

In comparison the Q1D system is less anisotropic, although its T_N/J is smaller, since it exhibits no staggering of the chains and has a shorter distance between the chains, approximately half the interlayer separation in the Q2D material.

In conclusion I show how a reduction of dimensionality can be achieved without significantly perturbing the magnitude of the primary interaction strengths. These results combined with the possibility to change the interaction strength whilst retaining the dimensionality, as presented in the previous sections, demonstrate how it is possible to take deliberate control over the magnetic properties of polymeric systems.

5.6 Halogen-halogen bonds in Spin- $\frac{1}{2}$ Heisenberg antiferromagnets

I will now introduce a series of systems, with closely related properties. Just like the other materials presented in this chapter $\text{CuX}_2(\text{pyz})$ and $\text{CuX}_2(\text{pyO})(\text{H}_2\text{O})_2$, where $X = \text{Cl}^{4+}$ and Br^{5+} , are self-organising systems. However these compounds have the distinction that they contain halogens (X) which interact with the Cu ions to form $\text{Cu-X} \cdots \text{X-Cu}$ bonds.

The importance of intermolecular halogen contacts in molecular systems has been increasingly studied in recent years [62]. These intermolecular interactions are important for the design of functional materials and play critical roles in conducting and magnetic systems. A large antiferromagnetic exchange of 234 K has been observed in $\text{Cu}(2,5\text{-me}_2\text{pyz})\text{Br}_2$ [15], which leads to new possibilities to use the halogen $\cdots$ superexchange pathway as a tool in generating new magnetic

5.6 Halogen-halogen bonds in Spin- $\frac{1}{2}$ Heisenberg antiferromagnets

systems.

The crystal structure of both systems with $X=\text{Br}$ are shown in Figure 5.15. The Cl-analogues are isostructural. $\text{CuX}_2(\text{pyz})$ consists of $\text{Cu}-X \cdots X-\text{Cu}$ bi-bridged chains that are linked through bridging pyrazine molecules resulting in a Q2D rectangular lattice with two possible exchange pathways J_1 and J_2 .

The crystal structure of $\text{CuBr}_2(\text{pyO})(\text{H}_2\text{O})_2$ is very similar. It is characterised by chains of $\text{Cu}-X \cdots X-\text{Cu}$. However the pyrazine ligands have been substituted by pyO so that weak $\text{OH} \cdots \text{O}$ hydrogen bonds form between the water molecules and pyO oxygen.

In contrast to the other materials described in this chapter the Cu^{2+} ion displays a Jahn-Teller elongation with the axial bonds towards the oxygen atoms of the pyzO [73] reveal that two of the lobes of the magnetic $d_{x^2-y^2}$ orbital of the Cu^{2+} ions in $\text{CuX}_2(\text{pyO})(\text{H}_2\text{O})_2$ are pointing along the direction of the $\text{Cu}-X_2-\text{Cu}$ bonds, so that magnetic Q1D chains form through $\text{Cu}-X \cdots X-\text{Cu}$ paths in $\text{CuX}_2(\text{pyO})(\text{H}_2\text{O})_2$. The other two lobes point in the direction of the $\text{Cu}-\text{O}$ bonds of the H_2O molecules. The bridging pyO-ligands serve as links between the chains.

The magnetic exchange via $\text{Cu}-X \cdots X-\text{Cu}$ is thought to occur as a result of spin delocalization from the Cu ions to the halogen atoms. This was shown to be true for materials based on Br [24]. Since the magnetism is mediated through the halogen contacts in both of the systems presented here, the substitution of Cl for Br is expected to have a large effect on the exchange interactions.

Previous μSR studies revealed that the $\text{CuX}_2(\text{pyz})$ compounds go through a transition to antiferromagnetic order at 3.2 K (Cl) and 3.6 K (Br) [56]. Keith *et al.* [47] and Butcher *et al.* [14] have fitted susceptibility data with the rectangular

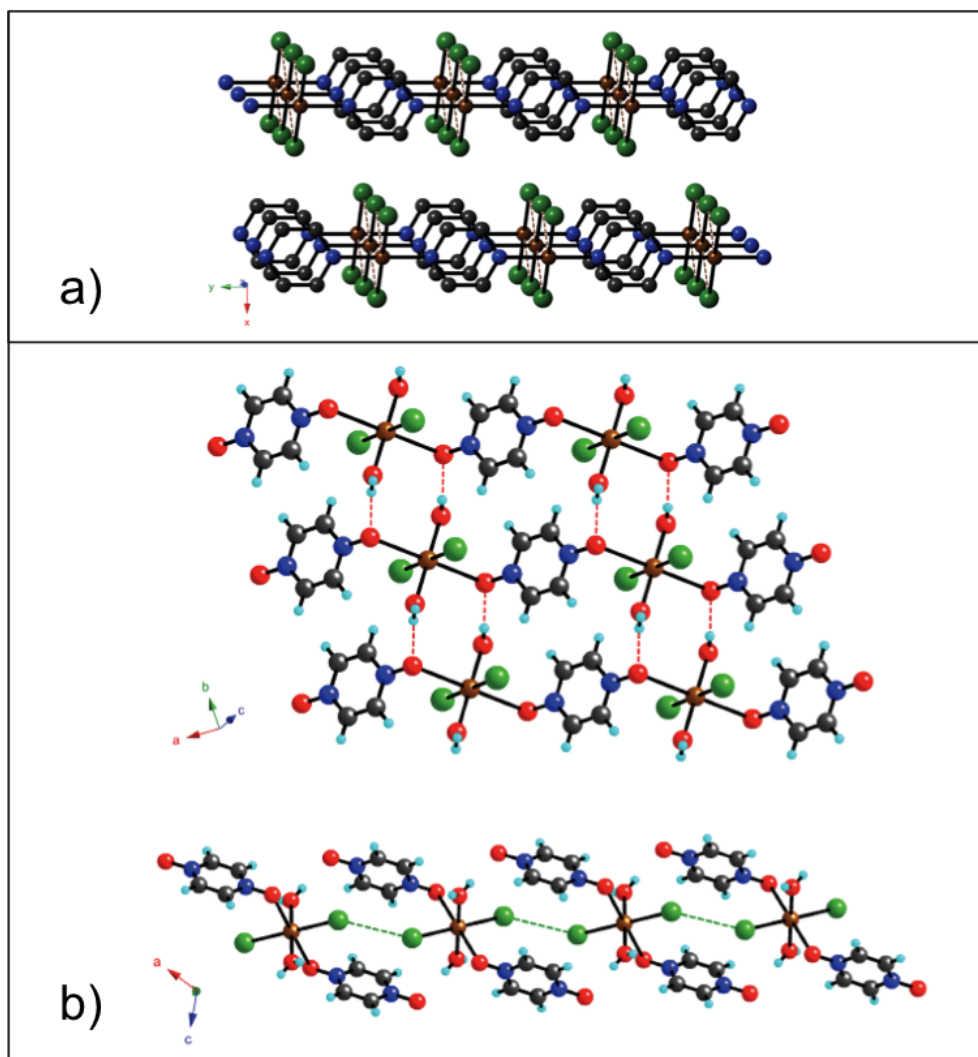


Figure 5.15: Crystal structure of (a) $\text{CuBr}_2(\text{pyz})$ and (b) $\text{CuBr}_2(\text{pyO})(\text{H}_2\text{O})_2$. In (a) the dashed lines indicate Cu-Br interactions. The dashed red lines in diagram b) illustrate how the hydrogen bonds link the Cu-pyz-Cu chains into layers. Halogen contacts along the c -axis link these planes into a 3D structure. Cu = brown, N = blue, C = black, Br = green, O = red, H = light-blue. Hydrogen bonds are omitted in (a). [73]

5.6 Halogen-halogen bonds in Spin- $\frac{1}{2}$ Heisenberg antiferromagnets

lattice antiferromagnetic Heisenberg model to determine the spin exchanges $J_1 = 28.4(5)$ K and $J_2 = 7.3(5)$ K for $X = \text{Cl}$, and $J_1 = -46(1)$ K and $J_2 = 9(1)$ K for $X = \text{Br}$.

Initial insights into the magnetism exhibited by these compounds were gained by measuring the magnetic susceptibility in the Quantum Design SQUID. Data from 2 K to 300 K were taken in a field of 0.1 T for the two $\text{CuX}_2(\text{pyO})(\text{H}_2\text{O})_2$ samples. High temperature susceptibility for $\text{CuBr}_2(\text{pyz})$ and $\text{CuCl}_2(\text{pyz})$ was not measured in this case since its susceptibility is known [14, 47]. The g -factor was estimated by fitting the reciprocal magnetic susceptibility, $\frac{1}{\chi}(\text{T})$, to the Curie-Weiss law Eqn. 5.6. This led to the following parameters: $g = 2.135(1)$ and $g = 2.101(2)$ for $\text{CuCl}_2(\text{pyO})(\text{H}_2\text{O})_2$ and $\text{CuBr}_2(\text{pyO})(\text{H}_2\text{O})_2$ respectively.

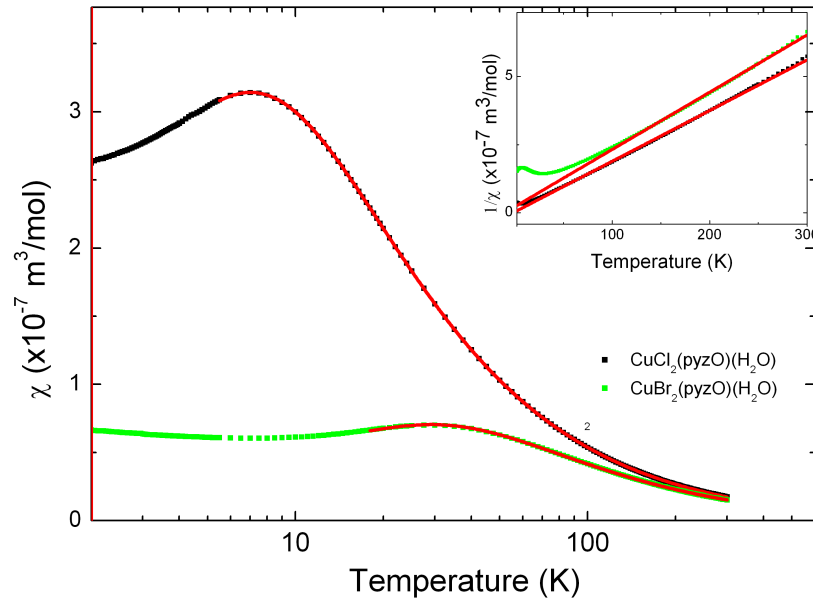


Figure 5.16: Susceptibility data for and $\text{CuX}_2(\text{pyO})(\text{H}_2\text{O})_2$ ($X=\text{Cl}, \text{Br}$). The inset presents reciprocal magnetic susceptibility and fits to the Curie-Weiss function (Eqn. 5.6)

The magnetic susceptibility of the two samples is shown in Figure 5.16 (Inset

5.6 Halogen-halogen bonds in Spin- $\frac{1}{2}$ Heisenberg antiferromagnets

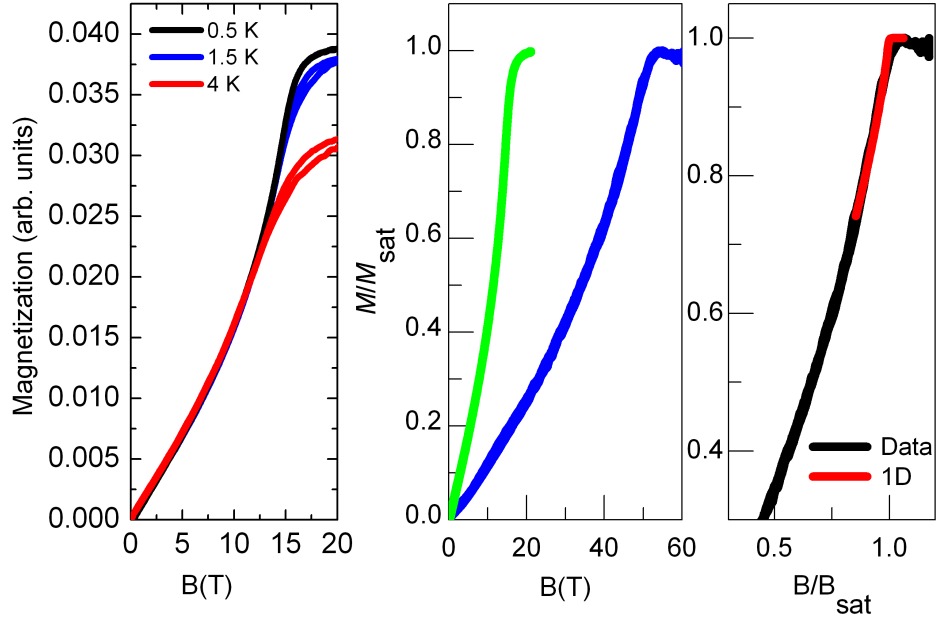


Figure 5.17: (a) Magnetisation data for $\text{CuCl}_2(\text{pyO})(\text{H}_2\text{O})_2$ at three different temperatures. (b) Normalised magnetisation against field for both $\text{CuCl}_2(\text{pyO})(\text{H}_2\text{O})_2$ and $\text{CuCl}_2(\text{pyz})$. (c) Normalised magnetisation against normalised field and quantum Monte Carlo simulations for Q1D model.

$\frac{1}{\chi}$ vs T). The best fit to the data of $\text{CuX}_2(\text{pyO})(\text{H}_2\text{O})_2$ ($X=\text{Cl}, \text{Br}$) was achieved using the 1D Heisenberg antiferromagnetic model for $S=\frac{1}{2}$ with eqn 5.12 and the extracted values for the primary exchange interaction were found to be $J = 11.5(3)$ and $J=46.9(4)$ respectively. The use of the 1D chain model is justified by the observation that the J values estimated solely from the form of the susceptibility fits are very close to those estimated from the pulsed-field magnetisation as described below.

The magnetisation was measured as a function of magnetic field up to 60 T. Figure 5.17 shows the data at three different temperatures for $\text{CuCl}_2(\text{pyO})(\text{H}_2\text{O})_2$, alongside the data for $\text{CuCl}_2(\text{pyz})$ (Figure 5.17 b)). The strong upward curvature

5.6 Halogen-halogen bonds in Spin- $\frac{1}{2}$ Heisenberg antiferromagnets

at lower fields, and approach to saturation at almost 90° in both systems is indicative of one-dimensional magnetism. In the case of $\text{CuCl}_2(\text{pyO})(\text{H}_2\text{O})_2$ and $\text{CuCl}_2(\text{pyz})$, the magnetisation saturates at a field of 16.1(3) T and 52.0(5) T. As described above in a Heisenberg chain, at a critical field Eqn. 5.2 holds: $g\mu_B B_c = 2J + 4J_\perp$. We assume that $J_\perp \ll J$ and, in the case of $\text{CuCl}_2(\text{pyO})(\text{H}_2\text{O})_2$ using the measured value of B_c , we obtain $J = 11.5(2)$ K, similar to the estimate derived from susceptibility.

$\text{CuCl}_2(\text{pyz})$ has antiferromagnetic rectangular lattice with two exchange pathways that are orthogonal to each other, the primary exchange J_1 and a second exchange $J_2 = mJ_1$. The Q1D model and the Q2D model have an AF square magnetic lattice corresponding to $m = 0$ and $m = 1$ respectively. Eqn. 5.2 in such a system becomes $g\mu_B B_c = 2(J_1 + J_2) + 2J_\perp$ so that the saturation field yields $(J_1 + J_2) = 35.5(6)$ K. Plugging in the previously reported values of $J = 28.4(5)$ and $J_2 = 7.3(5)$ results in $J_1 + J_2 = 35.7(5)$, in agreement with the value obtained from the critical field.

$\text{CuBr}_2(\text{pyO})(\text{H}_2\text{O})_2$ and $\text{CuBr}_2(\text{pyz})$ have stronger exchange couplings and therefore their critical saturation field is inaccessible with the 60 T magnet. We therefore used the 100 T magnet at the NHMFL in order to achieve saturation. Figure 5.18 shows the data obtained $\text{CuBr}_2(\text{pyO})(\text{H}_2\text{O})_2$ and $\text{CuBr}_2(\text{pyz})$ up to 85 T. The data was taken in the multi-shot 100 T magnet at the NHMFL by John Singleton. To reach such high fields the magnet is built out of generator-driven outsert and capacitor driven inserts. Due to this set-up the data at fields in excess of 60 T from the 100 T magnet are integrated and calibrated against the lower field data from the traditional 60 T magnets that we had measured previously. Therefore the magnetisation shown in Figure 5.18 is an amalgamation of the data

5.6 Halogen-halogen bonds in Spin- $\frac{1}{2}$ Heisenberg antiferromagnets

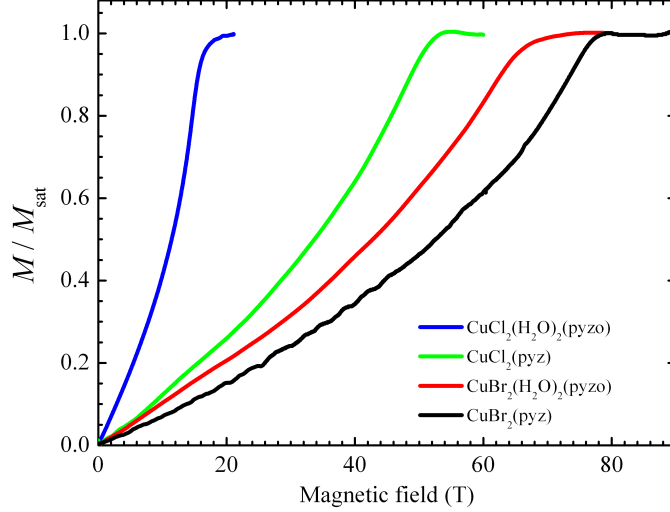


Figure 5.18: Magnetisation data for $\text{CuCl}_2(\text{pyz})$ and $\text{CuCl}_2(\text{pyO})(\text{H}_2\text{O})_2$ and $\text{CuBr}_2(\text{pyO})(\text{H}_2\text{O})_2$ and $\text{CuBr}_2(\text{pyz})$. The two Br compounds have higher critical fields than the Cl compounds and so the data was taken in the multi-shot 100 T magnet at the NHMFL.

from both experiments.

$\text{CuBr}_2(\text{pyO})(\text{H}_2\text{O})_2$ has a critical field of $B_c = 66.7(5)$ T, leading to an exchange interaction of $J=45.3(6)$ K, which agrees with the susceptibility data. In an analogous fashion $\text{CuBr}_2(\text{pyz})$ saturates at a higher magnetic field of $77.2(4)$ T, leading to exchange energies of $J_1 + J_2 = 56.3(5)$ K, which agrees with the exchange interactions of $J_1 = 49(1)$ and $J_2 = 9(1)$ extracted from susceptibility data. The exchange energies in the Br systems are a lot higher than in the Cl compounds and since the crystal structures are basically the same, it is reasonable to assume that $J_\perp$ will not have significantly altered and the Br materials should be more anisotropic than the Cl analogues.

No magnetic transitions are apparent in the susceptibility data and so muon spin rotation was used to investigate the materials. Zero field μSR was measured in ARGUS at the ISIS facility. The asymmetry spectra for $\text{CuCl}_2(\text{pyO})(\text{H}_2\text{O})_2$,

5.6 Halogen-halogen bonds in Spin- $\frac{1}{2}$ Heisenberg antiferromagnets

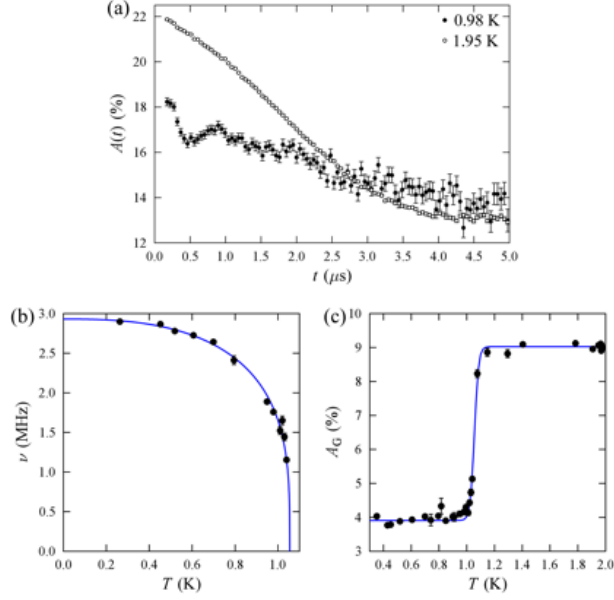


Figure 5.19: (a) Muon spin rotation asymmetry spectra for $\text{CuCl}_2(\text{pyO})(\text{H}_2\text{O})_2$ at 0.98 K and 1.95 K. (b) Evolution of the precession frequency with temperature. (c) Steplike transition in the Gaussian relaxing term as a function of temperature [73].

are shown in Figure 5.19. Above 1.1 K the asymmetry is purely relaxing and is described by a Gaussian relaxation function. Below 1.1 K oscillations appear in the signal, which are indicative of long-range magnetic order.

The muon signal can be described by a frequency term, a Gaussian relaxing term, characteristic of muons which experience a random distribution of local magnetic fields and a non-relaxing term that allows for background contributions:

$$\begin{aligned}
 A(t) = & A_1 \exp(-\lambda_1 t) \cos(2\pi\nu_1 t) \\
 & + A_2 \exp(-\lambda_2 t)^2 \\
 & + A_{bg}.
 \end{aligned}$$

The magnetic ordering temperature is most clearly extracted from the discontinuous change in the amplitude of the Gaussian component of the signal seen at T_N .

5.6 Halogen-halogen bonds in Spin- $\frac{1}{2}$ Heisenberg antiferromagnets

This is shown in Figure 5.19(c) where we see a step-like transition at $T_N = 1.06(1)$ K. In addition, as previously discussed, the precession frequency is an effective magnetic order parameter for this system, whose behavior may be parameterised through fitting to the phenomenological function Eqn. 3.3 allowing us to extract parameters $T_N = 1.0(1)$ K and $\beta = 0.28(1)$ describing the magnetic transition.

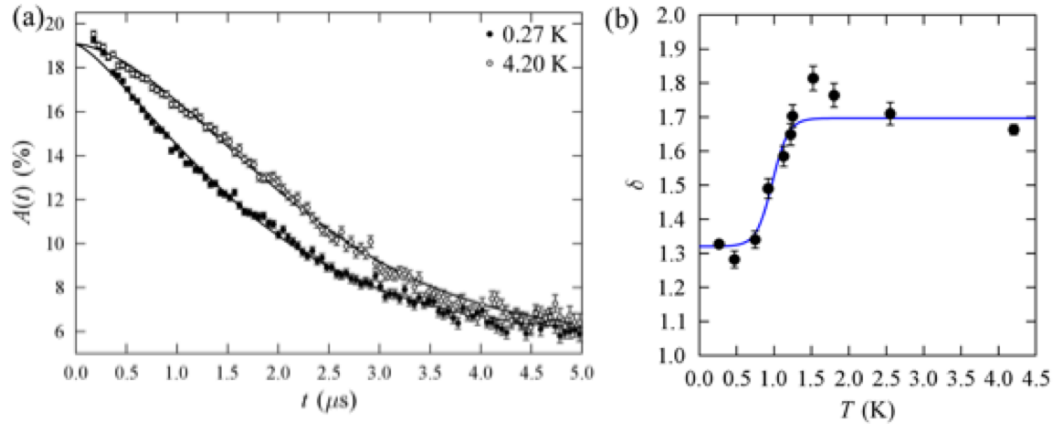


Figure 5.20: Muon spin rotation data for $\text{CuBr}_2(\text{pyO})(\text{H}_2\text{O})_2$. (a) No oscillations are observed in the signal but the asymmetry spectra become more exponential at higher temperatures. (b) The crossover apparent in δ could be a sign of a magnetic transition or the approach to magnetic order at lower temperatures. [73]

The μSR spectra for $\text{CuBr}_2(\text{pyO})(\text{H}_2\text{O})_2$ are shown in Figure 5.20. Again, the high temperature ($T \gg 1$ K) spectra have a Gaussian form as in the case of $\text{CuCl}_2(\text{pyO})(\text{H}_2\text{O})_2$. The spectra change their form below $T = 1$ K and become more exponential in character. Exponential relaxation is often the result of dynamic fluctuations of the local magnetic field at the muon site. The fact that there is no change in the apparent baseline of the relaxation strongly suggests that this is not a crossover to a static magnetic state. The crossover probably results from the fluctuations not being resolved at higher temperatures due to the limitations of the ISIS muon beam. The fluctuations then slow down until

5.6 Halogen-halogen bonds in Spin- $\frac{1}{2}$ Heisenberg antiferromagnets

they reach a regime where they are within the muon time window.

In order to parameterise the crossover, the spectra were fitted to a stretched exponential function :

$$A(t) = A_1 \exp(-\lambda_2 t)^\delta + A_{bg}, \quad (5.13)$$

where the final term accounts for those non-relaxing muons which stop in the sample mount or cryostat tails. The evolution of $\delta(T)$ is shown in Figure 5.20 where we see that quite a sharp crossover takes place at 0.98 K.

It is not clear whether this observed crossover is a sign of magnetic ordering which takes place around 1 K or due to the fact that such an ordered state occurs at a lower temperature, which could not be measured as the cryostat was limited to temperatures $T \geq 0.26$ K. It is puzzling that the low temperature magnetic behavior that we probe with μ SR should be so different for these two materials. The low transition temperatures explain why the critical field transition in these compounds is rounded off, as the magnetisation measurements were taken at temperature above the transition.

Combining the results from μ SR presented here for the $\text{CuX}_2(\text{pyO})(\text{H}_2\text{O})_2$ compounds with the magnetisation and susceptibility data makes it possible to extract exchange anisotropies for these systems. Based on Eqn. 5.3 from Q1D systems $J_\perp/J$ is 0.04(1) for $\text{CuCl}_2(\text{pyO})(\text{H}_2\text{O})_2$. We know that the ordering transition of $\text{CuBr}_2(\text{pyO})(\text{H}_2\text{O})_2$ has to be $T_N \ll 0.98$, which puts a limit on the exchange anisotropy of $J_\perp/J \ll 0.009(1)$.

Both $\text{CuCl}_2(\text{pyz})$ and $\text{CuBr}_2(\text{pyz})$ are based on a rectangular exchange lattice and so Eqn. 5.3 cannot be used to determine the exchange anisotropy in these

5.6 Halogen-halogen bonds in Spin- $\frac{1}{2}$ Heisenberg antiferromagnets

Compound	B_c (T)	g	J (K)	T_N (K)	$J_\perp/J$	J_2
$\text{CuCl}_2(\text{pyO})(\text{H}_2\text{O})_2$	16.1(3)	2.135(1)	11.5(2)	1.06	0.04(1)	-
$\text{CuCl}_2(\text{pyz})$	52.0(5)	2.21(1)	28.4(3)	3.2	-	7.3(5)
$\text{CuBr}_2(\text{pyO})(\text{H}_2\text{O})_2$	66.7(5)	2.101(2)	46.2(2)	≤ 0.98	$\leq 0.009(1)$	-
$\text{CuBr}_2(\text{pyz})$	77.2(4)	2.21(2)	46(1)	3.6	-	9(1)

Table 5.6: Main properties of the compounds discussed in the text. The critical fields B_c were extracted from pulsed field magnetisation, g -factors from Curie-Weiss fits to the inverse susceptibility, the primary exchange interaction J was calculated using Eqn. 5.2, transition temperatures were determined using μSR , and the exchange anisotropy was estimated with Eqn. 5.3. J_1 is the secondary exchange interaction in the Q2D rectangular lattice and was determined by Ref [47] and Ref [14]

systems.

In summary, I have presented the magnetism of the two systems $\text{CuX}_2(\text{pyO})(\text{H}_2\text{O})_2$ and $\text{CuX}_2(\text{pyz})$ ($X=\text{Cl}, \text{Br}$). The presence of chains in $\text{CuX}_2(\text{pyO})(\text{H}_2\text{O})_2$ leads to Q1D magnetism. The same chains are present in $\text{CuX}_2(\text{pyz})$ ($X=\text{Cl}, \text{Br}$) however an additional exchange pathway through the pyrazine ligands leads to the formation of a rectangular spin lattice in $\text{CuX}_2(\text{pyz})$ in contrast to the more one-dimensional $\text{CuX}_2(\text{pyO})(\text{H}_2\text{O})_2$. The substitution of Br for Cl has a similar effect in both systems. The exchange interactions are substantially higher in the Br-compounds. The strength of the exchange interactions is a function of the $X-X$ distance, $\text{Cu}-X-X$ angle, and the electronic nature of the halide ion, which explains why in this system the substitution of Cl by Br leads to such a big change in the exchange interactions.

Here we have confirmed that the dominant spin exchange involves superexchange through the halogen $\cdots$ halogen contacts. These can effectively be used to design new materials with significant super-superexchange.

5.7 Q1D magnetism in Cu(2.5-me₂pyz) (CH₃SO₃) (NO₃) (H₂O) and [Cu(2.3-me₂pyz) (CH₃SO₃) (H₂O)₂](CH₃SO₃)

	[Cu(2,3-me ₂ pyz)(CH ₃ SO ₃)(H ₂ O) ₂](CH ₃ SO ₃)	Cu(2,5-me ₂ pyz)(CH ₃ SO ₃)(NO ₃)(H ₂ O)
Cu-N (Å)	2.037, 2.038	2.041, 2.049
Cu-O _{ax} (Å)	2.211	2.263
Cu-O(Å)	1.956	1.951
Cu-O(Å)	1.941	1.949
CuCu(Å)	6.828	6.859
Cu-NN(°)	176.5, 176.9	176.04, 175.2
N-Cu-N(°)	174.00	164.53
O-Cu-O (°)	163.2	177.03
<i>J</i> (K)	7.8	6.4
<i>B_c</i> (T)	11.7	9.56

Table 5.7: Inter-atomic distances and angles, alongside the critical field and primary exchange interaction for **1** and **2**.

5.7 Q1D magnetism in Cu(2.5-me₂pyz) (CH₃SO₃) (NO₃) (H₂O) and [Cu(2.3-me₂pyz) (CH₃SO₃) (H₂O)₂](CH₃SO₃)

In this section I present two very similar Q1D compounds, which are both chain-like systems that have five-coordinate Cu²⁺ centres. In spite of their similarities they exhibit a small but significant difference in their primary exchange energies.

Figure 5.21 shows the crystal structures of [Cu(2,3-me₂pyz)(CH₃SO₃)(H₂O)₂](CH₃SO₃) **1** and Cu(2,5-me₂pyz)(CH₃SO₃)(NO₃)(H₂O) **2**. Both systems form chains of Cu²⁺ ions bridged by pyrazine chains to which two methyl (CH₃) groups are linked to either the second and third or the second and fifth carbon atom respectively.

There are non-bridging ligands in both samples. In **1**, one non-bridging ligand is CH₃SO₃ and two are H₂O, in both one oxygen coordinates directly to the copper. In addition another CH₃SO₃ acts as non-coordinated molecule. In **2**

5.7 Q1D magnetism in $\text{Cu}(\text{2.5-me}_2\text{pyz})(\text{CH}_3\text{SO}_3)(\text{NO}_3)(\text{H}_2\text{O})$ and
 $[\text{Cu}(\text{2.3-me}_2\text{pyz})(\text{CH}_3\text{SO}_3)(\text{H}_2\text{O})_2](\text{CH}_3\text{SO}_3)$

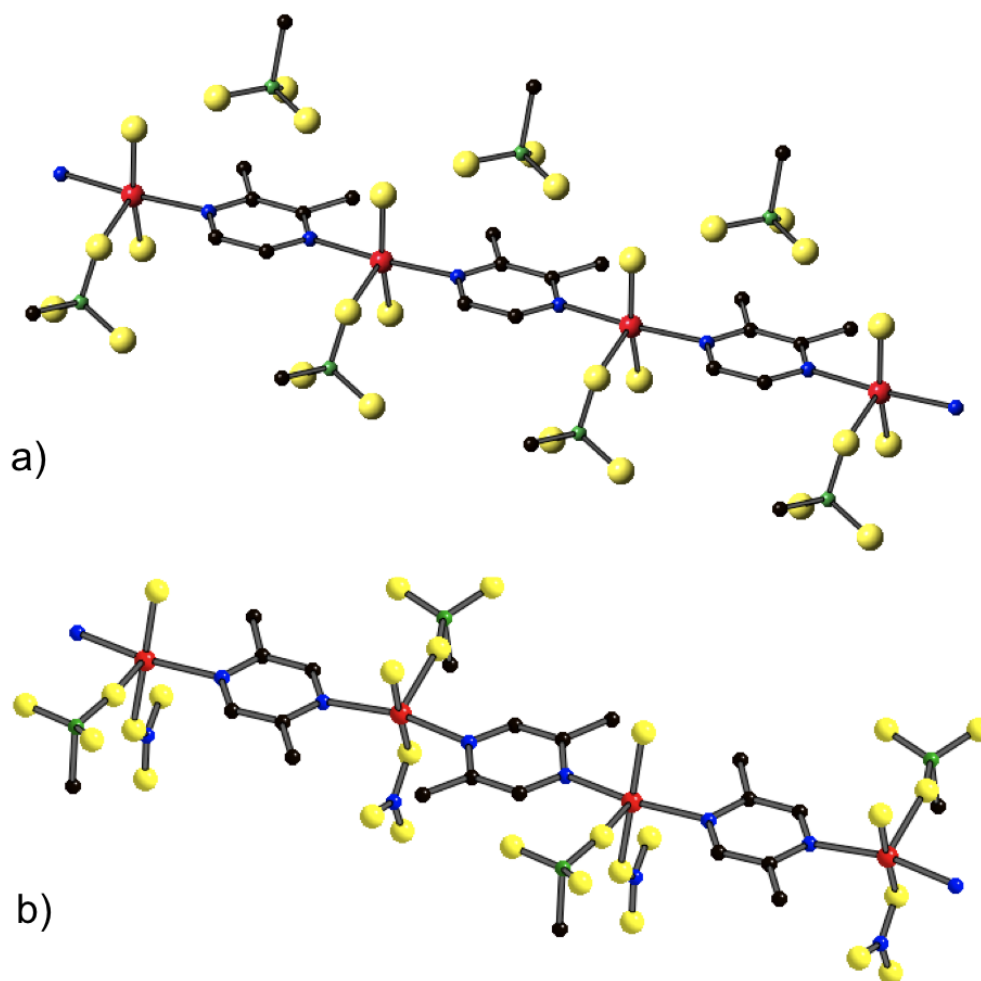


Figure 5.21: View of the Cu-pyz-Cu chains formed in a) **1** and b) **2**. Cu = red, N = blue, C = black, S = green, O = yellow. The hydrogens are omitted since they do not play a role in the magnetism.

5.7 Q1D magnetism in $\text{Cu}(\text{2.5-me}_2\text{pyz})(\text{CH}_3\text{SO}_3)(\text{NO}_3)(\text{H}_2\text{O})$ and $[\text{Cu}(\text{2.3-me}_2\text{pyz})(\text{CH}_3\text{SO}_3)(\text{H}_2\text{O})_2](\text{CH}_3\text{SO}_3)$

there is only one H_2O non-bridging ligand, another non-bridging ligand CH_3SO_3 as before, and an additional NO_3 that also forms a non bridging-ligand. In both compounds the Cu-ions are five-coordinate, with the remaining bonds are made up by two and one H_2O molecules respectively for **1** and **2**. Various structural parameters are tabulated in Table 5.7.

A first insight into the magnetism of these materials was obtained by measuring the magnetic susceptibility in the Quantum Design SQUID. Measurements were taken over the whole range of temperatures for for both samples.

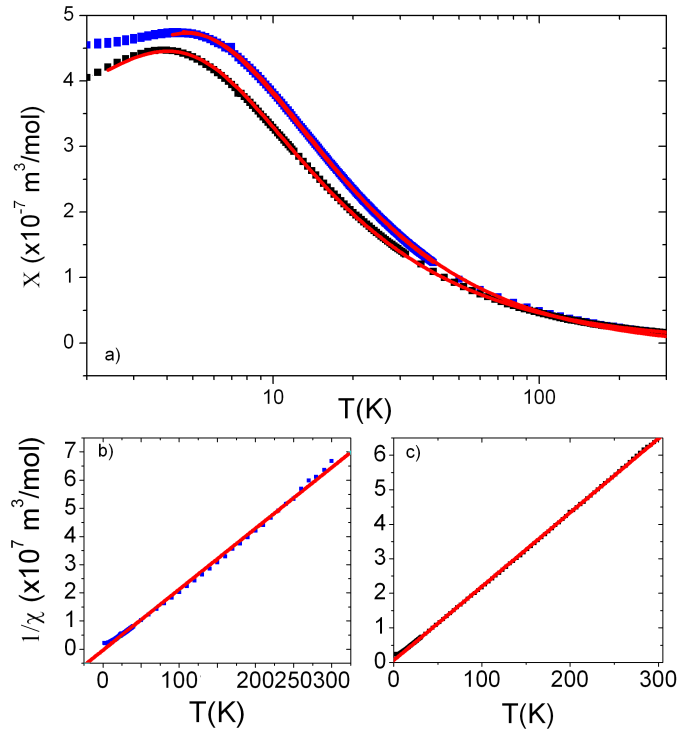


Figure 5.22: (a) Susceptibility of **1** (blue) and **2** (black). (b) and (c) show the inverse susceptibility for **1** and **2** respectively. The data (b) and (c) were fitted with the Curie-Weiss function and (a) with the Q1D Heisenberg model. The fits are shown in red.

The susceptibility data as a function of temperature are plotted in Figure 5.22a). They exhibit the broad hump seen in all the samples presented in this chapter.

5.7 Q1D magnetism in Cu(2.5-me₂pyz) (CH₃SO₃) (NO₃) (H₂O) and [Cu(2.3-me₂pyz) (CH₃SO₃) (H₂O)₂](CH₃SO₃)

The g-factors for both samples were evaluated by fitting the high-temperature inverse susceptibility with the Curie-Weiss function Eqn 5.6, resulting in $g = 2.2(1)$ for **1** and $g = 1.99(1)$ for **2**. The value for **1** is not as well defined due to the limited temperature range in this sample, resulting in the deviation from the linearity of $\frac{1}{\chi}$ having a stronger effect on the fitting. The values still agree with what would be expected for such a system although g for **2** is relatively low.

The susceptibility as a function of temperature was fitted with the Johnston model for Q1D Heisenberg spin- $\frac{1}{2}$ antiferromagnets (Equ. 5.12). The fits are in good agreement with the data down to temperatures just below the hump, with $g = 2.2(2)$ and $J = 7.86(2)$ for **1** and $g=1.9(1)$; $J=6.30(2)$ for **2**.

Magnetisation experiments in pulsed fields were performed to get another estimate of the dimensionality and exchange interactions in the two compounds. The data was taken in fields up to 60 T at the NHMFL. The results of data measured at 1.5 K are shown in Figure 5.23.

Figure 5.23 a) shows M/M_{sat} against reduced field B/B_c of both data sets. It is clear that both data sets exhibit a very similar curvature. Quantum Monte Carlo simulations plotted alongside the data in the Figure show that the Q1D model describes the data best.

The reduced magnetisation is plotted as a function of fields in Figure 5.23 b). The critical fields of the two compounds are close but clearly different, with $B_c = 11.4(3)$ T for **1** and $B_c = 9.5(3)$ T for **2**. Using these values in combination with the g -values obtained in the Curie-Weiss fits, in Eqn 5.2 results in a primary exchange value of $J = 7.9(2)$ T and $J = 6.2(2)$ T for **1** and **2** respectively. These values agree with the exchange magnitudes extracted for these compounds through the fits of magnetic susceptibility to the Q1D model.

5.7 Q1D magnetism in Cu(2.5-me₂pyz) (CH₃SO₃) (NO₃) (H₂O) and [Cu(2.3-me₂pyz) (CH₃SO₃) (H₂O)₂](CH₃SO₃)

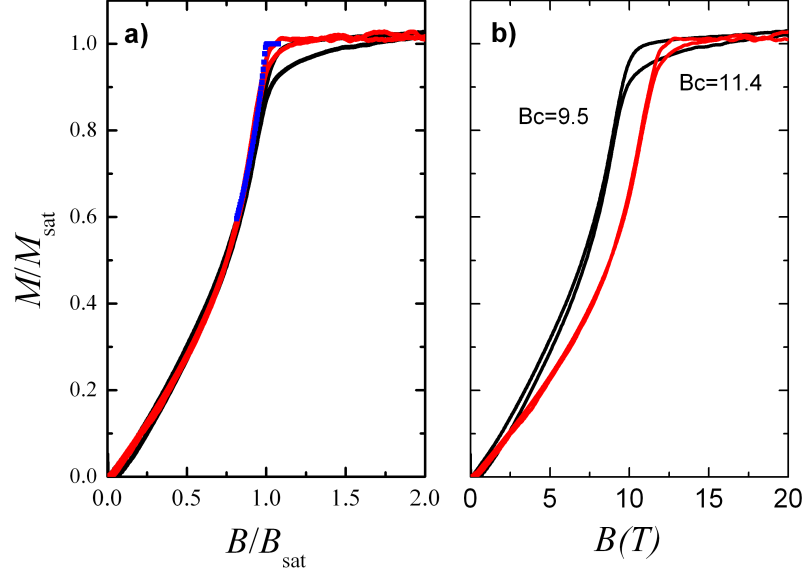


Figure 5.23: Magnetisation measurements of **1** (red) and **2** (black). a) Reduced magnetisation M/M_{sat} against reduced field B/B_c of both data sets and the Q1D model. b) Magnetisation as a function of field for both samples.

There is no available μ SR data that would give us information on the magnetic ordering transition in these two compounds.

Using Eqn. 5.3 the exchange anisotropy of **1** and **2** can be estimated based on the transition temperature of T_N . Assuming that the transition of both samples is at $T \leq 2$ K, then the exchange anisotropy in this system can be thought to be $J_{\perp}/J \leq 0.21(3)$.

In summary, these results confirm that these closely related compounds are Q1D magnetic systems in which the magnetism is mediated through Cu chains. The chains on which both materials are based are very similar. Although we do not have electron spin resonance data we can assume that the magnetism is mediated along the chain axis. In spite of these similarities **1** and **2** exhibit close but still significantly different primary exchange coupling.

A closer examination of the parameters in Table 5.7 provides an explanation for this observation. The obvious reason for different exchange couplings would be a variation in Cu···Cu separation. However the distance between two Cu centres is practically identical in both compounds.

Two differences between the two compounds that can be identified is that the Cu centre in the compound **1** is more symmetric, with Cu-N bonds being essentially identical, and that the N-Cu-N bond angle is more linear. The small difference in exchange coupling strength, could arise from the stronger antiferromagnetic interactions being mediated by the more linear bond. This would be in keeping with the semi-empirical Goodenough, Kanamori and Anderson rules of superexchange [8].

It would be of great interest to investigate these compounds with μ SR, in order to obtain reliable estimates of the transition temperatures. The results would then make it possible to compare the exchange anisotropies in those systems to find out to what extent the change in the non-bridging ligands affects $J_{\perp}$.

5.8 Conclusion

I have shown how the techniques of μ SR, high field pulsed magnetisation, low field experiments, ESR and Quantum Monte Carlo Simulations can be combined to investigate coordination polymers in order to take advantage of the benefits provided by each of the techniques.

Specific changes in the molecular architecture will lead to specific changes in the magnetism of these systems and the understanding of these effects in the materials presented in this thesis has given us valuable insights into how they

function and how their properties can be controlled. I have highlighted that we have the capacity to produce Q1D and Q2D systems, and also to tune the exchange coupling strengths. In addition I have demonstrated that we can preselect the exchange anisotropy without perturbing the magnitude of the primary interaction strengths and thus take control over the magnetic properties of polymeric systems. Thus these compounds represent a promising approach to magnetic crystal engineering of systems that exhibit higher ordering temperatures and other cooperative phenomena.

6

Conclusion

In this thesis I have presented the study of a number of magnetic materials that exhibit fascinating physical phenomena due to their low-dimensionality. The following conclusions summarise the findings of the experiments that were based on muon spin rotation and pulsed magnetic field experiments.

In Chapter 3 I describe an investigation of Fe-based superconductors, a new family of high temperature superconductors, that provide a breadth of possibilities for study leading to a better understanding of this phenomenon, in particular concerning the comparison and contrast with the cuprate superconductors. The interplay between magnetism and superconductivity in these materials is expected to be an essential contribution to understanding high temperature superconductivity.

A recurring question in these systems is whether the magnetic and structural transitions coincide, since this could give valuable information on what drives the magnetism in these materials. Although the occurrence of a structural and magnetic transition in the parent compound SrFeAsF is well established through earlier research, I identified that there is a 50 K difference between the two tran-

sitions. This does not exclude the possibility that there is an interplay between the two transitions, however it shows that the magnetic transition is not directly driven by the structural changes in SrFeAsF. In addition heat-capacity and μ SR reveal that the magnetism is more Q2D in SrFeAsF compared to the oxopnictide parent compound LaFeAsO **(a)**.

In contrast to SrFeAsF, the pnictide NaFeAs is superconducting at stoichiometric composition and we demonstrate that the electron count has a determinative role on the physics of the 111 pnictide systems **(g)**. In this thesis I present a significant contribution by providing the first observation of magnetism in the stoichiometric compound **(c)**. The magnetic moment is very small so that it was not detected in early neutron studies. However it was subsequently verified by Li *et al.* [58]. This magnetic phase is coexistent with superconductivity.

We were able to show the coexistence of antiferromagnetism and superconductivity in these compounds up to doping levels of 0.025 electrons per Fe. In a similar way to SrFeAsF the antiferromagnetic order has a primarily two-dimensional character, highlighting the importance of the low-dimensionality in these materials. The combination of μ SR and susceptibility measurements made it possible to obtain a phase diagram for Co-doped NaFeAs, revealing the clear competition between magnetism and superconductivity where the strengthening of the superconducting order parameter and the increasing volume fraction is seen directly to depress the magnetic and structural order parameters at low temperature **(m)**.

In Chapter 4, I presented a μ SR investigation of four different iridium oxide systems Ca_4IrO_6 , $\text{Ca}_5\text{Ir}_3\text{O}_{12}$, $\text{Sr}_3\text{Ir}_2\text{O}_7$, Sr_2IrO_4 **(j)**. The $J_{eff} = 1/2$ spin-orbit entangled Mott insulator Sr_2IrO_4 is particularly interesting and has even been suggested as a possible high temperature superconductor if appropriately

doped [86]. Although the μ SR data obtained on $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ is more complex with a large number of muon sites both the results of Ca_4IrO_6 and $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ are as expected for conventional ordered magnets. They exhibit 3D antiferromagnetic order and their Néel temperatures were determined from the data.

The results for $\text{Sr}_3\text{Ir}_2\text{O}_7$ and Sr_2IrO_4 are much more complicated. In $\text{Sr}_3\text{Ir}_2\text{O}_7$ a single muon precession frequency was observed between 20 K and 160 K. The disappearance of a precession signal below 20 K and above 160 K is mysterious. The change below 20 K does not correlate with any previously identified magnetic transition but corresponds to the temperature at which the field-cooled magnetisation becomes negative.

The high temperature behavior of Sr_2IrO_4 as determined in μ SR is conventional, with the appearance of one frequency below the transition temperature at 260 K and is clearly quasi-two-dimensional. However the low temperature behavior is very unusual with the development of a second precession signal. We have presented the potential explanation for this through the occurrence of a reorientation transition at low temperatures, which correlates with a change in the Ir–O–Ir bond-angle. This development of a reoriented phase is probably gradual and results from the balance of competing energies changing with temperature. This reorientation of the spins to a lower symmetry state could be at the root of the magnetoelectric behavior [22]. Ge *et al.*[36] observe a reduction in magnetic anisotropy M_a / M_c and propose that an emerging c-axis spin component generates a noncollinear spin structure and frustration at low temperatures. They suggest that this could explain the three different phases observed in the μ SR data and the occurrence of the reorientation transition.

The unconventional behaviour of both $\text{Sr}_3\text{Ir}_2\text{O}_7$ and Sr_2IrO_4 in contrast to

Ca_4IrO_6 and $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ is most probably a combined effect of the dimensionality and the competing energy scales in these systems.

In Chapter 5 I demonstrated how the coupling strengths and the type of magnetism in coordination polymers can be determined using a combination of magnetic susceptibility at low fields, magnetisation in pulsed magnetic fields, muon spin rotation and theoretical models. I presented a series of Cu-based systems, which are linked by molecular groups or ligands, forming chains and layers. I present how it is possible to make adjustments to the molecular architecture that will have a direct effect on the magnetic properties of the system. This enables the targeted design of magnetic systems that can be utilised as testing grounds to experimentally evaluate fundamental theories of magnetism (**b**, **f**, **n**).

It was possible for us to identify that the substitution of non-coordinated molecules X that share the same symmetry will affect the exchange interactions and anisotropy in the Q2D $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]X$ compounds in the same way. The octahedral class of counterion will lead to almost double the exchange interaction and a more anisotropic system than a tetragonal counterion.

We then presented a case in which the counterion becomes a non-bridging ligand, resulting in a material in which there was no non-coordinated molecule. In this system the primary exchange coupling is substantially enhanced. This effect was explained by introducing a reduced effective intralayer exchange $J_{eff} = J_1 - J_2$ where J_2 is mediated through the non-coordinated molecules. This model explains why a change in the class of counterion would affect the exchange interaction J_{eff} , as well as why the coupling is stronger when there is no non-coordinated molecule, resulting in a reduced value of J_2 .

It was also shown that the dimensionality of these materials can be tuned from

Q2D to Q1D (**n**), without significantly perturbing the magnitude of the primary interaction strengths, demonstrating that it is possible to take deliberate control over the dimensionality of these polymeric systems. We also demonstrated that changing the system so that the dominant spin exchange involves superexchange through halogen $\cdots$ halogen contacts, enables us to design systems with important superexchange, which can be significantly changed by the substitution of one halogen to another. Finally I also presented two Q1D materials with very similar structures and show that a change in the symmetry of the system has a direct effect on the coupling strengths.

We have demonstrated how the combination of μ SR, high field pulsed magnetisation, low field experiments, ESR and Quantum Monte Carlo Simulations provide a powerful technique for the study of coordination polymers. Some of the results presented here would benefit from μ SR and ESR that we were not able to do so far. In addition new coordination polymers will give new insights into the mechanisms at work here.

This thesis as part of these ongoing projects contributes to the understanding of the materials presented here, which has the potential to further our fundamental knowledge of condensed matter physics, and pave the way for great advances in technology.

List of publications

- (a) P. J. BAKER, **I. Franke**, T. LANCASTER, S. J. BLUNDELL, L. KERSLAKE, AND S. J. CLARKE. **Two-dimensional magnetism in the pnictide superconductor parent material SrFeAsF probed by muon-spin relaxation.** *Physical Review B*, **79**(6), 2009.
- (b) J. L. MANSON, J. A. SCHLUETER, K. A. FUNK, H. I. SOUTHERLAND, B. TWAMLEY, T. LANCASTER, S. J. BLUNDELL, P. J. BAKER, F. L. PRATT, J. SINGLETON, R. D. McDONALD, P. A. GODDARD, P. SENGUPTA, C. D. BATISTA, L. DING, C. LEE, M. WHANGBO, **I. Franke**, S. COX, C. BAINES, AND D. TRIAL. **Strong H · · F Hydrogen Bonds as Synthons in Polymeric Quantum Magnets: Structural, Magnetic, and Theoretical Characterization of [Cu(HF₂)-(pyrazine)₂](SbF₆), [Cu₂F(HF)(HF₂)(pyrazine)₄](SbF₆)₂, and [CuAg(H₃F₄)-(pyz)₅](SbF₆)₂.** *Journal of the American Chemical Society*, **131**(19), 2009.
- (c) D. R. PARKER, M. J. PITCHER, P. J. BAKER, **I. Franke**, T. LANCASTER, S. J. BLUNDELL, AND S. J. CLARKE. **Structure, antiferromagnetism and superconductivity of the layered iron arsenide NaFeAs.** *Chemical Communications*, (16):2189–2191, 2009.
- (d) P. J. BAKER, T. LANCASTER, **I. Franke**, W. HAYES, S. J. BLUNDELL, F. L. PRATT, P. JAIN, Z. M. WANG, AND M. KURMOO. **Muon spin relaxation investigation of magnetic ordering in the hybrid organic-inorganic perovskites [((CH₃)₂NH₂)M(HCOO)₃ (M=Ni, Co, Mn, Cu).** *Physical Review B*, **82**(1), 2010.
- (e) P. J. BAKER, H. J. LEWTAS, S. J. BLUNDELL, T. LANCASTER, **I. Franke**, W. HAYES, F. L. PRATT, L. BOHATY, AND P. BECKER. **Muon-spin relaxation and heat capacity measurements on the magnetoelectric and multiferroic pyroxenes LiFeSi₂O₆ and NaFeSi₂O₆.** *Physical Review B*, **81**(21), 2010.
- (f) T. LANCASTER, S. J. BLUNDELL, F. L. PRATT, **I. Franke**, A. J. STEELE, P. J. BAKER, Z. SALMAN, C. BAINES, I. WATANABE, S. CARRETTA, G. A. TIMCO, AND R. E. P. WINPENNY. **Relaxation of muon spins in molecular nanomagnets.** *Physical Review B*, **81**(14), 2010.

-
- (g) D. R. PARKER, M. J. P. SMITH, T. LANCASTER, A. J. STEELE, **I. Franke**, P. J. BAKER, F. L. PRATT, M. J. PITCHER, S. J. BLUNDELL, AND S. J. CLARKE. **Control of the Competition between a Magnetic Phase and a Superconducting Phase in Cobalt-Doped and Nickel-Doped NaFeAs Using Electron Count.** *Physical Review Letters*, **104**(5), 2010.
 - (h) M. J. PITCHER, T. LANCASTER, J. D. WRIGHT, **I. Franke**, A. J. STEELE, P. J. BAKER, F. L. PRATT, W. T. THOMAS, D. R. PARKER, S. J. BLUNDELL, AND S. J. CLARKE. **Compositional Control of the Superconducting Properties of LiFeAs.** *Journal of the American Chemical Society*, **132**(30), 2010.
 - (i) J. SINGLETON, C. DE LA CRUZ, R. D. McDONALD, S. L. LI, M. ALTARAWNEH, P. GODDARD, **I. Franke**, D. RICKEL, C. H. MIELKE, X. YAO, AND P.C. DAI. **Magnetic Quantum Oscillations in $\text{YBa}_2\text{Cu}_3\text{O}_{6.61}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.69}$ in Fields of Up to 85 T: Patching the Hole in the Roof of the Superconducting Dome.** *Physical Review Letters*, **104**(8), 2010.
 - (j) **I. Franke**, P. J. BAKER, S. J. BLUNDELL, T. LANCASTER, W. HAYES, F. L. PRATT, AND G. CAO. **Measurement of the internal magnetic field in the correlated iridates Ca_4IrO_6 , $\text{Ca}_5\text{Ir}_3\text{O}_{12}$, $\text{Sr}_3\text{Ir}_2\text{O}_7$ and Sr_2IrO_4 .** *Physical Review B*, **83**(9), 2011.
 - (k) A. J. STEELE, P. J. BAKER, T. LANCASTER, F. L. PRATT, **I. Franke**, S. GHANNADZADEH, P. A. GODDARD, W. HAYES, D. PRABHAKARAN, AND S. J. BLUNDELL. **Low-moment magnetism in the double perovskites Ba_2MOsO_6 ($M = \text{Li}, \text{Na}$).** *Physical Review B*, **84**(14), 2011.
 - (l) S. GHANNADZADEH, M. COAK, **I. Franke**, P. A. GODDARD, J. SINGLETON, AND J. L. MANSON. **Measurement of magnetic susceptibility in pulsed magnetic fields using a proximity detector oscillator.** *Rev. Sci. Instrum.*, **82**(113902), 2011.
 - (m) J. D. WRIGHT, T. LANCASTER, **I. Franke**, A. J. STEELE, J. S. MOLLER, M. J. PITCHER, A. J. CORKETT, D. R. PARKER, F. L. PRATT, P. J. BAKER, S. J. CLARKE, AND S. J. BLUNDELL. **The gradual destruction of magnetism in the superconducting family $\text{NaFe}_{1-x}\text{Co}_x\text{As}$.** *submitted*, 2011.

-
- (n) P. A. GODDARD, J. L. MANSON, J. SINGLETON, **I. Franke**, T. LANCASTER, A. J. STEELE, S. J. BLUNDELL, C. BAINES, F. L. PRATT, R. D. McDONALD, O. A. VALENZUELA, J. F. CORBEY, H. I. SOUTHERLAND, P. SENGUPTA, J. A. SCHLUETER. **Dimensionality selection in a molecule-based magnet.** *submitted*, 2011.
- (o) J. L. MANSON, K. E. CARREIRO, S. H. LAPIDUS, P. W. STEPHENS, P. A. GODDARD, R. E. DEL SESTO, J. BENDIX, **I. Franke**, S. GHANNADZADEH, J. SINGLETON, T. LANCASTER, J. S. MILLER, P. J. BAKER, F. L. PRATT, S. J. BLUNDELL, J. KANG, C. LEEH, M. WHANGBOH. **Influence of HF_2^- geometry on magnetic interactions elucidated from polymorphs of the bifluoride-bridged coordination polymer $[\text{Ni}(\text{HF}_2)(\text{pyz})_2]\text{PF}_6$ (pyz = pyrazine).** *submitted*, 2011.
- (p) J. A. SCHLUETER, H. PARK, G. J. HALDER, W. R. ARMAND, C. DUNMARS, K. W. CHAPMAN, J. L. MANSON, J. SINGLETON, R. McDONALD, A. PLONCZAK, J. KANG, C. LEE, M. WHANGBO, T. LANCASTER, A. J. STEELE, **I. Franke**, J. D. WRIGHT, S. J. BLUNDELL, F. L. PRATT, J. DEGEORGE, MARK M. TURNBULL, AND C. P. LANDEEH. **Importance of Halogen $\cdots$ Halogen Contacts for the Structural and Magnetic Properties of $\text{CuX}_2(\text{pyrazine-}N,N'\text{-dioxide})(\text{H}_2\text{O})_2$ ($X = \text{Cl}$ and Br).** *Inorganic Chemistry*, 2011.

References

- [1] D. ANDREICA. **Muon Spin rotation**. <http://esm.neel.cnrs.fr/2011/notes/andreica-notes.pdf>, 2011.
- [2] N. W. ASHCROFT AND N. D. MERMIN. *Solid State Physics*. Saunders, 1976.
- [3] P. J. BAKER. *Tuning the dimensionality and interactions in transition metal oxides: a μ SR study*. PhD thesis, University of Oxford, 2008.
- [4] P. J. BAKER, I. FRANKE, T. LANCASTER, S. J. BLUNDELL, L. KERSLAKE, AND S. J. CLARKE. **Two-dimensional magnetism in the pnictide superconductor parent material SrFeAsF probed by muon-spin relaxation**. *Physical Review B (Condensed Matter and Materials Physics)*, **79**, 2009.
- [5] P. J. BAKER, S. R. GIBLIN, F. L. PRATT, R. H. LIU, G. WU, X. H. CHEN, M. J. PITCHER, D. R. PARKER, S. J. CLARKE, AND S. J. BLUNDELL. **Heat capacity measurements on FeAs-based compounds: a thermodynamic probe of electronic and magnetic states**. *New Journal of Physics*, **11**(2):025010, 2009.
- [6] D. N. BASOV AND A. V. CHUBUKOV. **Manifesto for a higher T(c)**. *Nature Physics*, **7**(4):272–276, 2011.
- [7] S. J. BLUNDELL. **Spin-polarized muons in condensed matter physics**. *Contemporary Physics*, **40**, 1999.
- [8] S. J. BLUNDELL. *Magnetism in Condensed Matter*. Oxford University Press, 2001.

REFERENCES

- [9] S. J. BLUNDELL. **Muon-spin rotation : a brief introduction.** <http://users.ox.ac.uk/~sjb/musr/musr.html>, 2009.
- [10] S. J. BLUNDELL AND F. L. PRATT. **Organic and molecular magnets.** *J. Phys.: Condens. Matter*, **16**:R771R828, 2004.
- [11] S. J. BLUNDELL AND M. VERDAGUER. **Muon-Spin-Rotation Studies of Organic Magnets [and Discussion].** *Philosophical Transactions: Mathematical, Physical and Engineering Sciences*, **357**(1762):2923–2937, 1999.
- [12] J. C. BONNER AND M. E. FISHER. **Linear Magnetic Chains with Anisotropic Coupling.** *Phys. Rev.*, **135**(3A):A640–A658, Aug 1964.
- [13] S. V. BORISENKO, V. B. ZABOLOTNYY, D. V. EVTUSHINSKY, T. K. KIM, I. V. MOROZOV, A. N. YARESKO, A. A. KORDYUK, G. BEHR, A. VASILIEV, R. FOLLATH, AND B. BÜCHNER. **Superconductivity without Nesting in LiFeAs.** *Phys. Rev. Lett.*, **105**:067002, 2010.
- [14] R. T. BUTCHER, C. P. LANDEE, M. M. TURNBULL, AND F. XIAO. **Rectangular two-dimensional antiferromagnetic systems: Analysis of copper(II) pyrazine dibromide and dichloride.** *Inorganica Chimica Acta*, **361**(12-13):3654 – 3658, 2008.
- [15] R. T. BUTCHER, J. J. NOVOA, J. RIBAS-ARINO, A. W. SANDVIK, M. M. TURNBULL, C. P. LANDEE, P. CHRISTOPHER, B. M. WELLS, AND F. F. AWWADI. **Strong through-space two-halide magnetic exchange of –234 K in (2,5-dimethylpyrazine)copper(II) bromide.** *Chem. Commun.*, pages 1359–1361, 2009.
- [16] P. C. CANFIELD, S. L. BUD’KO, N. NI, J. Q. YAN, AND A. KRACHER. **Decoupling of the superconducting and magnetic/structural phase transitions in electron-doped BaFe₂As₂.** *Phys. Rev. B*, **80**:060501, 2009.
- [17] G. CAO, J. BOLIVAR, S. MCCALL, J. E. CROW, AND R. P. GUERTIN. **Weak ferromagnetism, metal-to-nonmetal transition, and negative differential resistivity in single-crystal Sr₂IrO₄.** *Phys. Rev. B*, **57**(18):R11039, 1998.

REFERENCES

- [18] G. CAO, V. DURAIRAJ, S. CHIKARA, S. PARKIN, AND P. SCHLOTTMANN. **Partial antiferromagnetism in spin-chain $\text{Sr}_5\text{Rh}_4\text{O}_{12}$, $\text{Ca}_5\text{Ir}_3\text{O}_{12}$, and Ca_4IrO_6 single crystals.** *Phys. Rev. B*, **75**(13):134402, 2007.
- [19] G. CAO, Y. XIN, C. S. ALEXANDER, J. E. CROW, P. SCHLOTTMANN, M. K. CRAWFORD, R. L. HARLOW, AND W. MARSHALL. **Anomalous magnetic and transport behavior in the magnetic insulator $\text{Sr}_3\text{Ir}_2\text{O}_7$.** *Phys. Rev. B*, **66**(21):214412, 2002.
- [20] J. A. CHAKHALIAN. *Local magnetic susceptibility of the positive muon in graphite and the quasi 1D spin 1/2 chain CPC.* PhD thesis, The University of British Columbia, 2002.
- [21] G. F. CHEN, W. Z. HU, J. L. LUO, AND N. L. WANG. **Multiple Phase Transitions in Single-Crystalline $\text{Na}_{1-\delta}\text{FeAs}$.** *Phys. Rev. Lett.*, **102**:227004, 2009.
- [22] S. CHIKARA, O. KORNETA, W. P. CRUMMETT, L. E. DELONG, P. SCHLOTTMANN, AND G. CAO. **Giant magnetoelectric effect in the $J_{eff}=1/2$ Mott insulator Sr_2IrO_4 .** *Phys. Rev. B*, **80**(14):140407, 2009.
- [23] S. V. CHONG, S. HASHIMOTO, H. YAMAGUCHI, AND K. KADOWAKI. **Neodymium-Doping Induced Superconductivity in 1111- SrFeAsF Iron-Pnictide System.** *Journal of Superconductivity and Novel Magnetism*, **23**(8):1479–1484, 2010.
- [24] C. CHOW, K. CHANG, AND R. D. WILLETT. **Electron spin resonance spectra and covalent bonding in the square-planar CuCl_4^{2-} and CuBr_4^{2-} ions.** *The Journal of Chemical Physics*, **59**(5):2629–2640, 1973.
- [25] C. W. CHU, F. CHEN, M. GOOCH, A. M. GULOY, B. LORENZ, B. LV, K. SASMAL, Z. J. TANG, J. H. TAPP, AND Y. Y. XUE. **The Synthesis and Characterization of LiFeAs and NaFeAs .** *Physica C Superconductivity*, **469**(9-12):326–331, 2009.
- [26] J. CHU, J. G. ANALYTIS, C. KUCHARCZYK, AND I. R. FISHER. **Determination of the phase diagram of the electron-doped superconductor $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$.** *Phys. Rev. B*, **79**:014506, 2009.

REFERENCES

- [27] NATIONAL RESEARCH COUNCIL COMMITTEE IN OPPORTUNITIES IN HIGH MAGNETIC FIELD SCIENCE, SOLID STATE SCIENCE COMMITTEE. *Opportunities In High Magnetic Field Science*. The national academic press, 2005.
- [28] M. K. CRAWFORD, M. A. SUBRAMANIAN, R. L. HARLOW, J. A. FERNANDEZ-BACA, Z. R. WANG, AND D. C. JOHNSTON. **Structural and magnetic studies of Sr_2IrO_4** . *Phys. Rev. B*, **49**(13):9198, 1994.
- [29] E. DAGOTTO. **Complexity in Strongly Correlated Electronic Systems**. *Science*, **309**(5732):257–262, 2005.
- [30] J. DARRIET, G. DEMAZEAU, AND M. POUCHARD. **Une modelisation du comportement magnetique d’un compose de l’iridium pentavalent**. *Mater. Res. Bull.*, **16**(8):1013–1017, 1981.
- [31] M. J. DAVIS, M. D. SMITH, AND H. LOYE. **Ca_4IrO_6 , $\text{Ca}_3\text{MgIrO}_6$ and $\text{Ca}_3\text{ZnIrO}_6$** . *Acta Crystallographica Section C*, **57**(11):1234–1236, 2001.
- [32] THE MAGNET DEVELOPMENT AND APPLIED SUPERCONDUCTIVITY GROUP. <http://www.physics.ox.ac.uk/magnet/>, 2011.
- [33] F. J. J. DIJKSMA, J. F. VENTE, E. FRIKKEE, AND D. J. W. IJDO. **The Structure of a Calcium-Deficient Hexagonal Calcium Iridium Oxide Compound**. *Mater. Res. Bull.*, **28**(11):1145–1151, 1993.
- [34] A. J. DREW, C. NIEDERMAYER, P. J. BAKER, F. L. PRATT, S. J. BLUNDELL, T. LANCASTER, R. H. LIU, G. WU, X. H. CHEN, I. WATANABE, V. K. MALIK, A. DUBROKA, M. ROSSLE, K. W. KIM, C. BAINES, AND C. BERNHARD. **Coexistence of static magnetism and superconductivity in $\text{SmFeAsO}_{1-x}\text{F}_x$ as revealed by muon spin rotation**. *Nat Mater*, **8**(4):310–314, 2009/04//print.
- [35] I. FRANKE, P. J. BAKER, S. J. BLUNDELL, T. LANCASTER, W. HAYES, F. L. PRATT, AND G. CAO. **Measurement of the internal magnetic field in the correlated iridates Ca_4IrO_6 , $\text{Ca}_5\text{Ir}_3\text{O}_{12}$, $\text{Sr}_3\text{Ir}_2\text{O}_7$ and Sr_2IrO_4** . *Physical Review B*, **83**(9), 2011.

REFERENCES

- [36] M. GE, T. F. QI, O. B. KORNETA, D. E. DE LONG, P. SCHLOTTMANN, W. P. CRUMMETT, AND G. CAO. **Lattice-driven magnetoresistivity and metal-insulator transition in single-layered iridates.** *Phys. Rev. B*, **84**:100402, 2011.
- [37] P. A. GODDARD, J. SINGLETON, P. SENGUPTA, R. D. McDONALD, T. LANCASTER, S. J. BLUNDELL, F. L. PRATT, S. COX, N. HARRISON, J. L. MANSON, H. I. SOUTHERLAND, AND J. A. SCHLUETER. **Experimentally determining the exchange parameters of quasi-two-dimensional Heisenberg magnets.** *New Journal of Physics*, **10**(8):083025 (11pp), 2008.
- [38] P. M. GRANT. **Superconductivity: Prospecting for an iron age.** *Nature*, **453**(7198):1000–1001, 2008.
- [39] F. HAN, X. ZHU, G. MU, P. CHENG, AND H. WEN. **SrFeAsF as a parent compound for iron pnictide superconductors.** *Phys. Rev. B*, **78**:180503, 2008.
- [40] K. HAYASHI, G. DEMAZEAU, M. POUCHARD, AND P. HAGENMULLER. **Preparation and magnetic study of a new iridium (V) perovskite: $\text{LaLi}_{0.5}\text{Ir}_{0.5}\text{O}_3$.** *Mater. Res. Bull.*, **15**(4):461–467, 1980.
- [41] F. HERLACH AND N. MIURA, editors. *High Magnetic Fields, Science and Technology, Volume 1*. Scientific publishing company, 2003.
- [42] M. IMADAI, A. FUJIMORI, AND Y. TOKURA. **Metal-insulator transitions.** *Rev. Mod. Phys.*, **70**(4):1039, 1998.
- [43] G. JACKELI AND G. KHALIULLIN. **Mott Insulators in the Strong Spin-Orbit Coupling Limit: From Heisenberg to a Quantum Compass and Kitaev Models.** *Phys.Rev. Lett.*, **102**(1):017205, 2009.
- [44] A. JESCHE, N. CAROCA-CANALES, H. ROSNER, H. BORRMANN, A. ORMECI, D. KASINATHAN, H. H. KLAUSS, H. LUETKENS, R. KHASANOV, A. AMATO, A. HOSER, K. KANEKO, C. KRELLNER, AND C. GEIBEL. **Strong coupling between magnetic and structural order parameters in SrFe_2As_2 .** *Physical Review B (Condensed Matter and Materials Physics)*, **78**(18):180504, 2008.

-
- [45] H. JIN, H. JEONG, T. OZAKI, AND J. YU. **Anisotropic exchange interactions of spin-orbit-integrated states in Sr_2IrO_4 .** *Phys. Rev. B*, **80**(7):075112, 2009.
 - [46] D. C. JOHNSTON, R. K. KREMER, M. TROYER, X. WANG, A. KLUMPER, S. L. BUD'KO, A. F. PANCHULA, AND P. C. CANFIELD. **Thermodynamics of spin $S = 1/2$ antiferromagnetic uniform and alternating-exchange Heisenberg chains.** *Phys. Rev. B*, **61**:9558–9606, 2000.
 - [47] B. C. KEITH, C. P. LANDEE, T. VALLEAU, M. M. TURNBULL, AND N. HARRISON. **Two-dimensional spin- $\frac{1}{2}$ rectangular Heisenberg antiferromagnets: Simulation and experiment.** *Phys. Rev. B*, **84**:104442, 2011.
 - [48] S. L. LEE, S. H. KILCOYNE AND R. CYWINSKI. *Muon Science, Muons in Physics, Chemistry and Materials*. SUSSP Publications and Institute of Physics Publishing, 1999.
 - [49] B. J. KIM, H. JIN, S. J. MOON, J. Y. KIM, B. G. PARK, C. S. LEEM, J. YU, T. W. NOH, C. KIM, S. J. OH, J. H. PARK, V. DURAIRAJ, G. CAO, AND E. ROTENBERG. **Novel $J_{eff}=1/2$ Mott State Induced by Relativistic Spin-Orbit Coupling in Sr_2IrO_4 .** *Phys. Rev. Lett.*, **101**(7):076402, 2008.
 - [50] B. J. KIM, H. OHSUMI, T. KOMESU, S. SAKAI, T. MORITA, H. TAKAGI, AND T. ARIMA. **Phase-Sensitive Observation of a Spin-Orbital Mott State in Sr_2IrO_4 .** *Science*, **323**(5919):1329–1332, 2009.
 - [51] N. S. KINI, A. M. STRYDOM, H. S. JEEVAN, C. GEIBEL, AND S. RAMAKRISHNAN. **Transport and thermal properties of weakly ferromagnetic Sr_2IrO_4 .** *Journal of Physics: Condensed Matter*, **18**(35):8205, 2006.
 - [52] Y. KOHAMA, M. JAIME, O. E. AYALA-VALENZUELA, R. D. McDONALD, E. D. MUN, F. J. CORBEY, AND J. L. MANSON. **Field-induced XY and Ising ground states in a quasi-two-dimensional $S = \frac{1}{2}$ Heisenberg antiferromagnet.** *Phys. Rev. B*, **84**:184402, Nov 2011.
 - [53] O. B. KORNETA, T. QI, S. CHIKARA, S. PARKIN, L. E. DE LONG, P. SCHLOTTMANN, AND G. CAO. **Electron-doped $\text{Sr}_2\text{IrO}_{4-\delta}$ ($0 \leq \delta \leq 0.04$): Evolution of a disordered $J_{eff} = \frac{1}{2}$ Mott insulator into an exotic metallic state.** *Phys. Rev. B*, **82**(11):115117, 2010.

REFERENCES

- [54] T. LANCASTER. *Muon-spin relaxation and its application to magnetic systems of differing dimensionality*. PhD thesis, University of Oxford, 2004.
- [55] T. LANCASTER, S. J. BLUNDELL, M. L. BROOKS, P. J. BAKER, F. L. PRATT, J. L. MANSON, M. M. CONNER, F. XIAO, C. P. LANDEE, F. A. CHAVES, S. SORIANO, M. A. NOVAK, T. P. PAPAGEORGIOU, A. D. BIANCHI, T. HERMANNSDÖRFER, J. WOSNITZA, AND J. A. SCHLUETER. **Magnetic order in the $S = 1/2$ two-dimensional molecular antiferromagnet copper pyrazine perchlorate $\text{Cu}(\text{Pz})_2(\text{ClO}_4)_2$** . *Phys. Rev. B*, **75**:094421, 2007.
- [56] T. LANCASTER, S. J. BLUNDELL, F. L. PRATT, M. L. BROOKS, J. L. MANSON, E. K. BRECHIN, C. CADIOU, D. LOW, E. J. L. MCINNES, AND R. E. P. WINPENNY. **Muons as a probe of magnetism in molecule-based low dimensional magnets**. *Journal of Physics: Condensed Matter*, **16**(40):S4563, 2004.
- [57] C. LEE, A. IYO, H. EISAKI, H. KITO, M. T. FERNANDEZ-DIAZ, T. ITO, K. KIHOU, H. MATSUHATA, M. BRADEN, AND K. YAMADA. **Effect of Structural Parameters on Superconductivity in Fluorine-Free LnFeAsO_{1-y} ($\text{Ln} = \text{La}, \text{Nd}$)**. *Journal of the Physical Society of Japan*, **77**(8):083704, 2008.
- [58] S. LI, C. DE LA CRUZ, Q. HUANG, G. F. CHEN, T. L. XIA, J. L. LUO, N. L. WANG, AND P. DAI. **Structural and magnetic phase transitions in $\text{Na}_{1-\delta}\text{FeAs}$** . *Phys. Rev. B*, **80**:020504, 2009.
- [59] S. MATSUISHI, Y. INOUE, T. NOMURA, H. YANAGI, M. HIRANO, AND H. HOSONO. **Superconductivity Induced by Co-Doping in Quaternary Fluoroarsenide CaFeAsF** . *Journal of the American Chemical Society*, **130**(44):14428–14429, 2008.
- [60] I. I. MAZIN, D. J. SINGH, M. D. JOHANNES, AND M. H. DU. **Unconventional Superconductivity with a Sign Reversal in the Order Parameter of $\text{LaFeAsO}_{1-x}\text{F}_x$** . *Phys. Rev. Lett.*, **101**:057003, 2008.
- [61] M. A. MCGUIRE, A. D. CHRISTIANSON, A. S. SEFAT, B. C. SALES, M. D. LUMSDEN, R. JIN, E. A. PAYZANT, D. MANDRUS, Y. LUAN, V. KEPENS, V. VARADARAJAN, J. W. BRILL, R. P. HERMANN, M. T. SOUGRATI,

REFERENCES

- F.GRANDJEAN, AND G. J. LONG. **Phase transitions in LaFeAsO: Structural, magnetic, elastic, and transport properties, heat capacity and Mossbauer spectra.** *Physical Review B (Condensed Matter and Materials Physics)*, **78**, 2008.
- [62] P. METRANGOLO, G. RESNATI, T. PILATI, R. LIANTONIO, AND F. MEYER. **Engineering functional materials by halogen bonding.** *Journal of Polymer Science Part A: Polymer Chemistry*, **45**(1):1–15, 2007.
- [63] S. J. MOON, H. JIN, W. S. CHOI, J. S. LEE, S. S. A. SEO, J. YU, G. CAO, T. W. NOH, AND Y. S. LEE. **Temperature dependence of the electronic structure of the $J_{eff}=1/2$ Mott insulator Sr_2IrO_4 studied by optical spectroscopy.** *Phys. Rev. B*, **80**(19):195110, 2009.
- [64] M. MOTOKAWA. **Physics in high magnetic fields.** *Reports on Progress in Physics*, **67**(11):1995, 2004.
- [65] I. NAGAI, Y. YOSHIDA, S. I. IKEDA, H. MATSUHATA, H. KITO, AND M. KOSAKA. **Canted antiferromagnetic ground state in $Sr_3Ir_2O_7$.** *J. Phys.: Condens. Matter*, **19**(13):136214, 2007.
- [66] LOS ALAMOS NATIONAL LABORATORY NHMFL. **National High Magnetic Field Laboratory, Pulsed Field Facility.** <http://www.lanl.gov/orgs/mpa/nhmfl/>, 2009.
- [67] M. R. NORMAN. **High-temperature superconductivity in the iron pnictides.** *Physics*, **1**:21, 2008.
- [68] UNIVERSITY OF FRIBURG. <http://physics.unifr.ch>, 2009.
- [69] J. PAGLIONE AND R. L. GREENE. **High-temperature superconductivity in iron-based materials.** *Nature Physics*, **6**(9):645–658, 2010.
- [70] T. PARK, E. PARK, H. LEE, T. KLIMCZUK, E. D. BAUER, F. RONNING, AND J. D. THOMPSON. **Pressure-induced superconductivity in $CaFe_2As_2$.** *Journal of Physics: Condensed Matter*, **20**(32):322204, 2008.

REFERENCES

- [71] D. R. PARKER, M. J. P., P. J. BAKER, I. FRANKE, T. LANCASTER, S. J. BLUNDELL, AND S. J. CLARKE. **Structure, antiferromagnetism and superconductivity of the layered iron arsenide NaFeAs**. *Chemical Communications*, **16**:2189–91, 2009.
- [72] D. R. PARKER, J. P. MATTHEW SMITH, T. LANCASTER, A. J. STEELE, I. FRANKE, P. J. BAKER, F. L. PRATT, M. J. PITCHER, S. J. BLUNDELL, AND S. J. CLARKE. **Control of the Competition between a Magnetic Phase and a Superconducting Phase in Cobalt-Doped and Nickel-Doped NaFeAs Using Electron Count**. *Phys. Rev. Lett.*, **104**:057007, 2010.
- [73] J. A. SCHLUETER, H. PARK, G. J. HALDER, W. R. ARMAND, C. DUNMARS, K. W. CHAPMAN, J. L. MANSON, J. SINGLETON, R. McDONALD, A. PLONCZAK, J. KANG, C. LEE, M. WHANGBO, T. LANCASTER, A. J. STEELE, I. FRANKE, J. D. WRIGHT, S. J. BLUNDELL, F. L. PRATT, J. DEGEORGE, MARK M. TURNBULL, AND C. P. LANDEEH. **Importance of Halogen-Halogen Contacts for the Structural and Magnetic Properties of $\text{CuX}_2(\text{pyrazine-}N,N'\text{-dioxide})(\text{H}_2\text{O})_2$ ($X = \text{Cl}$ and Br)**. *Inorganic Chemistry*, 2011.
- [74] N. SEGAL, J. F. VENTE, T. S. BUSH, AND P. D. BATTLE. **Structural and magnetic properties of $\text{Sr}_{4-x}\text{M}_x\text{IrO}_6$ ($\text{M}=\text{Ca}, \text{Zn}, \text{Cd}, \text{Li}, \text{Na}$)**. *J. Mat. Chem.*, **6**(3):395–401, 1996.
- [75] P. SENGUPTA, A. W. SANDVIK, AND R. R. P. SINGH. **Specific heat of quasi-two-dimensional antiferromagnetic Heisenberg models with varying interplanar couplings**. *Phys. Rev. B*, **68**:094423, 2003.
- [76] T. SENTHIL AND F. WANG. <http://www.tpi.umn.edu/workshops/2010-2011/supercon/Talks/Senthil/>, 2010.
- [77] A. SHITADE, H. KATSURA, J. KUNEŠ, X. QI, S. ZHANG, AND N. NAGAOSA. **Quantum Spin Hall Effect in a Transition Metal Oxide Na_2IrO_3** . *Phys. Rev. Lett.*, **102**:256403, Jun 2009.

-
- [78] Y. SINGH AND P. GEGENWART. **Antiferromagnetic Mott insulating state in single crystals of the honeycomb lattice material Na_2IrO_3 .** *Phys. Rev. B*, **82**:064412, 2010.
 - [79] A. J. STEELE, T. LANCASTER, S. J. BLUNDELL, P. J. BAKER, F. L. PRATT, C. BAINES, M. M. CONNER, H. I. SOUTHERLAND, J. L. MANSON, AND J. A. SCHLUETER. **Magnetic order in quasi-two-dimensional molecular magnets investigated with muon-spin relaxation.** *Physical Review B*, **84**:064412, 2011.
 - [80] H. TAKAHASHI, K. IGAWA, K. ARII, Y. KAMIHARA, HIRANO M, AND H. HOSONO. **Superconductivity at 43K in an iron-based layered compound $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$.** *Nature*, **453**(7193):378, 2008.
 - [81] A. TARONI, S. T. BRAMWELL, AND P. C. W. HOLDSWORTH. **Universal window for two-dimensional critical exponents.** *Journal of Physics: Condensed Matter*, **20**(27):275233 (15pp), 2008.
 - [82] M. TEGEL, S. JOHANSSON, V. WEI, I. SCHELLENBERG, W. HERMES, R. PTTGEN, AND D. JOHRENDT. **Synthesis, crystal structure and spin-density-wave anomaly of the iron arsenide-fluoride SrFeAsF .** *EPL (Europhysics Letters)*, **84**(6):67007 (5pp), 2008.
 - [83] M. TROPEANO, A. MARTINELLI, A. PALENZONA, E. BELLINGERI, E. GALLEANI D’AGLIANO, T. D. NGUYEN, M. AFFRONTI, AND M. PUTTI. **Thermal properties of $\text{SmFeAsO}_{1-x}\text{F}_x$ as a probe of the interplay between electrons and phonons.** *Phys. Rev. B*, **78**:094518, 2008.
 - [84] N. TSYRULIN, T. PARDINI, R. R. P. SINGH, F. XIAO, P. LINK, A. SCHNEIDWIND, A. HIESS, C. P. LANDEE, M. M. TURNBULL, AND M. KENZELMANN. **Quantum Effects in a Weakly Frustrated $S = 1/2$ Two-Dimensional Heisenberg Antiferromagnet in an Applied Magnetic Field.** *Phys. Rev. Lett.*, **102**:197201, May 2009.
 - [85] M. WAKESHIMA, N. TAIRA, Y. HINATSU, AND Y. ISHII. **Electrical and magnetic properties of pseudo-one-dimensional calcium iridium oxide $\text{Ca}_5\text{Ir}_3\text{O}_{12}$.** *Solid State Commun.*, **125**(6):311–315, 2003.

REFERENCES

- [86] F. WANG AND T. SENTHIL. **Twisted Hubbard Model for Sr_2IrO_4 : Magnetism and Possible High Temperature Superconductivity.** *Phys. Rev. Lett.*, **106**:136402, 2011.
- [87] H. WATANABE, T. SHIRAKAWA, AND S. YUNOKI. **Microscopic Study of a Spin-Orbit-Induced Mott Insulator in Ir Oxides.** *Phys. Rev. Lett.*, **105**:216410, 2010.
- [88] F. M. WOODWARD, A. S. ALBRECHT, C. M. WYNN, C. P. LANDEE, AND M. M. TURNBULL. **Two-dimensional $S = \frac{1}{2}$ Heisenberg antiferromagnets: Synthesis, structure, and magnetic properties.** *Phys. Rev. B*, **65**:144412, 2002.
- [89] F. M. WOODWARD, P. J. GIBSON, G. B. JAMESON, C. P. LANDEE, M. M. TURNBULL, AND R. D. WILLETT. **Two-Dimensional Heisenberg Antiferromagnets: Syntheses, X-ray Structures, and Magnetic Behavior of $[\text{Cu}(\text{pz})_2](\text{ClO}_4)_2$, $[\text{Cu}(\text{pz})_2](\text{BF}_4)_2$, and $[\text{Cu}(\text{pz})_2(\text{NO}_3)](\text{PF}_6)$.** *Inorganic Chemistry*, **46**(10):4256–4266, 2007.
- [90] J. D. WRIGHT, T. LANCASTER, I. FRANKE, A. J. STEELE, J. S. MOLLER, M. J. PITCHER, A. J. CORKETT, D. R. PARKER, F. L. PRATT, P. J. BAKER, S. J. CLARKE, AND S. J. BLUNDELL. **the gradual destruction of magnetism in the superconducting family $\text{NaFe}_{1-x}\text{Co}_x\text{As}$.** *submitted*, 2011.
- [91] G. WU, Y. L. XIE, H. CHEN, M. ZHONG, R. H. LIU, B. C. SHI, Q. J. LI, X. F. WANG, T. WU, Y. J. YAN, J. J. YING, AND X. H. CHEN. **Superconductivity at 56 K in samarium-doped SrFeAsF .** *Journal of Physics: Condensed Matter*, **21**(14):142203, 2009.
- [92] F. XIAO, F. M WOODWARD, C. P. LANDEE, M. M. TURNBULL, C. MIELKE, N. HARRISON, T. LANCASTER, S. J. BLUNDELL, P. J. BAKER, P. BABKEVICH, AND F. L. PRATT. **Two-dimensional XY behavior observed in quasi-two-dimensional quantum Heisenberg antiferromagnets.** *Phys. Rev. B*, **79**:134412, 2009.
- [93] Y. XIAO, T. SU, R. MITTAL, T. CHATTERJI, T. HANSEN, S. PRICE, C. M. N. KUMAR, J. PERSSON, S. MATSUISHI, Y. INOUE, H. HOSONO, AND

REFERENCES

- T. BRUECKEL. **Neutron diffraction study of phase transitions and thermal expansion of SrFeAsF**. *Phys. Rev. B*, **81**:094523, 2010.
- [94] C. YASUDA, S. TODO, K. HUKUSHIMA, F. ALET, M. KELLER, M. TROYER, AND H. TAKAYAMA. **Néel Temperature of Quasi-Low-Dimensional Heisenberg Antiferromagnets**. *Phys. Rev. Lett.*, **94**:217201, Jun 2005.
- [95] J. ZHAO, Q. HUANG, S. DE LA CRUZ, S. LI, J. W. LYNN, Y. CHEN, M. A. GREEN, G. F. CHEN, G. LI, Z. LI, J. L. LUO, N. L. WANG, AND P. DAI. **Structural and magnetic phase diagram of CeFeAsO_{1-x}F_x and its relation to high-temperature superconductivity**. *Nat Mater*, **7**(12):953–959, 2008.
- [96] YI ZHOU, PATRICK A. LEE, TAI-KAI NG, AND FU-CHUN ZHANG. **Na₄Ir₃O₈ as a 3D Spin Liquid with Fermionic Spinons**. *Phys. Rev. Lett.*, **101**:197201, 2008.