

Investigating magnetism and superconductivity using high magnetic fields

Saman Ghannadzadeh
Lincoln College, University of Oxford



A thesis submitted for the degree of
Doctor of Philosophy

Trinity Term 2014

Investigating magnetism and superconductivity using high magnetic fields

Saman Ghannadzadeh
Lincoln College, University of Oxford

Trinity Term 2014

A thesis submitted for the Degree of Doctor of Philosophy

This thesis investigates a number of transition-metal coordination polymers and iron-pnictide superconductors through the use of high magnetic fields, low temperatures, and on occasion, high pressures.

The thesis will begin by describing my development of the proximity detector dynamic susceptometer, a novel technique that can be used for magnetometry and transport measurements in high magnetic fields. This technique is highly compact and has no moving parts, making it suitable for use in pressure cells, hence opening the way for a variety of new experiments.

Through high-field magnetometry and other measurements, I will demonstrate that the pressure can be used to directly control the magnetic properties of the polymeric magnet $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyrazine})$. In particular, I observe a transition from quasi-two-dimensional to quasi-one-dimensional antiferromagnetism at 9 kbar, driven by the rotation of the Jahn-Teller axis.

I will then present a series of measurements on two coordination polymers, showing how a small chemical difference can lead to drastically different magnetic properties. I show that $[\text{Cu}(\text{pyrazine})\text{H}_2\text{O}(\text{glycine})_2]\text{ClO}_4$ is an excellent spin-chain, while the sister compound $[\text{Cu}(\text{pyrazine})(\text{glycine})]\text{ClO}_4$ is a dimerised material that shows a spin-gap and is disordered down to very low temperatures, but then undergoes a field-induced phase transition to an ordered phase.

I will also describe a series of pulsed-field measurements of the upper critical field of the iron-based superconductors $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ across the whole of the doping phase diagram. It is shown that paramagnetic pair-breaking effects dominate the critical field when the field is parallel to the crystal planes. In the parent compound the paramagnetic limit is equal to that expected from BCS theory, but becomes significantly enhanced above the BCS limit upon doping. It is shown that the multi-band nature of the superconductivity leads to a convex curvature in the evolution of the critical field as the temperature is reduced.

Acknowledgements

I would like to thank my supervisor **Paul Goddard** for his support, advice, encouragement, humour, and for trusting me with the lab. I also thank **Stephen Blundell** for his invaluable support through my career as a postgraduate student.

This thesis has benefitted greatly from collaborations with a number of people. In particular I would like to thank **Johannes Möller** and **Tom Lancaster** for various projects. Thanks are also due to **Jamie Manson**, **John Schlueter**, and **Jack Wright**, for growing the high quality samples used in this thesis. My work using high pressures would not have been possible without the excellent technical support of **David Graf** (thanks for the crash course into American football) and **Stanley Tozer**.

I am grateful to past and present members of the pulsed-field group: **Isabel Franke**, **Francesca Foronda**, **Junjie Liu**, **John Singleton**, and **Richard Lewin**. I also thank **Roger Johnston**, **Dharmalingam Prabhakaran**, **Moon-Sun Nam**, **Tony Hickman**, and **Robert Storey**.

I thank all members of the Clarendon Laboratory, and specially my friends in the Quantum Matter group (who are too numerous to mention here) for making Oxford the incredible place it is. In particular, I thank my office mates **Johannes Möller** (for putting up with my bad squash skills, and the midnight ice cream rendezvous), and **Ben Williams** (for his unmatched humour, and the photo opportunities).

I am grateful to **Paul Goddard**, **Stephen Blundell**, and **Ben Williams** for proof-reading this thesis.

My final thanks goes to the pulsed-field magnet **HJ45**, which never exploded despite all the abuse it suffered from me, and is now in well-deserved retirement.

This work was supported by **Engineering and Physical Sciences Research Council** through grants EP/H00324X/2 and EP/H00324X/1. A portion of this work was also performed at the National High Magnetic Field Laboratory, USA, which is supported by NSF Cooperative Agreement No. DMR-0654118, the State of Florida, and the DOE. Pressure measurements were performed with technical assistance of David Graf and Stanley Tozer, who are supported by DOE/NNSA Grants No. DE-FG52-10NA29659 and DE-NA0001979. Sample growth by Jamie Manson was supported by NSF Grant No. DMR-1005825. Sample growth by John Schlueter was supported by Argonne national Laboratory, a DOE Office of Science laboratory, operated under Contract No. DE-AC02-06CH11357.

List of publications

1. T. Lancaster, S. J. Blundell, F. R. Foronda, S. Ghannadzadeh, P. A. Goddard, J. S. Möller, P. J. Baker, F. L. Pratt, C. Baines, L. Hang, J. Wosnitza, J. Singleton, C. V. Topping, T. A. W. Beale, J. L. Manson, *The structure-magnetism relationship in a molecule-based magnetic system: magnetic order and quantum disorder in one and zero dimensions*, Phys. Rev. Lett., **112**, 207201 (2014)
2. S. Ghannadzadeh, J. D. Wright, F. R. Foronda, S. J. Blundell, S. J. Clarke, P. A. Goddard, *The upper critical field of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ superconductors*, Phys. Rev. B. **89**, 054502 (2014)
3. S. Ghannadzadeh, J. S. Möller, P. A. Goddard, T. Lancaster, F. Xiao, S. J. Blundell, A. Maisuradze, R. Khasanov, J. L. Manson, S. W. Tozer, D. Graf, J. A. Schlueter, *Evolution of magnetic interactions in a pressure-induced Jahn-Teller driven magnetic dimensionality switch*, Phys. Rev. B. **87**, 241102(R) (2013)
4. A. Kohn, N. Tal, A. Elkayam, A. Kovcs, D. Li, S. Wang, S. Ghannadzadeh, T. Hesjedal, and R. C. C. Ward, *Structure of epitaxial $\text{L1}_0\text{-FePt/MgO}$ perpendicular magnetic tunnel junctions*, Appl. Phys. Lett., **102**, 062403 (2013)
5. S. H. Lapidus, J. L. Manson, H. Park, A. J. Clement, S. Ghannadzadeh, P. Goddard, T. Lancaster, J. S. Möller, S. J. Blundell, M. T. F. Telling, J. Kang, M.-H. Whangbo, and J. A. Schlueter, *Antiferromagnetic ordering through a hydrogen-bonded network in the molecular solid $\text{CuF}_2(\text{H}_2\text{O})_2(3\text{-chloropyridine})$* , Chem. Commun., **49**, 499 (2013)
6. J. L. Manson, A. G. Baldwin, B. L. Scott, J. Bendix, R. E. Del Sesto, P. A. Goddard, Y. Kohama, H. E. Tran, S. Ghannadzadeh, J. Singleton, T. Lancaster, J. S. Möller, S. J. Blundell, F. L. Pratt, V. S. Zapf, J. Kang, C. Lee, M.-H. Whangbo, and C. Baines, *$[\text{Ni}(\text{HF}_2)(3\text{-Clpy})_4]\text{BF}_4$ ($\text{py} = \text{pyridine}$): Evidence for Spin Exchange Along Strongly Distorted $\text{F}\cdots\text{H}\cdots\text{F}^-$ Bridges in a One-Dimensional Polymeric Chain*, Inorg. Chem., **51**, 7520 (2012)
7. J. L. Manson, K. E. Carreiro, S. H. Lapidus, P. W. Stephens, P. A. Goddard, R. E. Del Sesto, J. Bendix, S. Ghannadzadeh, I. Franke, J. Singleton, T. Lancaster, J. S. Möller, P. J. Baker, F. L. Pratt, S. J. Blundell, J. Kang, C. Lee, and M.-H. Whangbo, *Influence of HF_2 -geometry on magnetic interactions elucidated from polymorphs of the metal-organic framework $[\text{Ni}(\text{HF}_2)(\text{pyz})_2]\text{PF}_6$ ($\text{pyz} = \text{pyrazine}$)*, Dalton Trans., **41**, 7235 (2012)

8. 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. of Scien. Instrum., **82**, 113902 (2011)
9. 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 ($M = Li, Na$)*, Phys. Rev. B, **84**, 144416 (2011)

Dedicated to my grandfather

*Tis all a chequer-board of nights and days,
Where Destiny with Men for Pieces plays:
Hither and thither moves, and mates, and slays,
And one by one back in the Closet lays.*
– Omar Khayyám (1048–1131)

Contents

1	Introduction	1
1.1	Low-dimensional magnetism in coordination polymers	3
1.2	Iron-pnictide superconductivity	7
1.3	Outline	13
2	Experimental methods	15
2.1	Generating magnetic fields	16
2.1.1	Pulsed magnets	16
2.1.2	Continuous resistive magnets	18
2.1.3	Superconducting magnets	20
2.2	Magnetisation measurements	20
2.2.1	Pulsed-field compensated magnetometry	21
2.2.2	DC low-field susceptibility	23
2.3	Heat capacity	24
2.4	Muon-spin relaxation	26
3	The Proximity Detector Oscillator	29
3.1	Introduction	30
3.2	Advantages	32
3.3	Experimental details	33
3.4	Theory	36
3.5	Magnetoresistance of circuit elements	39
3.6	Samples	41
3.7	Susceptibility	41
3.8	Magnetisation	44
3.9	Conclusion	46
4	Controlling magnetic interactions of Jahn-Teller active systems with pressure	49
4.1	Introduction	50
4.2	Previous work	51
4.3	Experimental details	54
4.3.1	Piston cylinder cells	54
4.3.2	Pressure calibration and hydrostaticity	56
4.3.3	PDO measurements	59
4.4	Magnetisation	60
4.5	Muon-spin relaxation	64

4.6	Further discussion	67
4.7	Another Jahn-Teller active material: $\text{Cu}(\text{NO}_3)_2(\text{pyz})$	70
4.8	Conclusion	72
4.9	Further work: a second phase transition in $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})?$. . .	73
5	Field-induced transitions in molecular magnets	79
5.1	Introduction	80
5.2	A spin chain: $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$	81
5.3	Field-induced transitions in $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$	84
5.3.1	Results	84
5.3.2	Discussion	89
5.3.3	Bose-Einstein condensation of triplons	93
5.4	Conclusion	96
6	The upper critical field of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ superconductors	97
6.1	Introduction	98
6.2	Experimental details	101
6.3	Results	106
6.4	Discussion	107
6.4.1	Dirty or clean?	111
6.4.2	Single-band model	112
6.4.3	Two-band model	114
6.4.4	Enhancement of the paramagnetic limit	116
6.4.5	$(dH_{c2}/dT)_{T=T_c}$	120
6.4.6	Anisotropy	121
6.4.7	Coherence length and the superfluid stiffness	123
6.5	Conclusion	125
6.6	Further work	126
7	Conclusion and outlook	129
A	Diamond anvil cell measurements	135
	Bibliography	139

Chapter 1

Introduction

“Door meten tot weten - through measurement to knowledge.”
– Heike K. Onnes (1853–1926)

Condensed matter physics is a wide field of research that covers fundamental questions, as well as new cutting-edge technologies. The properties of materials are determined by the Coulomb interactions between the electrons and constituent atoms; the motion of the electrons as governed by the laws of quantum mechanics; and other fundamental laws of physics. Research seeks to address how the microscopic laws of physics lead to the huge diversity of macroscopic behaviour seen in different materials and devices. Furthermore, one is often concerned not just with why a material behaves the way it does, but also how the material properties can be tuned to meet technological needs. In absence of a universal theory that explains the wide range of physical phenomena seen in solid state systems, empirical experimental research continues to be of great importance.

This thesis focuses on investigations of low-dimensional magnetism and superconductivity using high magnetic fields. The magnetic field is an extremely important tool in exploring the physics of materials. It couples directly to the motion of charge carriers and the magnetic moments within a system, which are often the crucial ingredients in determining how the system behaves. Thus the magnetic field has access to the magnetic, electronic, and structural degrees of freedom, and enables

the use of experimental techniques that can reveal the underlying electronic or magnetic properties of the system, which might have been otherwise inaccessible. In some cases strong magnetic fields can noticeably alter the material properties and even induce phase transitions. An important property of a magnetic field is that it is directional, which allows for an exploration of the anisotropy of the electronic and magnetic interactions within a material. Some of the applications of high magnetic fields include: exploring the Fermi surface topology through quantum oscillations [1, 2], aligning spins in magnetic systems [3], and identifying quantum phase transition or inducing new phases [4], amongst others [5].

Often high magnetic fields are needed to sufficiently probe a system and its interactions. For example, an interaction of strength $1\text{ K} \approx 0.1\text{ meV}$ is roughly equivalent to a field of 1 T in energy, meaning that high magnetic fields are required to perturb interactions of even modest strength. High magnetic fields are defined as *magnetic fields whose attainment tests the limit of current technological abilities* [5], and are achieved through the use of steady-field or pulsed-field electromagnets. High-field experiments can be very challenging. This is due to a number of factors which, for example in the case of pulsed magnetic fields, may include (a) the small space in which the high magnetic field is realised and in which the experiment must take place, (b) the presence of significant vibrations, (c) the time-scale within which the experiment must take place (as low as microseconds), and (d) the rate of change of field (as high as 10^8 T/s). These factors can serve to restrict the type of experiments that can be performed and the number of samples that can be investigated.

In Chapter 3 of this thesis I will focus on my development of the proximity detector oscillator dynamic susceptometer, a novel contactless technique that can be used for both magnetometry and transport measurements. This technique is relatively insensitive to the challenges listed above, and is well-suited for use in high magnetic fields. Furthermore, this new technique has a very small spatial footprint and uses no moving parts, meaning that it can be used in pressure cells or rota-

tors, where high-field magnetometry measurements have previously been extremely difficult. Thus it opens the way for a number of new experiments.

The remaining chapters of this thesis then focus on using this technique, in combination with others, to investigate a number of low-dimensional polymeric magnets and iron-pnictide superconductors. These materials are introduced, and the motivation for studying them given, in the following sections.

1.1 Low-dimensional magnetism in coordination polymers

Much of the early work on magnetism has been performed on inorganic elements and alloys [6], partly due to the availability and prevalence of these materials, and also due to the belief that these would most easily reveal information on the underlying physical processes [7]. While such work has been relatively fruitful,¹ it suffers from several disadvantages for our purposes. One is that these materials have relatively large magnetic interactions that may even cause ordering at room temperature. The large energy scale of the interactions, which can be as high as ~ 1000 K, means that extremely high fields of ~ 1000 T are required to probe the magnetism. Another disadvantage is often the difficulty of modifying such systems in a desired and controlled manner without severely distorting the crystal structure or the electronic behaviour [9].

However, it has now become recognised that it is possible to experimentally study fundamental physical processes in chemically complex systems, such as transition-metal coordination polymers [7]. These are molecular systems that consist of a regular array of transition-metal spin centres, linked together by halogens or coordination molecules, which act as bridging ligands. The magnetism is facilitated by the unpaired electrons of the transition metal, and the bridging ligands, which readily mediate magnetic exchange between the metal centres.

¹Perhaps one of the most significant breakthroughs was the discovery of magnetic tunnelling junctions [8], which are now the basis for data storage in computer hard disks.

Through the use of ligands with different exchange strengths, and variations in the metal–ligand environment, it becomes possible to introduce anisotropy into the system, where the strength of the magnetic exchange along different crystal directions is different. If this anisotropy is significant, then a quasi-low-dimensional system has been realised. In a quasi-two-dimensional (Q2D) system, the exchange between neighbouring spins within a two-dimensional plane is significantly larger than the magnetic exchange between two spins on different planes. Alternatively, in a quasi-one-dimensional (Q1D) system, the system has strong magnetic coupling along the chains, whereas the inter-chain coupling is much weaker.

In coordination polymers often the spins do not prefer a specific direction, and thus the magnetism can be described by the Heisenberg Hamiltonian,

$$\mathcal{H} = J \sum_{\langle i,j \rangle_{\parallel}} \mathbf{S}_i \cdot \mathbf{S}_j + J_{\perp} \sum_{\langle i,j \rangle_{\perp}} \mathbf{S}_i \cdot \mathbf{S}_j$$

where J is the strength of exchange coupling within the planes (in Q2D systems) or chains (in Q1D systems), $J_{\perp}$ is the exchange normal to the planes or chains, and the summations are over the unique nearest neighbours between which the exchange couplings take place.² In a perfect Heisenberg low-dimensional system with $J_{\perp} = 0$, the presence of fluctuations means that system will not reach long-range ordering at any temperature down to absolute zero, as embodied in Mermin-Wagner theorem [10]. However, in physical systems a small $J_{\perp}$ is always present. This small exchange coupling becomes important at low temperatures, and means that long-range ordering at finite temperatures becomes possible, although the ordering temperature will be significantly lower than that of fully three-dimensional systems. The presence of anisotropic interactions, low dimensionality and quantum fluctuations in low-dimensional magnets allows for the emergence of interesting quantum phenomena, for example the formation of a Haldane gap or spin-Peierls transition [7].

Coordination polymers have a number of important advantages. These include:

²Note that through this thesis I use the single- J convention, such that in a system with just two exchange-coupled spin-1/2 spins, the energy difference between the $S = 0$ singlet and $S = 1$ triplet at zero magnetic field is J .

- The rich carbon-based chemistry of the molecular ligands, which allows for synthesis of highly tuneable systems. Through chemistry it is possible to modify the magnetic centres, the exchange ligands, and the surrounding molecular groups [11, 12].
- The solution-based ‘self-assembly’ chemistry of the growth process, which means that the samples are often high quality large single crystals [13].
- The low values of the exchange couplings, typically of order of 10 K [3], which means that magnetic fields ~ 10 T can be enough to probe the magnetic properties. Thus direct laboratory access to the magnetism becomes possible.

Coordination polymers are currently subject to significant global research interest [7]. This stems partially from their high degree of tunability, which allows for controlled modification of the system structure, and enables for a systematic study of the effects on magnetic behaviour. The ability to synthesise materials with specific structures that mediate magnetic interactions means that there is huge potential in the use of coordination polymers for bespoke design of materials for technological applications, as well as testing grounds for investigating models of magnetism [9]. Finally the tunability of the systems, and the almost ‘Lego’-like manner in which the structure can be designed, means that it may be possible to use custom-designed molecular magnets as purely-magnetic analogues of more complex systems where it may be desirable to isolate the magnetic behaviour from other effects, for example in cuprate superconductors.

The polymeric magnets considered in this thesis are based on $S = 1/2$ Cu^{2+} ions, and use three different bridging ligands: (a) pyrazine ($\text{C}_4\text{H}_4\text{N}_2$, abbreviated as *pyz*), (b) glycine ($\text{C}_2\text{H}_5\text{NO}_2$, abbreviated as *gly*), and (c) the linear bifluoride ion $[\text{HF}_2]^-$, which forms via strong, yet flexible, $\text{F} \cdots \text{H} \cdots \text{F}$ bonds. The structure of pyrazine and glycine ligands are given in Fig. 1.1. Pyrazine is an aromatic ring that is known to be an effective mediator of magnetic exchange within these systems, with $J \sim 10$ K [3]. To ensure charge neutrality counter-ions such as $[\text{ClO}_4]^-$ or $[\text{PF}_6]^-$ are also used. These counter-ions tend to position themselves in the empty spaces

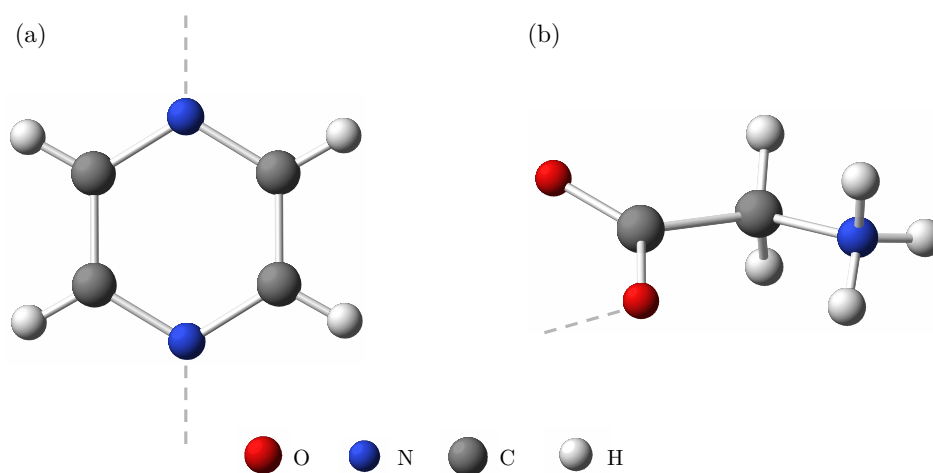


Figure 1.1: Two of the ligands used in the compounds discussed in this thesis: (a) pyrazine, and (b) glycine. The dashed lines indicate bonds to other parts of the structure.

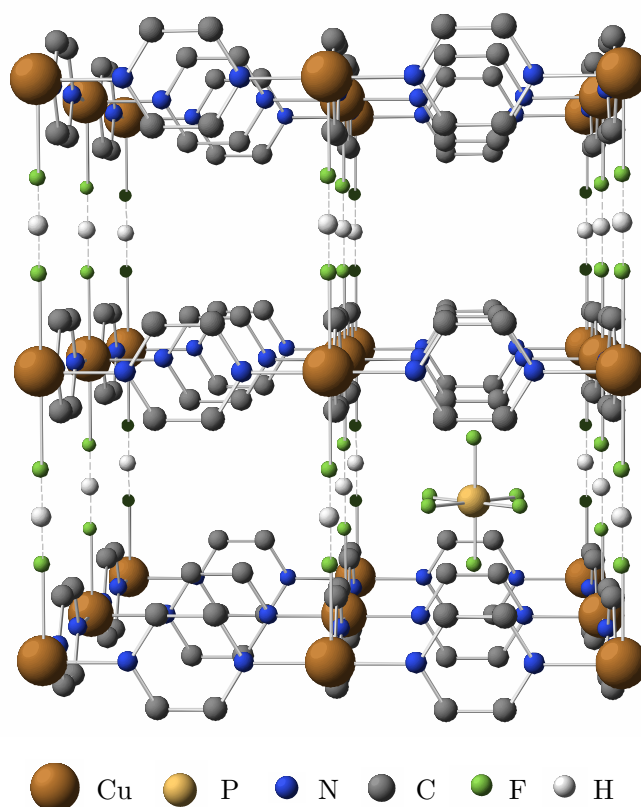


Figure 1.2: The coordination polymer $[\text{Cu}(\text{pyrazine})(\text{HF}_2)]\text{PF}_6$. Pyrazine and HF_2 are the bridging ligands, and also act as the exchange pathways. PF_6 fills the empty space between the planes and acts as a counter-ion, ensuring charge neutrality. For clarity, the H atoms on the pyrazine are not shown, and only one of the eight PF_6 counter-ions is shown. Dashed lines represent $\text{H} \cdots \text{F}$ bonds.

between the planes or chains. In the notation used in the rest of this thesis I will omit the charge on the ligand or counter-ion.

The structure of an archetypal coordination polymer $[\text{Cu}(\text{pyz})_2(\text{HF}_2)]\text{PF}_6$ is given in Fig. 1.2 [3, 14]. This system consists of Cu atoms that are joined in planes by Cu–pyz–Cu bonds. The $\text{Cu}(\text{pyz})_2$ planes are then connected via HF_2 ligands, forming the overall cubic structure of the system. The counter-ion PF_6 is placed in the centre of each cube. In this compound, the pyrazine molecules mediate strong antiferromagnetic exchange within the planes, whereas as the HF_2 ligands mediate a much weaker inter-plane coupling. Therefore this system becomes a Q2D antiferromagnet, as confirmed by magnetometry measurements [3], giving $J \approx 12.4$ K and $J_\perp \approx 10^{-2}J$. One can see how the use of different ligands can give rise to diverse array of different magnetic systems, including quasi-three-dimensional [15], quasi-two-dimensional [3, 12, 16], and quasi-one-dimensional [12, 17–19] spin networks, as well as spin-ladders [20, 21] and geometrically frustrated systems [22].

This thesis will focus on the tunability of coordination polymers, and the ability to control the magnetic parameters and behaviour via external parameters. In particular, in Chapter 4 I will discuss how the application of high pressures allows one to control the magnetic exchange couplings in $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyrazine})$, tipping the balance of interactions and leading to a change in the magnetic dimensionality. Chapter 5 will discuss how a small modification at the synthesis stage can lead to a huge change in the magnetic properties, causing the formation of an unusual magnetic ground state in $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$ that allows for the magnetic field to control the energy levels, leading to a field-induced phase transition.

1.2 Iron-pnictide superconductivity

Superconductivity was discovered serendipitously in 1911 by Heike K. Onnes, who was investigating the validity of the Drude theory of transport at low temperatures. Onnes found that pure mercury, upon cooling to a critical temperature $T_c \approx 4.2$ K, undergoes a sudden transition to a state with zero DC electrical resistance. The

discovery of this so-called superconducting phase, amongst other low-temperature work, won Onnes the Nobel prize two years later in 1913 [23]. Yet, despite the passage of more than a century, a full theoretical understanding of the superconductivity seen in a range of materials remains elusive, and superconductivity to this day remains one of most intensely studied subjects in physics.

The significant yet intricate effect of magnetic fields on superconductivity was first investigated by Meissner, who discovered that a superconductor will actively expel and exclude an applied magnetic field at temperatures below T_c [24, 25]. This effect now bears his name, and cannot be attributed to a metal with zero resistivity, but is an intrinsic property of the superconducting state itself [26]. The presence of the Meissner effect is now the universally accepted signature of a superconducting phase.

The problem of superconductivity was thought to have been solved in 1957 by Bardeen, Cooper, and Schrieffer (BCS) [27], who showed that electron-phonon interactions lead to formation of pairs of electrons with opposite spin and momentum (now called Cooper pairs). It was demonstrated that this brings about the formation of an energy gap and a coherent superconducting state that can last over “miles of dirty lead cable” in Bardeen’s own words [5]. The BCS theory could account for all the features seen in superconducting materials of the day [26, 28], and so the phenomena of superconductivity was assumed to be fully accounted for.

A particular prediction of the phonon-mediated coupling in BCS theory is that superconductivity becomes impossible above ~ 30 K [27, 28]. This assumption was disproven in 1986 upon the discovery of “possible high- T_c superconductivity in the Ba-La-Cu-O system” by Bednorz and Müller [29].³ The remarkable discovery of a superconductor that violates the conventional BCS model led to an unprecedented resurgence in the field of superconductivity,⁴ and soon afterwards a range of similar high- T_c superconductors were discovered, with a Hg-based ceramic having the high-

³The 1987 Nobel physics prize was awarded to Bednorz and Müller for this discovery.

⁴This sudden resurgence was highlighted by the marathon session on high- T_c superconductivity at the American Physical Society’s March meeting in 1986, now known as the “Woodstock of Physics”. It is estimated that around one-third of all physicists over the world tried to contribute to the topic [30].

est T_c of 133 K at ambient pressure [31]. These unconventional superconductors all have a highly two-dimensional structure and are based on layers of Cu–O atoms, and became known as ‘cuprates’. Despite intense research activity, the underlying mechanism for superconductivity in these materials still remains not understood.

It seemed that the presence of Cu–O layers was crucial for high-temperature superconductivity. However, this was changed in 2008 by the discovery of “superconductivity at 43 K in an iron-based layered compound doped system $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ ” by Takahashi *et al.* [32]. The discovery of superconductivity with such a high critical temperature in a material that contains iron, an element that is frequently ferromagnetic, came as a surprise to all. This is because magnetism is thought to be antagonistic to superconductivity, such that in the BCS model magnetic interactions lead to the breaking up of the spin-singlet Cooper pairs [26]. The discovery of iron-based superconductivity triggered a second tsunami of research on superconductivity [33–35], and a wide number of Fe-based superconductors have been discovered to date. After almost three decades of research in cuprates, iron-pnictides now provide an alternative path into research in high- T_c superconductivity. It is hoped that study of Fe-based superconductors will lead to new ideas and insights into the mechanisms of the unconventional superconductivity.

Similar to cuprates, Fe-based superconductors have a layered structure, consisting of FeX layers, where X is a pnictogen (As, P) or chalcogen (Se, Te) atom. These layers are formed out of edge sharing FeX_4 tetrahedra, with the Fe atom sitting at the centre. The simplest Fe-based superconductors are FeTe and FeSe, as shown in Fig. 1.3. Superconductivity is thought to be associated with these layers [36]. In more complex materials, the FeX layers are separated by spacer species. It is common to group these into ‘families’ based on stoichiometry of the spacer layer. The most common families are [37],

- the “111” family: $(\text{Li, Na})\text{FeAs}$
- the “122” family: $(\text{Ca, Sr, Ba, Eu, K})\text{Fe}_2\text{As}_2$
- the “1111” family: $(\text{La, Ce, Pr, Nd})\text{OFeAs}$

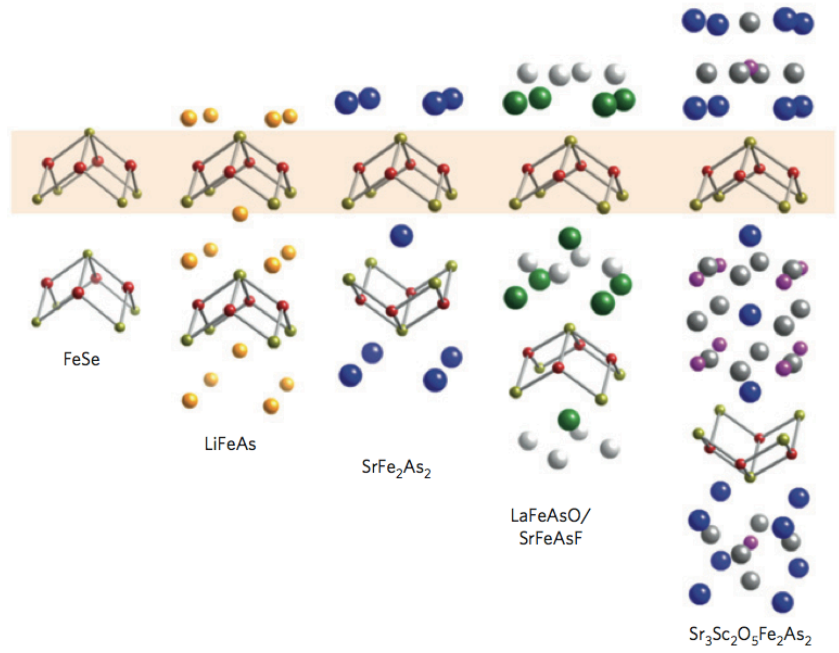


Figure 1.3: Crystallographic structure of the iron-based superconductor families, showing the most common tetragonal structures that are known to mediate superconductivity. All compounds contain a FeX layer as highlighted, with X = pnictogens or chalcogens. From Ref. [36].

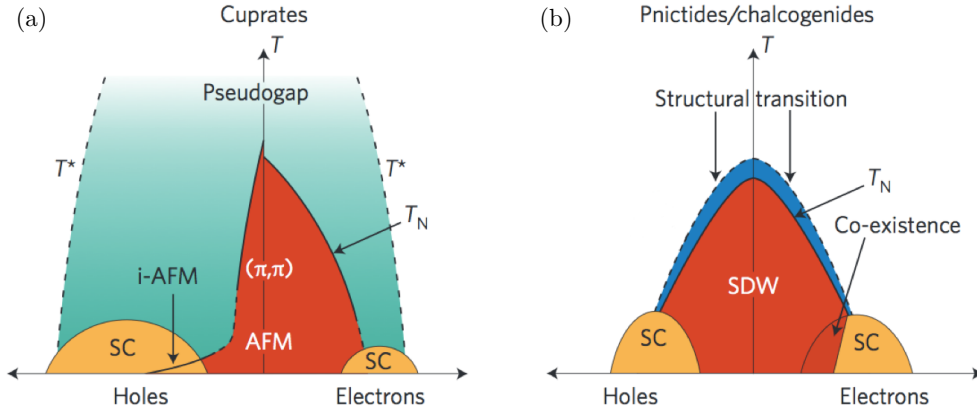


Figure 1.4: Typical phase diagrams of (a) cuprates and (b) iron-pnictides, as a function of electron or hole doping. In both systems the parent compound is usually antiferromagnetic and non-superconducting at low doping, and becomes superconducting upon some doping. Superconductivity in pnictides can also be induced by pressure. The presence of a pseudogap phase in cuprates is a marked difference between the two sets of compounds, although hints of a pseudogap have been seen in some iron-pnictides [40]. Note that each specific material has a unique phase diagram that may be slightly different from what is shown here. From Ref. [41].

Note that this is not a comprehensive list and more complex systems exist, for example the iron-arsenide-oxides (such as $\text{Sr}_3\text{Sc}_2\text{O}_5\text{Fe}_2\text{As}_2$) [38] or the recently discovered intercalated chalcogenides [39].

The generic phase diagrams of cuprate and iron-pnictide superconductors are given in Fig. 1.4. In both systems the parent compound tends to be non-superconducting, and is insulating in case of cuprates, or semi-metallic in case of Fe-based systems. Both systems undergo a transition to an antiferromagnetic phase upon cooling below a temperature T_N . In pnictides the magnetic ordering is stripe-like [36] and is accompanied by a structural transition from tetragonal to orthorhombic structure, although whether the magnetic and structural transition occur together or separately depends on the family. For example, in “122” systems the transitions occur almost simultaneously [42], but in the “1111” family they are far from each other [43]. Superconductivity is induced by (a) electron or hole doping, for example by replacing one atom with another atom from a nearby group [44], (b) application of physical pressure [45], or (c) modification of structure by isovalent chemical substitution of one atom by another (*i.e.* chemical pressure) [46]. With the application of these perturbations the system is tuned away from magnetism, and bulk superconductivity eventually appears, leading to formation of a superconducting dome in the phase diagram. Interestingly, in pnictide superconductors the highest T_c tends to occur in the vicinity of the point at which the magnetism is completely suppressed. Further application of doping/pressure past this leads to suppression of T_c , and the material eventually becomes non-superconducting again. See Fig. 1.4.

Traditionally, magnetism and superconductivity have been thought to be at odds to each other. However, the proximity of the antiferromagnetic and superconducting phases in cuprates and iron-pnictides hints that interplay between superconductivity and magnetism may play an important role in unconventional superconductivity. It is now generally believed that magnetic fluctuations are the source of the unconventional superconductor pairing [35], in a similar way that electron-phonon interactions

are responsible for formation of BCS Cooper pairs. The resulting superconducting gap symmetry is suggested to be *d*-wave in cuprates [30, 47] and *s*-wave in iron-pnictides [35, 48].

One of the main properties of these materials is the high value of the upper critical field (H_{c2}) above which the superconducting state becomes destroyed. This can be as high as tens or even hundreds of tesla, especially in the case of optimally doped systems [49]. Application of fields above H_{c2} breaks the superconducting pairs (for details see Chapter 6) and allows for characterisation of the low-temperature regime ($T < T_c$) in the normal state, which would have been otherwise inaccessible. For example, high magnetic fields have facilitated the observation of quantum oscillations in clean samples [50], providing a direct measurement of the Fermi surface. The ability to perform measurements at high magnetic fields is critical for research in superconductivity [5], and enables detailed exploration of the phase diagram. Pnictide superconductors are found to be less anisotropic and have lower H_{c2} [51] than cuprates. This allows for further exploration of the phase diagram with laboratory-accessible fields.

As well as for fundamental science, the exploration of the high-field behaviour and determination of H_{c2} is also important for technological applications where high magnetic fields may be present [5]. This for example includes power generation and transmission, magnetic resonance imaging, and particle accelerators, amongst others. The high T_c , high H_{c2} , and relative isotropy of Fe-based superconductors makes them potential candidates for use in industry [52].

As it is often application of doping that induces superconductivity in Fe-based superconductors, it is important to characterise its effect on the magnetic and electronic structure of these systems. Chapter 6 of this thesis will focus on high-field characterisation of the “111” superconductor NaFeAs, when doped with cobalt. In particular, the upper critical field of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ is measured across the whole of the doping phase diagram. The measurement of H_{c2} , as well as being important in its own right, allows for extraction of other physical parameters such as the co-

herence and penetration depths. Furthermore, the behaviour of H_{c2} as a function of temperature provides hints toward the origin of the field-induced pair-breaking in these systems.

1.3 Outline

This thesis is organised as follows:

Chapter 2 The various methods of achieving high magnetic field are briefly described. Also discussed are the measurement techniques of pulsed-field magnetometry, low-field susceptibility, heat capacity, and muon-spin relaxation.

Chapter 3 The development of the proximity detector dynamic oscillator, a novel radio-frequency based system that is capable of operating in high magnetic fields and high pressures, is outlined. This is the basis measurement technique used in this thesis.

Chapter 4 It is shown that high pressures can be used to take control of the magnetic exchange parameters in $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyrazine})$, where the presence of a Jahn-Teller active metal centre leads to a dramatic pressure-induced change in magnetic dimensionality from quasi-two-dimensional to quasi-one-dimensional.

Chapter 5 The magnetic behaviour of two coordination polymers that were synthesised using the same starting chemicals and growth process is investigated. It is shown that one system is a quasi-two-dimensional magnet that orders at very low temperatures, while the other is a quantum-disordered paramagnet down to absolute zero, but undergoes a phase transition as a function of field.

Chapter 6 The upper critical field of the iron-pnictide superconductor $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ is measured across the whole of the doping phase dia-

gram. The behaviour of the upper critical field as a function of temperature, and the effect of doping on this, is discussed. It is shown that $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ is likely a multi-band superconductor, and that with the magnetic field parallel to the Fe–As planes, the Cooper pairs are broken by paramagnetic effects. The coherence length, penetration depth, and other physical parameters, are extracted and discussed.

Chapter 7 An overview of the results obtained in different chapters is given, and an outlook of future work is presented.

Chapter 2

Experimental methods

“More than the diamond Kooh-e-Noor, which glitters among their crown jewels, they prize the dull pebble which is wiser than a man, whose poles turn themselves to the poles of the world, and whose axis is parallel to the axis of the world. Now, their toys are steam and galvanism.”

– Ralph W. Emerson (1803–1882)

The above quote reflects the fascination of Victorian England with magnetism and electricity. Ever since the unification of electromagnetism by Maxwell, Ampère, and others, there has been a race to reach higher and higher magnetic fields using bigger, more powerful, and more efficient electromagnets. Today, a wide range of magnet systems are available, from the extreme of kilotesla explosive pulsed magnets to the more mundane room-temperature electromagnet. The majority of the experimental work presented in this thesis was performed in high magnetic fields generated by pulsed, steady resistive, or superconducting magnets. Here each magnet system is briefly discussed, including a description of the advantages, disadvantages, and the method of operation. Additionally, the techniques for measurement of pulsed-field magnetisation, low-field magnetic susceptibility, heat capacity, and muon-spin relaxation are described.

2.1 Generating magnetic fields

The design of high-field magnets requires a good knowledge of the physics of magnets, understanding of the material properties, and a large amount of computer-aided optimisation. The highest magnetic fields can only be provided by solenoid electromagnets, which provide the most efficient design [53].

2.1.1 Pulsed magnets

Pulsed magnetic fields are currently the only method of generating magnetic fields above 45 T, and 100 T is regularly accessed at the National High Magnetic Field Laboratory (NHMFL), Los Alamos, USA. Even higher fields can be achieved in destructive single-turn magnets, and explosive flux compression techniques have produced fields of order of 2800 T. In these systems a magnetic-field pulse is generated by pushing a large pulse of current through a resistive magnet, typically made of copper alloys. The maximum field is limited by the amount of resistive heating that is generated within the magnetic coil and the amount of the Lorentz-force stress that the magnet can withstand. The stress is roughly proportional to magnetic field strength squared and can be up to several GPa [54, 55]. The magnets are usually energised by releasing the energy stored in a series of capacitors or an inertial motor generator.

The advantages of pulsed magnets are the high magnetic fields and the low operational cost. However, disadvantages include the small magnet bore which restricts the sample space, and the long cooling time required between each pulse. The high dB/dt is useful in that it will amplify the measurement signal in compensated magnetometry experiments, however it can cause heating via eddy currents in metallic samples. Furthermore, the short pulse-width means that often experiments are performed in semi-adiabatic conditions and thus the magnetocaloric effect [56] can become a problem.

My measurements were carried out at the Nicholas Kurti High Magnetic Field Laboratory at Oxford [55]. The system has a total stored energy of 0.8 MJ stored

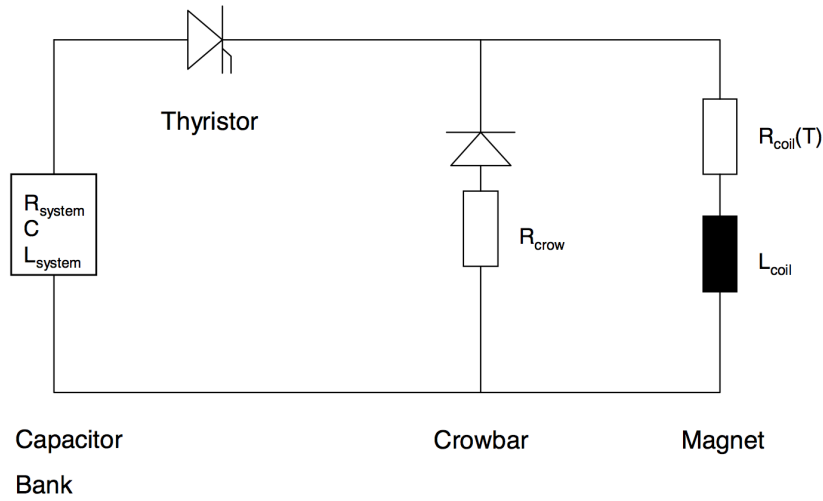


Figure 2.1: Schematic diagram of the pulsed field facility at the Nicholas Kurti High Magnetic Field Laboratory.

in four sets of 8 mF, 7 kV capacitor banks, and is capable of reaching fields in excess of 45 T — the highest magnetic field in the UK. The number of capacitors for each pulse can be varied, allowing for dB/dt of 9000 to 18000 T/sec.

A schematic diagram of the facility is given in Fig. 2.1. The system effectively forms a very large LCR circuit, with the inductance being defined by the magnet, the capacitance being defined by the capacitor bank used to energise the magnet, and the resistance defined by the the magnet coil. The LCR circuit is in series with a high voltage thyristor, which is used as a fast-acting bi-stable switch, meaning that it will switch from the insulating to conducting when triggered and will stay conducting as long as the voltage across is is not reversed. The system operates as follows: once the capacitors are charged to the desired voltage, the thyristor is triggered by a laser. Thus the LCR circuit is closed, and current begins to flow through the magnet. The LCR circuit is underdamped, and if left to its own will begin to resonate. To prevent this a diode and ‘crow-bar’ resistor are placed in parallel, which also stop the capacitors from being negatively charged. Thus the magnetic-field pulse is produced by allowing the first half-oscillation of the LCR circuit. The width of the pulse is half the LCR oscillation period $\sqrt{LC}/2\pi$, and can be varied by changing the capacitance as shown in Fig. 2.2.

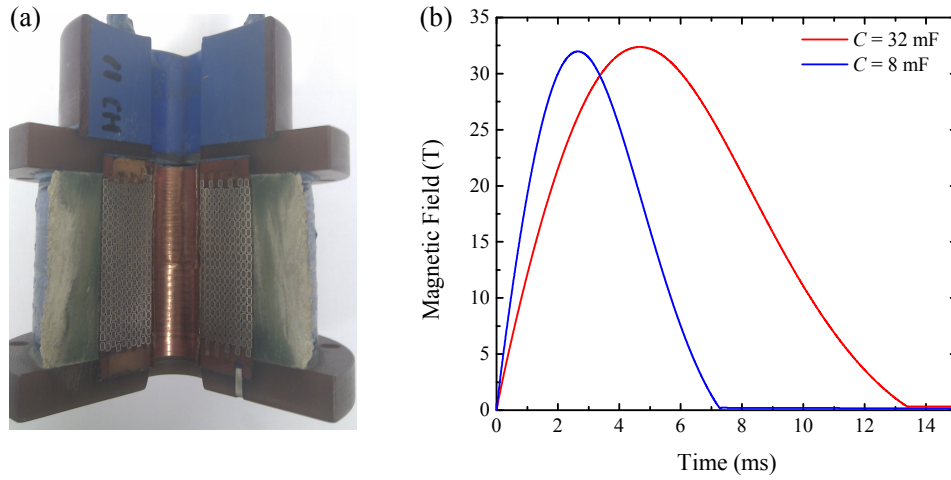


Figure 2.2: (a) Cross-section image of a pulsed field magnet, and (b) the typical profile of the produced magnetic field, showing the change in pulse-width with capacitance.

The pulsed-field work presented in this thesis was done using magnet HJ45, a 45 T magnet with a bore of 1.5 cm. The magnet coil is formed out of hardened copper, encased in steel sheeting for added strength as shown in Fig. 2.2(a) [55, 57]. The magnet is structurally reinforced using a combination of Stycast 2850, a strong epoxy with good thermal conductivity, and Zylon, a synthetic fibre with a tensile strength 1.6 times that of Kevlar [58]. The magnet is immersed in liquid nitrogen, and it typically takes 60 minutes for the magnet to cool down after a 32 mF, 45 T pulse, which has a nominal energy of 0.32 MJ.

2.1.2 Continuous resistive magnets

Continuous steady-fields are produced by passing a large DC current through a resistive electromagnet. The larger the current the larger the magnetic field. However an increase in the current means more resistive heating, which needs to be dissipated to prevent a meltdown. Steady-field resistive magnets are limited by the heating and the amount of cooling that can be provided, as well as the maximum Lorentz-stress that the magnet can withstand. The advantage of such magnets is the large magnet bore and the high homogeneity of the field, which allows for a large sample space and hence for a large variety of different experiments; and the low dB/dt which al-

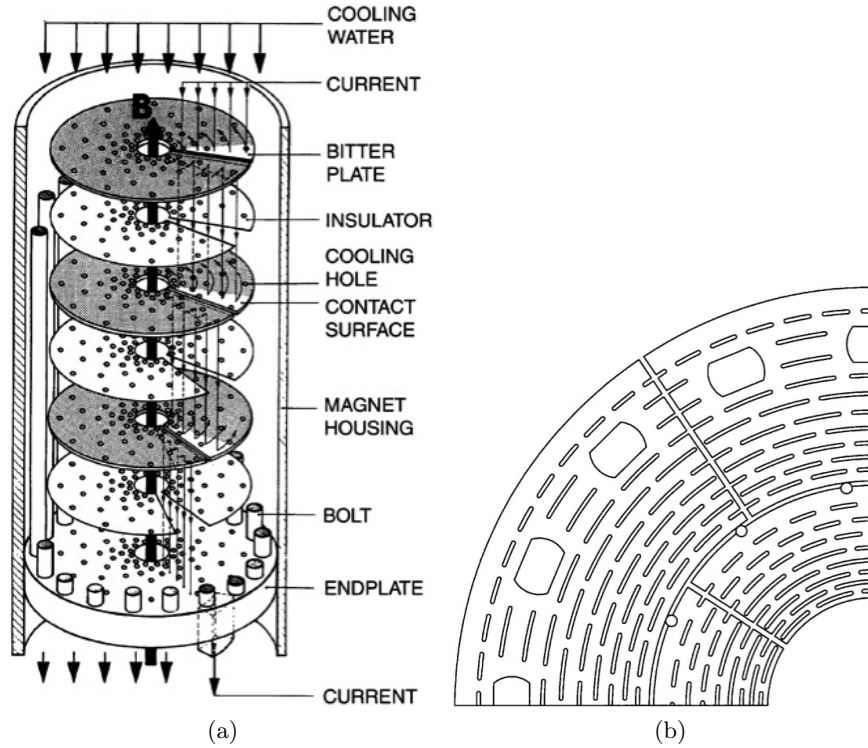


Figure 2.3: Schematic diagram of (a) a typical Bitter magnet, and (b) the improved Florida-Bitter disc [53].

lows for isothermal conditions. However, this is offset by the high operational costs due to the complexity of the magnet, the amount of current needed, and the cooling requirements.

Experiments were performed using facilities at NHMFL, Tallahassee, USA. The magnetic fields were created by a Florida-Bitter magnet, an improved version of well-known Bitter design [59]. A Bitter magnet is formed of circular disks which are interleaved with insulators and stacked to form a monolayer helical winding. The insulators cover less than 360° to allow contact between the plates. The magnet is cooled by high-pressure water flowing through circular holes in the plates, as shown in Fig. 2.3a. The Florida-Bitter design improves on this by replacing the circular holes with long thin slits, which optimise the cooling without affecting the resistance, improve the power density three-fold, and reduce the Lorentz force stress [53]. Fields up to 38 T with a 32 mm bore have been achieved with this design, at a nominal power usage of 20 MW.

2.1.3 Superconducting magnets

In superconducting magnets the solenoid is made of superconducting wires. The magnet is immersed in cryogens in order to cool it below the critical temperature, at which point the wires become superconducting, showing zero resistance to direct current. Superconducting magnets have excellent homogeneity and field quality, and do not suffer from the vibrational noise present in resistive magnets [53]. The magnet is relatively cheap to run, with the main operational cost being that of the cryogens required to keep the magnet cool. Commercially available magnets are made of low-temperature superconductors, cooled using liquid ^4He . The maximum field is limited by the critical current density and temperature, the desired magnet bore and homogeneity, and the mechanical properties. One challenge in superconducting magnet design is safe handling of a magnet quench, where the magnet coil switches from the superconducting to its normal phase near-instantaneously due to fluctuations in temperature, current, or field. This leads to a sudden de-energisation of the magnet and significant mechanical stress. Currently fields up to 22 T are available commercially.

To energise the magnet a small portion of the superconducting coil is put into the normal state via a heater, and the magnet current is increased until the desired magnetic field has been reached. The magnet can then be placed in persistent mode by turning off the heater switch, creating a loop of current that should theoretically last as long as the magnet is below the critical temperature. However, in reality small resistances within the magnet joints prevent this.

2.2 Magnetisation measurements

The magnetisation $\mathbf{M}$ is defined as the total moment per unit volume of the sample, and is related to the magnetic flux density $\mathbf{B}$ and the magnetic field strength $\mathbf{H}$ via

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) .$$

Under most circumstances the magnetic moment is parallel to the applied magnetic field, and thus the magnetisation is usually given as a scalar. By tracking the variation of magnetisation as a function of magnetic field, temperature, pressure, or other external perturbations, one can learn a lot about the nature of the magnetism and magnetic interactions within a material [3].

2.2.1 Pulsed-field compensated magnetometry

In pulsed magnetic fields the magnetisation can be measured using a compensated extraction magnetometer. This consists of a system where the sample is placed inside a magnetometer coil, and the induced voltage in the coil during the magnetic field pulse is measured. The induced voltage is given as

$$V = V_{\text{field}} + V_{\text{sample}},$$

where $V_{\text{field}} \propto dH/dt$ and $V_{\text{sample}} \propto dM/dt$ are due to the change in the applied field and sample magnetisation respectively, as defined by Lenz's law. In order to make a successful measurement the signal produced by the applied field H must be removed. This is achieved via a multistep procedure. Firstly, the magnetometer coil is made out of out of high-purity 50 gauge wire, which is wound 1000 turns in one direction, and then counter-wound 500 turns in the opposite direction. Fractions of a turn are then added or removed as needed, so as to equalise the effective area of the two portions of the coil. Such compensation means that the application of a uniform magnetic field H will not induce a voltage within the coil; however the magnetisation of the sample placed inside the coil will be non-uniform, inducing different voltages in the counter-wound portions of the coil and resulting in an overall signal. To further fine-tune the compensation, an additional single-turn compensation coil is used. The signal from the magnetometer coil and the compensation coil are fed to custom-designed electronics, where the two signals are added or subtracted such that there is no induced voltage in an empty-coil 10 T shot. The signal is also amplified as needed, up to a factor of 250,000.

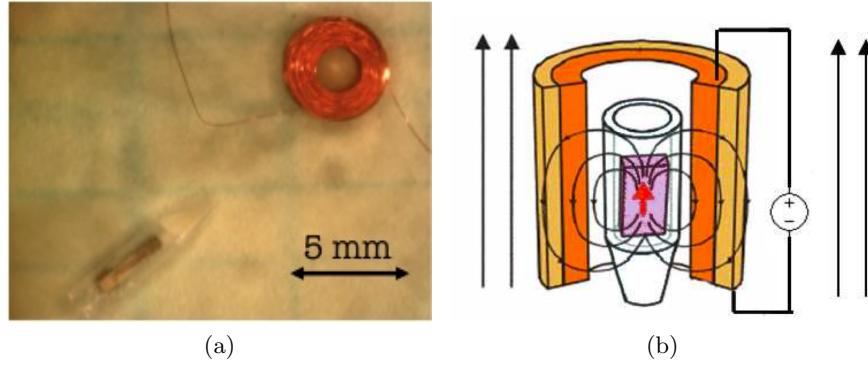


Figure 2.4: (a) Image of the magnetometer coil, and a sample inside an ampoule. (b) Schematic diagram of the measurement position, with the sample inside the coil [60].

To measure the applied magnetic field a calibrated pickup coil is used. The voltage across the pickup coil is $-a dB/dt$, where a is the coil area. The magnetic field can then be calculated via integration. The magnetometer setup is shown in Fig. 2.4. The sample is placed in a 1.3 mm diameter ampoule made of polychlorotri-fluoroethylene [61]. The measurement probe is designed such that the sample can be extracted from the magnetometer coil *in-situ*. For each measurement two magnetic field pulses are performed under identical conditions, with the sample in and out; and the results subtracted from each other. In the resulting dataset, the remaining signal is due to the rapid change of the sample magnetic moment,

$$\begin{aligned} V &\propto -\frac{dM}{dt} \\ &\propto -\frac{dM}{dB} \frac{dB}{dt}. \end{aligned}$$

Therefore the sample moment can then be extracted by dividing by $\frac{dB}{dt}$ and integrating with respect to the magnetic field. Notice how the sample signal is amplified by $\frac{dB}{dt}$, which is of order of 10^3 T/s. This makes this technique extremely sensitive to small changes in magnetisation, such as in spin-flip transitions. The measured magnetisation can then be converted to absolute values by calibration to low-field measurements performed using other techniques.

2.2.2 DC low-field susceptibility

The low-field static molar susceptibility is defined as

$$\chi = \frac{m_N}{m} \frac{\mu}{H}$$

where μ is the measured moment, m is the sample mass, and m_N is the sample molar mass. Evolution of the magnetic susceptibility can provide an insight into the magnetism of the sample, such as the average magnetic moment, the nature of magnetic interactions, and the critical temperature of any phase transitions. Given suitable theoretical models, the data can also be fitted to extract further information on exchange interactions within the sample.

A Quantum Design Magnetic Properties Measurement System (MPMS) [62] was used for low-field measurements. This system uses a 7 T superconducting magnet, and the sample temperature is controlled in the range $1.8 \text{ K} \leq T \leq 400 \text{ K}$ by a variable temperature insert (VTI) and a heater. The magnetometer consists of four-loops of superconducting wire in the ‘second derivative’ configuration, with the upper and lower loops having the opposite sense to the two loops at the centre, as shown in Fig. 2.5. This configuration is insensitive to any linear gradient in the external field. The superconducting wire is then coupled to a radio-frequency Superconducting QUantum Interference Device (SQUID), and thus acts as a flux transformer [63].

Single crystal samples were oriented inside a glucose ampoule using Apiezon N grease. The capsule was placed in the centre of a thin drinking straw, which was then mounted in the MPMS. The magnetic moment is measured using the DC SQUID option, where the sample is moved mechanically through the magnetometer coils. The sample moment produces a current in the pickup coils that is proportional to the flux that crosses each coil [63]. This current is then passed on to the secondary winding of the flux transformer, which is coupled to the SQUID. The SQUID signal is converted to a voltage that is proportional to the total flux through the pickup coils. As the sample is moved through the magnetometer, the resulting voltage takes

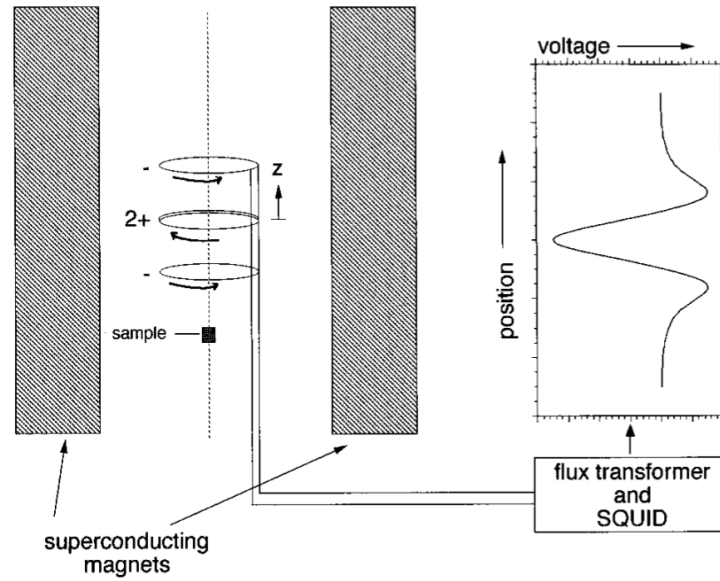


Figure 2.5: Schematic diagram of the Magnetic Properties Measurement System magnetometry setup. Diagram from Ref. [63].

the form of a $\sin z/z$ function, where z is the position within the magnetometer coils (see Fig. 2.5). The sample moment is calculated by fitting to this voltage.

Best results are obtained with a sample that shows dipolar field distribution: that is, the sample must be significantly smaller than the pickup coils, but large enough to give a good signal [63, 64]. Care must be taken to precisely centre the sample with respect to the pickup coils, and to make sure that the sample holder is symmetrical with respect to the sample position. Failure to do so will result in poor fitting, leading to erroneous results that may resemble phase transitions [65].

2.3 Heat capacity

The heat capacity is defined as,

$$C_p = \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta Q}{\Delta T} \right)_p$$

where ΔQ is the heat input that causes a temperature change ΔT within the sample at constant pressure p . The heat capacity is closely related to the system entropy and is therefore a sensitive probe of phase transitions [66].

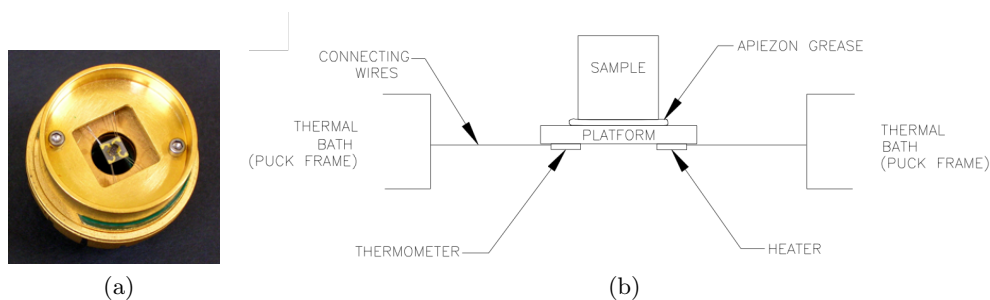


Figure 2.6: (a) Picture and (b) schematic diagram of the PPMS heat capacity setup. Diagram from Ref [67].

The heat capacity was measured using a Quantum Design Physical Properties Measurement System (PPMS). This system consists of a 14 T superconducting magnet, and a VTI with a temperature range of $1.8 \text{ K} \leq T \leq 400 \text{ K}$. The PPMS is highly customisable and has a variety of sample platforms for heat capacity, AC and DC transport, Hall effect, and AC magnetisation measurements [62]. The calorimeter platform consists of a thin $3 \times 3 \text{ mm}$ alumina crystal, with a heater and a thermometer on one side. The calorimeter is isolated from the rest of the system, and is connected to a heat-sink by 8 thin wires which provide thermal and electrical links [67, 68]. The sample is mounted on the calorimeter using Apiezon N grease, which has good thermal conductivity, and the system is pumped down to 0.01 mTorr. The heat capacity is measured by a heat-pulse relaxation technique: for each measurement the sample platform is heated by a heat pulse of width $\Delta t = \tau$, after which the platform temperature is measured for a time 2τ , where τ is the time constant of the thermal relaxation between the sample platform and the heat sink [68]. Knowing the thermal conductivity between the sample platform and heat sink, the sample heat capacity can be determined by fitting the temperature relaxation curve [69]. The thermal response of the empty calorimeter platform—the addenda—is measured separately and subtracted from the dataset.

To maximise the thermal coupling between the sample and the calorimeter platform, crystals with a large flat face are typically used. To obtain high-accuracy

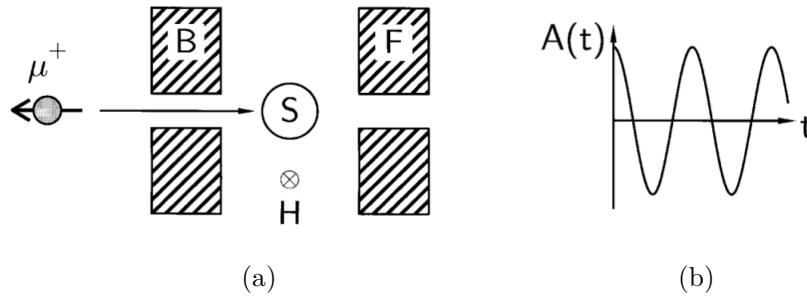


Figure 2.7: (a) Schematic diagram of a muon-spin relaxation experiment, and (b) the resulting decay asymmetry for a long-range ordered sample. Diagrams from Blundell [70].

data, samples should be large enough such that $C_{\text{sample}}/C_{\text{addenda}} > 0.5$ for metallic samples, and > 1.5 for insulating samples [68].

2.4 Muon-spin relaxation

In this section I briefly describe the technique of muon-spin relaxation measurements, which although not performed by myself, is highly complementary to the other techniques used, and will aid in understanding the materials studied within this thesis. In a muon-spin relaxation (μ^+ SR) experiment, spin-polarised positive muons are implanted inside the sample. The muons usually occupy interstitial positions in the crystal [70], and are sensitive to the local magnetic field of the sample, thus acting as a probe of the microscopic magnetism of a system. The property of interest is the time evolution of the spin polarisation of the muons.

The muons are unstable, and will decay with an average lifetime of $2.2\mu\text{s}$ into a positron and two neutrinos. The positrons are detected at detectors placed at the front and back of the sample. The positrons are emitted preferentially in the instantaneous direction of the μ^+ spin, and so the number of the emitted positrons in a given direction is a measurement of the polarisation of the ensemble of μ^+ spins [70, 71]. The measured property is the time dependence of the asymmetry $A(t)$ of

the number of positrons detected at the front (N_F) and back (N_B) of the sample,

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

where α is an experimental constant. In samples that are long-range ordered, the implanted muons experience a quasi-static magnetic field, and begin to precess coherently. This precession causes an oscillation in the decay asymmetry $A(t)$. Therefore, μ^+ SR experiments are an excellent probe of the long-range ordered state of a system, with the Néel temperature being deduced from the temperature at which these oscillations appear.

Chapter 3

The Proximity Detector Oscillator

“The career of a young theoretical physicist consists of treating the harmonic oscillator in ever-increasing levels of abstraction.”

– Sidney Coleman (1937–2007)

Harmonic oscillators are everywhere in physics. This chapter describes the development of the Proximity Detector Oscillator Dynamic Susceptometer (PDODS), a novel radio-frequency susceptometer based on an LCR circuit. The PDODS is the primary measurement technique used in this thesis. Here I present the experimental and the theoretical details of this new technique, and discuss its advantages. The PDODS is used to measure the magnetisation of the polymeric magnets $\text{Cu}(\text{H}_2\text{O})_5(\text{VOF}_4)(\text{H}_2\text{O})$ and $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$, and by comparing the results to that of the extraction susceptometer it is confirmed that the new system can be used to measure and observe magnetic susceptibilities and phase transitions. This chapter is based on work published in Ref. [72].

3.1 Introduction

Radio frequency (RF) techniques have been widely used to measure a range of physical properties [73–82]. Most resonant techniques work by using a simple LCR circuit, where either the capacitance or inductance of the circuit is coupled to the sample, acting as a probe of its physical properties. Depending on the coupling, changes in the magnetic, dielectric or conductive properties of the sample can affect the inductance and/or capacitance, which in turn will modify the resonant frequency.

There are several advantages in using RF techniques. The first is that such techniques are contactless, an important consideration for measurements of resistivity in samples where surface contacts can be poor, those which cannot be exposed to the atmosphere for various reasons [83], or for very small samples where contacts cannot be made easily [79]. Additionally RF transducers can have extremely high sensitivity due to the high stability of the resonator and the accuracy to which frequency can be measured. Sensitivities down to $1 : 10^9$ are possible [81, 84]. Also significant is the relatively high speed of data acquisition—signals with frequencies of order of 10 MHz can be digitised directly, and so changes in sample response can be measured in time scales of 0.1 μ s. This is particularly important for experiments in pulsed magnetic fields [1, 77, 85, 86], where the pulse duration is very short.

One of the most widely used of such techniques has been the Tunnel Diode Oscillator (TDO) [87], coupled to a sensor coil containing a sample. Despite the high stability of the TDO system under optimum conditions, it has a relatively small stable operating range due to the narrow bias voltage region over which the TDO oscillates [88–90]. A TDO-driven circuit is prone to jumping to parasitic frequencies and can be taken out of its stable operating condition by changes in the circuit temperature, inductance, sample size or by the voltages induced in uncompensated coils during experiments using pulsed magnetic fields [90].

Recently a new RF circuit, the Proximity Detector Oscillator (PDO), has been reported by Altarawneh *et al.* [90]. The circuit is based on the widely available proximity detector chip that is used in modern metal detectors. It does not suffer

from the above issues and can be similarly coupled to a sensor coil containing the sample. The PDO can operate across a wide range of temperatures and inductances, and works with coils of various sizes and shapes, has a broad dynamic resonant frequency range and is insensitive to bias changes [90]. This insensitivity to bias voltages makes the proximity detector system suited for use in pulsed magnetic fields, where significant voltages can be induced due to the high dB/dt . The PDO has been successfully used to measure the skin depths of UIrGe and $\text{Ba}_{0.55}\text{K}_{0.45}\text{Fe}_2\text{As}_2$ in high magnetic fields [91, 92], to observe quantum oscillations [86, 93], Fermi-liquid behaviour [94], and the metal-insulating quantum critical point in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [1].

The transport measurements listed above depend on observing relative changes in the resonator filling factor. The filling factor is defined as the ratio of the volume of the sample penetrated by the RF field, to the overall volume of the RF sensor coil [95]. Thus, in metals the filling factor is representative of the skin depth, and in superconductors the penetration depth [96]. Consequently the PDO, when coupled to an RF sensor coil, is highly sensitive to relative changes in the conductivity of metals and semi-metals—allowing for observation of Shubnikov-de Haas oscillations [93], as well as superconducting transitions as will be demonstrated in Chapter 6. Whilst changes in skin (penetration) depth dominate the response of metals (superconductors) to RF fields, I will show in this chapter that the magnetic susceptibility¹ dominates the response of insulators. Hence a PDO system can be used to observe magnetic phase transitions and susceptibility of insulators. I believe that this is the first such application of PDOs.

The PDO can thus be used to observe transport in metals and superconductors, and magnetism in insulators. Being able to probe both properties using a single instrument is highly useful and convenient — there are many systems which have magnetic insulating phases neighbouring metallic or superconducting phases in

¹In early application of TDO-driven RF coils to organic metals and superconductors, it was assumed that changes in susceptibility would dominate the response, and that the quantum oscillations observed were de Haas–van Alphen oscillations [97–99]. Subsequent experience has showed that it is the skin depth changes that dominate, and that the quantum oscillations observed were Shubnikov–de Haas instead [81, 85, 88].

their pressure/temperature phase diagram, such as topological insulators [100, 101], cuprates [102], and the newly discovered iron chalcogenide [103] superconductors.

I will call this magnetic measurement technique/setup, which consists of a sample placed in a sensor coil that is coupled inductively to the proximity detector, a PDO dynamic susceptometer (PDODS), to avoid confusion with the oscillator itself (PDO).

3.2 Advantages

There are many advantages to the PDODS. The sensor coil typically consists of only 5 to 10 turns, and I have used coils with diameters down to 200 μm . Only the sensor coil needs to be placed inside the cryostat — the proximity detector circuit and the power supply can be placed conveniently outside the measurement probe. Thus, the part of PDODS system within the cryostat has a highly compact and small spatial footprint. This, together with the fact that it does not contain any moving parts, means that it is highly suitable for use in systems with limited space where such measurements may not have been previously possible. Such systems include pulsed magnetic fields [92, 104] and pressure cells [105, 106], allowing for an exploration of the magnetic, metallic and superconducting regions of the phase diagram as a function of pressure. For samples where the angle-dependent behaviour is of interest [107, 108], the PDODS can also be used in rotators, thus for example enabling Fermi surface characterisation via angle-dependent de Haas-van Alphen oscillations [109].

The small spatial footprint means that several sensor coils can be used concurrently on the same measurement probe, even within restrictive magnet bores. This allows for the empty-coil and sample measurements to be performed simultaneously, or even for several samples to be measured during a single experiment. Since typically a cooling time of order an hour is needed between each pulsed-field measurement, this can also save significant time and expense when compared to a

traditional extraction susceptometer, where at least two pulsed shots are needed for each dataset.

Moreover, the lack of moving parts makes the PDODS significantly insensitive to vibrational noise. This, as well as the insensitivity to dB/dt and the pulse profile, makes it suitable for use in multi-stage extremely high pulsed-field (e.g. $\mu_0 H > 70$ T) systems [110], where a traditional extraction susceptometer has the potential to become unreliable. This insensitivity to vibrational noise, in addition to the possibility of using several sensor coils simultaneously, means that the PDODS may also be suitable for use in multi-megagauss destructive single-turn magnets [111], where the magnet is destroyed after one experiment.

Another advantage of the PDODS is that it works equally well in steady and pulsed magnetic fields. The ability to work in steady fields allows for study of samples which would otherwise have been perturbed by the high dB/dt of pulsed magnetic fields via eddy current heating, the magnetocaloric effect, or other phenomena. A comparison of the steady and pulsed field measurements would then allow for quantitative elucidation of the effect of dB/dt on such samples.

3.3 Experimental details

The PDODS technique was developed and tested using the pulsed field facility at the Nicholas Kurti High Magnetic Field Laboratory. A schematic diagram of the PDODS probe design, and the cryostat, is given in Fig. 3.1. The cryostat consists of a large bath of liquid nitrogen used for cooling the magnet, with an insulated space within the magnet bore containing ^4He . A simple non-metallic ^3He jacket containing the measurement probe is then inserted into the ^4He cryostat. This arrangement allows for temperatures as low as 300 mK upon de-pressurisation of the $^3\text{He}/^4\text{He}$ baths.

A schematic diagram of the PDODS circuitry [90] is given in Fig. 3.2. The system uses the commercially available TDA0161 proximity detector integrated circuit (IC) used in metal detectors. The proximity detector essentially acts as a noise-triggered

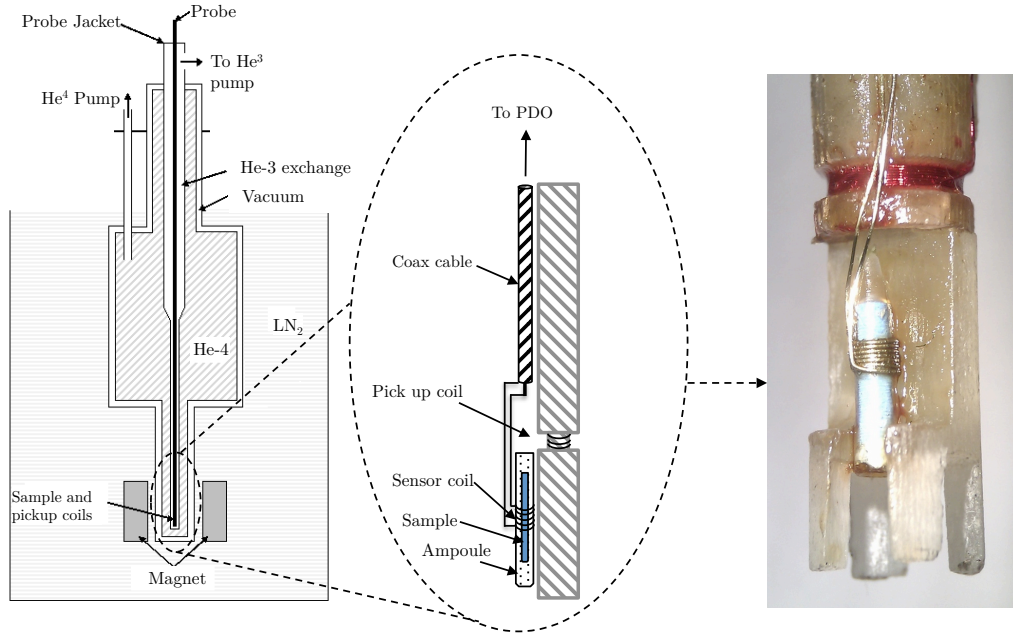


Figure 3.1: Diagram of the cryostat and PDODS probe design. Image shows a powder sample ready for measurement.

negative resistor, which compensates for any loss within the sensor circuit and thus creates sustained oscillations [112]. The negative resistance is achieved through a combination of amplifiers and transistors within the IC [113]. The sensor coil is inductively coupled to pins 3 and 7 of the IC, and the proximity detector works by comparing the load impedance R_{3-7} to the resistance R_{2-4} across pins 2 and 4. The oscillations are sustained if $|R_{3-7}| > R_{2-4}$; and when the sensor coil experiences an extra inductive load, the change in R_{3-7} will modify the current drawn from pin 1 [90, 113]. This change in current leads to a modification of the metal detector signal.

For our purposes, pins 2 and 4 are short-circuited ($R_{2-4} = 0$) to ensure that the IC will always resonate, and the resonant frequency can be read from the coupling capacitor C_4 on pin 6. Additionally C_3 and R_2 are used to maintain a stable operating voltage. The sample penetration depth λ is related to the oscillation frequency ω via

$$\lambda = \sqrt{\frac{2\rho}{\omega\mu_r\mu_0}},$$

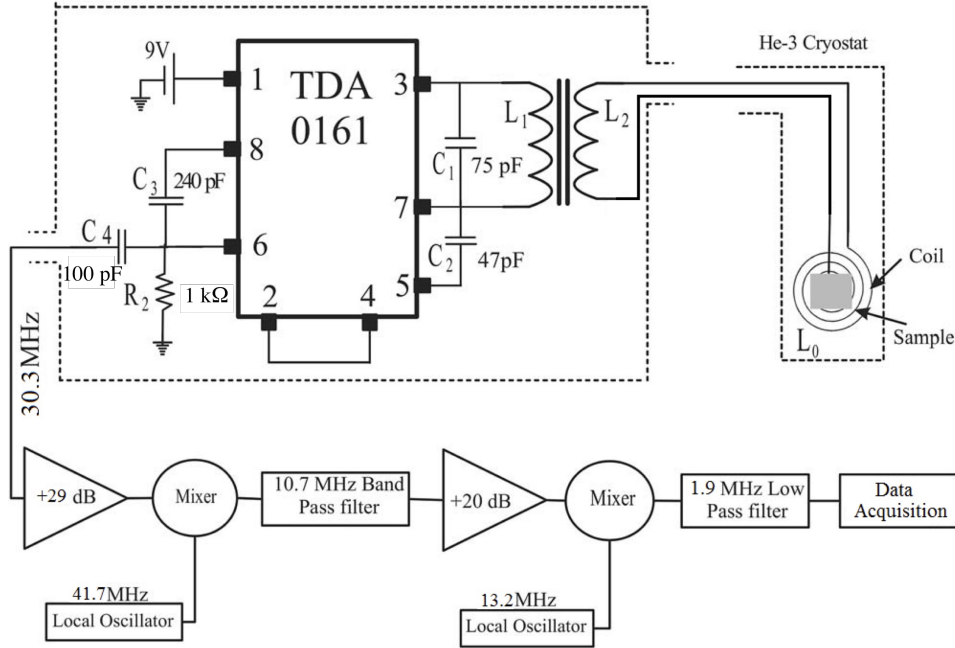


Figure 3.2: Schematic diagram of the PDODS system, modified from Ref. [90]. L_0 is the sensor coil inductance, which is then coupled to the proximity detector chip through inductances L_1 and L_2 . C and R represent capacitors and resistors respectively. $L_2 = L_1 \simeq 0.45 \mu\text{H}$.

where ρ is the sample resistivity and μ_r is the the sample magnetic permeability relative to free space. Transport measurements are performed by monitoring the response of the PDO to changes in λ , and so it is important that in such measurements λ be always smaller than the sample radius; otherwise the RF waves will completely penetrate the sample and the PDO loses sensitivity to changes in λ . The frequency ω is therefore maximised to minimise λ , to allow for measurement of small samples. C_1 and C_2 are used to tune the resonance frequency to about 30 MHz, although higher frequencies are possible.

Powdered samples are usually held in the same ampoule as that used for extraction magnetometry measurements, while single crystal samples are usually used without such protection. To maximise the coupling of the sensor coil to the sample, the sensor coil is made to match the sample or ampoule size and shape as much as possible. The sample/ampoule is placed in the coil and then mounted on the measurement probe. Note that the same coil can be used for both transport and

magnetic measurements — in metals it is transport that dominates the system response, while in insulators it is magnetism. The PDO circuitry is then placed at the top of the probe and is connected to the sensor coil using a semi-rigid coaxial cable.

The output signal from the proximity detector chip is amplified, and undergoes two stages of mixing and filtering to remove high frequency noise. The output is then recorded by a fast data-acquisition card, and the frequency is found by performing a traveling fast Fourier transform. To improve the Fourier transform resolution, extra zeros are added to either side of the time interval (zero padding) [114].

The PDO setup during this thesis used $C_1 = 75$ pF, $C_2 = 47$ pF, $C_3 = 240$ pF, $C_4 = 100$ pF, and $R_2 = 1$ k Ω . The internal isolation transformer was made by wrapping two 18 AWG Cu wires eight times around a hollow G10 tube of diameter 1.2 cm, giving $L_2 = L_1 \simeq 0.45$ μ H. The PDO was powered by a standard 9V battery. The battery and the C_4 read-out capacitor were housed in a separate box, which was connected to the PDO circuit using a 2 m SMA cable. The distance between the sample coil and the PDO circuit was approximately 1.8 m in pulsed-field experiments, and 2.5–3.5 m in steady-field experiments. The PDO was electrically isolated from the probe body.

3.4 Theory

In a system where the sample is inductively coupled to the sensor coil, the inductance L_0 of the coil can be calculated as the sum of the inductances due to the RF field outside and within the skin/penetration depth λ of the sample,

$$\begin{aligned} L_0 &= L_{\text{space}} + L_{\text{sample}} \\ &= \frac{\gamma}{l} \mu_0 \pi N^2 (R^2 - r^2) + \frac{\gamma}{l} \mu_0 \mu_r \pi N^2 \left[r^2 - (r - \lambda)^2 \right] \\ &= \frac{\gamma}{l} \mu_0 \pi N^2 \left[R^2 - r^2 + \mu_r (2r\lambda - \lambda^2) \right], \end{aligned} \quad (3.1)$$

where R is sensor coil radius, r is sample radius, N is the total number of turns, l is the coil length, and $\gamma \simeq 0.8$ is the geometrical factor for non-infinite coils [115]. I

have assumed that both the sample and the coil are cylindrical, that sample length² $l_{\text{sample}} \geq l$ and have neglected any edge effects. Differentiating, this gives

$$\Delta L_0 = \frac{\gamma}{l} \mu_0 \pi N^2 [2\mu_r (r - \lambda) \Delta \lambda + (2r - \lambda) \lambda \Delta \mu_r]. \quad (3.2)$$

Thus we can see the effect of changes in the sample skin/penetration depth, which can be used for transport measurements, and changes in relative magnetic permeability, which can be used to probe magnetism. In metals and superconductors it is changes in the skin/penetration depth $\Delta \lambda$ which dominate the coil inductance. However, in insulators the RF field penetrates the whole of the sample — in effect loading the coil with a constant volume [88], and so the system becomes insensitive to changes in the skin/penetration depth. In this case small changes in the magnetic permeability μ_r can become noticeable.

Therefore, setting $\Delta \lambda = 0$ and $\lambda = r$ for insulators,³ equation 3.1 can be reduced to:

$$\begin{aligned} L_0 &= \frac{\gamma}{l} \mu_0 \pi N^2 (R^2 - r^2 + \mu_r r^2) \\ &= L_{\text{empty}} (1 + f\chi), \\ \Delta L_0 &= L_{\text{empty}} f \Delta \chi \end{aligned} \quad (3.3)$$

where $L_{\text{empty}} = \gamma \mu_0 \pi R^2 N^2 / l$ is the empty coil inductance, $f = r^2 / R^2$ is the coil filling factor, and $\chi = \mu_r - 1$.

Applying circuit theory to the schematic in Fig. 3.2, one has

$$V = I_1 R_1 + L_1 \frac{dI_1}{dt} - m \frac{dI_0}{dt}, \quad (3.4)$$

$$0 = R_0 I_0 + L_0 \frac{dI_0}{dt} - m \frac{dI_1}{dt} + L_2 \frac{dI_0}{dt}, \quad (3.5)$$

²If $l_{\text{sample}} \leq l$ instead, then Eqn. 3.1 is scaled by l_{sample}/l and a constant $\gamma \mu_0 \pi N^2 R^2 (l - l_{\text{sample}})/l^2$ is also added to inductance. Equation 3.3 then becomes $\Delta L_0 = l_{\text{sample}} L_{\text{empty}} f \Delta \chi / l$. Thus all equations still hold, but with a scaling of l_{sample}/l .

³In reality $\lambda \gg r$, however for the purposes of Eqn. 3.1 we have to set $\lambda = r$

where R_0 is the sensor coil and coaxial cable resistance, R_1 is the resistance of inductor L_1 , m is coupling factor between L_1 and L_2 , I_0 and I_1 are the currents through inductors L_0 and L_1 , and V is the voltage across pins 3 and 7 of the proximity detector chip. Substituting Eqn. 3.5 into 3.4, and setting $I_0 \propto I_1 \propto \exp(j\omega t)$ we have:

$$V = \left[R_1 + j\omega L_1 + \frac{m^2 \omega^2}{R_0 + j\omega(L_0 + L_2)} \right] I_1.$$

By considering the imaginary component of the above equation, one gets the effective inductance of the circuit,

$$L_{\text{eff}} = L_1 \left[1 - \frac{m^2 \omega^2}{R_0^2 + \omega^2(L_0 + L_2)^2} \left(\frac{L_0 + L_2}{L_1} \right) \right]. \quad (3.6)$$

Being an LCR circuit, the overall angular resonance frequency is $\frac{1}{\sqrt{L_{\text{eff}}C}}$, in which C is the overall circuit capacitance. We can differentiate to obtain

$$\frac{\Delta\omega}{\omega} = -\frac{\Delta L_{\text{eff}}}{2L_{\text{eff}}}, \quad (3.7)$$

where $\Delta\omega = \omega(H) - \omega(0)$ is the change in resonant frequency when a magnetic field H is applied, and similarly $\Delta L_{\text{eff}} = L_{\text{eff}}(H) - L_{\text{eff}}(0)$. Substitution of Eqn. 3.6 into the above equation results in a rather complicated expression, which upon assuming small changes in variables⁴ ($\Delta\omega \ll \omega$, $\Delta L_0 \ll L_0$, $\Delta R_0 \ll R_0$) results in

$$\Delta\omega = -a\Delta L_0 - b\Delta R_0, \quad (3.8)$$

where a, b are positive constant functions of R_0 , ω , C and the inductances; and ΔR_0 represents the magnetoresistance of the coax cable and the sensor coil in the presence of a magnetic field.

⁴This assumption is valid as typical changes in $\omega/2\pi$ is of order of tens of KHz, while $\omega/2\pi$ itself is about 30 MHz.

Finally, after substituting Eqn. 3.3, one can relate changes in the dynamic susceptibility of insulating samples to frequency:

$$\Delta\omega = -a'\Delta\chi - b\Delta R_0, \quad (3.9)$$

where $a' = afL_{\text{empty}}$.

We can isolate the susceptibility by taking a background measurement, where an identical empty coil is used. In that case, assuming that changes in the permeability of the exchange medium are negligible, we can set $\Delta\chi_{\text{background}} = 0$ to get

$$\Delta\omega_{\text{background}} = -b\Delta R_0.$$

By subtracting the background measurement from that with the sample,

$$\Delta\chi = \frac{1}{a'} (\Delta\omega_{\text{background}} - \Delta\omega_{\text{with sample}}),$$

and setting $\Delta\chi = \chi(H) - \chi_0$, where χ_0 is a constant, we get

$$\chi(H) = \frac{1}{a'} (\Delta\omega_{\text{background}} - \Delta\omega_{\text{with sample}}) + \chi_0. \quad (3.10)$$

3.5 Magnetoresistance of circuit elements

The response of the PDO, when coupled to empty coils made from aluminium or copper, is shown in Fig. 3.3 as a function of field. The changes in ω can be attributed to magnetoresistance and other second order affects not considered in the previous calculations.⁵

⁵This background can also include a noticeable drop in frequency at low fields due to the superconducting transition of the solder used. Typically a 60%/40% tin/lead solder is used, which has a critical field of 0.08 T and transition temperature of 7.05 K [116].

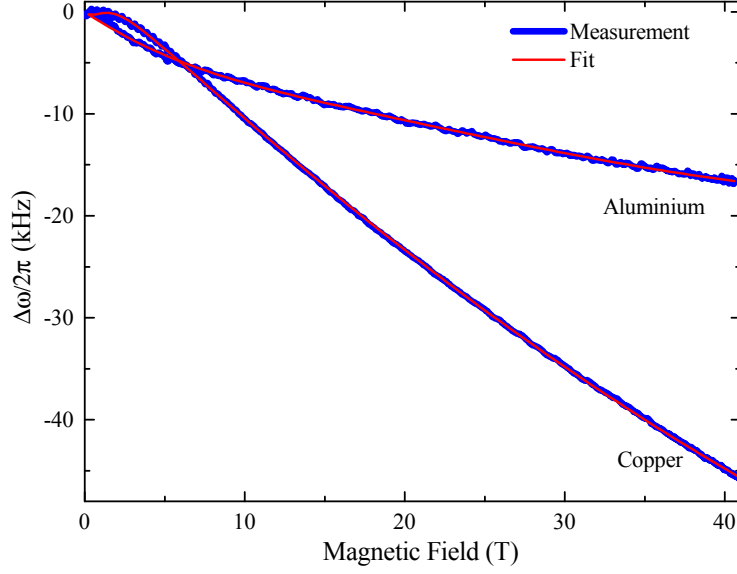


Figure 3.3: Relative shift in resonant frequency at 4.2 K when using empty coils made with 8 turns of 75 μm -thick copper or 100 μm -thick aluminium wire. Also plotted are least-squares fits using Eqn. 3.11.

The magnetoresistance background of a coil can be approximated as

$$\begin{aligned}\Delta\omega_{\text{background}} &= -b\Delta R_0 \\ &= \frac{\alpha}{H^{-2} + \beta} + \gamma H^2 + \eta H,\end{aligned}\tag{3.11}$$

where α , β , γ and η are constants. The first and second terms respectively represent the closed and open quasiparticle orbits around the Fermi surface in the limit $\omega_c\tau \rightarrow \infty$ (ω_c is the cyclotron frequency, τ is the relaxation time) [117]. The last term is a phenomenological term associated with linear transverse magnetoresistance at high magnetic fields [118–120]. As shown in Fig. 3.3, this equation closely matches the background response of both copper and aluminium coils. The list of fit parameters is given in Table 3.1. The magnetoresistance was found to be largely temperature-independent below 20 K.

From Fig. 3.3, it is clear that aluminium has a considerably lower magnetoresistance than copper. However, it still may be desirable to use copper in some applications (such as pressure cells) due to its superior structural and tensile properties, and the ease with which electrical contacts can be applied.

	Copper	Aluminium
$\alpha/2\pi$ (Hz/T ²)	2050	31.43
β (T ⁻²)	0.5	0.0022
$\gamma/2\pi$ (Hz/T ²)	7.45	8.83
$\eta/2\pi$ (Hz/T)	-1520	-1041

Table 3.1: Parameters from least-square fits of Eqn. 3.11 to the frequency response of empty copper and aluminium coils.

3.6 Samples

The PDODS was tested with a single crystal of $\text{Cu}(\text{H}_2\text{O})_5(\text{VOF}_4)(\text{H}_2\text{O})$. This material has a spin-gap at zero field (see Chapter 5 for the physics of spin-gapped systems). At low temperatures ($T < 4\text{ K}$) the magnetisation is close to zero up to around 13 T, at which point it undergoes a sharp phase transition, leading to a step-like increase in magnetisation. This transition becomes less noticeable with increasing temperature, and eventually disappears at $T \approx 10\text{ K}$ to give way to a gradual rise in magnetisation. This material is therefore ideal for testing the response of the PDODS to sharp magnetic transitions, as well as more gradual variations in magnetisation, as a function of the magnetic field.

The second material to be measured is a powdered sample of the metal-organic coordination polymer $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$. This is a well-studied quasi-two dimensional Heisenberg antiferromagnet, with a g -factor of 2.13, primary exchange coupling $|J|$ of 6.3 K, exchange anisotropy $|J_\perp/J|$ of 9×10^{-4} and a Néel temperature of 1.54 K. This system shows a gradual concave rise in magnetisation with increasing field, saturating at 18 T [3].

3.7 Susceptibility

A $1.5 \times 0.6 \times 0.3\text{ mm}^3$ single crystal of $\text{Cu}(\text{H}_2\text{O})_5(\text{VOF}_4)(\text{H}_2\text{O})$ was placed in an ampoule and measured using an 8 turn coil made of 100 μm -thick aluminium wire, with coil diameter of 1.3 mm. Measurements were done at a range of temperatures, a selection of which are shown in Fig. 3.4(a).

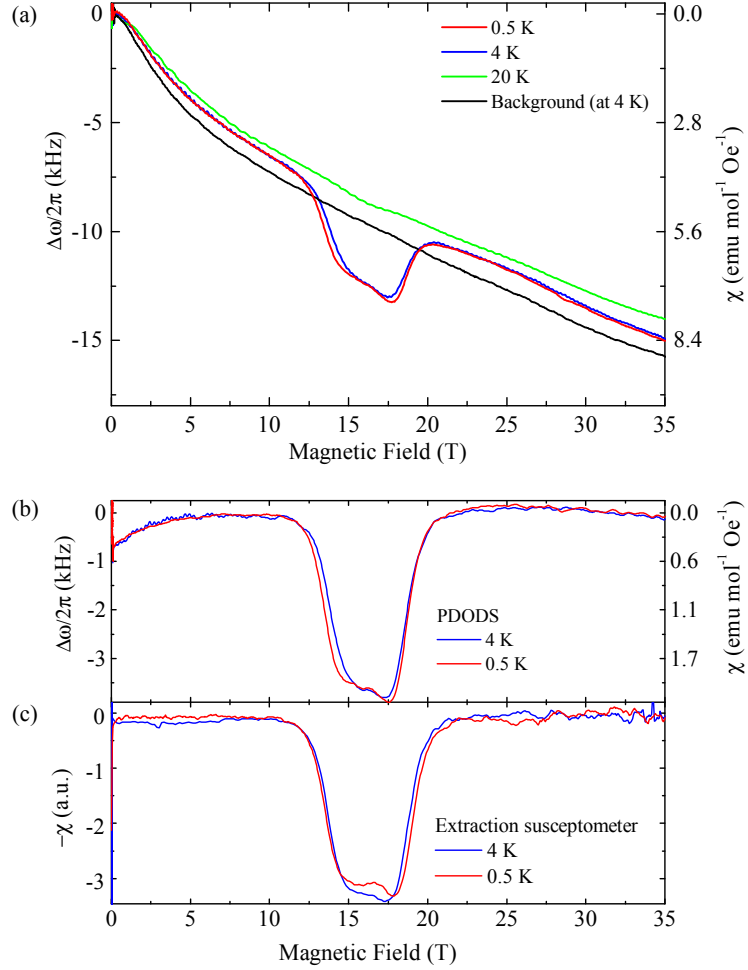


Figure 3.4: (a) PDODS frequency shifts for a sample of $\text{Cu}(\text{H}_2\text{O})_5(\text{VOF}_4)(\text{H}_2\text{O})$ at various temperatures. Some smoothing has been performed to reduce high frequency noise. The resonance frequency at zero field was 28.4 MHz. (b) PDODS frequency shift with the background and the $a'\chi_0$ constant removed. The data has been calibrated (right-hand axis) using SQUID data, which gives a saturation magnetisation of $2.2 \mu_{\text{B}}/\text{formula-unit}$. Data can be converted to S.I. units using the relation $1 \text{ emu mol}^{-1} \text{ Oe}^{-1} = 4\pi \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. (c) Data from the extraction susceptometer.

Equation 3.9 implies that $\Delta\omega \propto -\Delta\chi$, and the changes in magnetic susceptibility are quite clear at low temperatures without any need to subtract the background or perform any further analysis: relative frequency shifts of about 4 kHz are seen at 12 T and 20 T, representing the magnetic transition. Also note how this transition is no longer seen at 20 K implying that at high temperatures the changes in the magnetisation are much more gradual.

The data with the background subtracted are shown in Fig. 3.4(b). The magnetic transition at low temperatures is well pronounced, and the resonant frequency is shown to be constant at $\mu_0 H < 13$ T and $\mu_0 H > 20$ T — in these regions we know there is no change in the magnetisation, implying $\chi = 0$. However, $\Delta\omega$ is still non-zero due to the χ_0 constant term in equation 3.10. The data from a traditional extraction susceptometer is shown in Fig. 3.4c, for the same sample. It is clear that both datasets are qualitatively very similar.

The PDODS response to powdered sample of $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$ was similarly measured using a coil of 6 turns of 100 μm aluminium wire, and is shown in the inset of Fig. 3.5b. As expected, $\Delta\omega$ varies smoothly at low fields, and a sudden change is seen at around 18 T as the system becomes saturated. This sample was also measured using the traditional extraction susceptometer, which shows the same behaviour.

In addition, both samples were measured with magnetic pulses of different magnitudes with rise-times ranging from 2.6 μs to 4.6 μs , corresponding to dB/dT varying from 4.7 T/ms to 16 T/ms, and no change was observed in the PDODS behaviour at such rates. $\text{Cu}(\text{H}_2\text{O})_5(\text{VOF}_4)(\text{H}_2\text{O})$ was also measured successfully in a 17 T superconducting magnet, and similar features were seen. It was found that in DC magnets the magnetoresistance background is larger than in pulsed fields, likely due to the extensive fringe field of the magnets.

In summary, the fact that the PDODS and the extraction susceptometer data look the same for both samples shows that χ dominates the resonator response,

and so the PDODS system can be used for dynamic susceptibility measurements in insulators.

3.8 Magnetisation

Once the background is removed from the data, the magnetisation can be calculated from Eqn. 3.10 by subtracting a constant corresponding to the $a'\chi_0$ term and then numerically integrating. In samples which saturate during the pulse, the susceptibility should be zero after saturation and so any non-zero susceptibility can be attributed to this $a'\chi_0$. For samples which are not known to saturate fully, the correct $a'\chi_0$ can be found by comparing the PDODS results to low field data from other magnetometers, such as a SQUID magnetometer (for which commercial pressure cells are available) [62].

Both of the samples measured above become saturated at high fields, and at 4 K $a'\chi_0/2\pi$ is found to be around 0.75 kHz for $\text{Cu}(\text{H}_2\text{O})_5(\text{VOF}_4)(\text{H}_2\text{O})$ and 0.5 kHz for $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$.

A comparison is made between the PDODS and extraction susceptometer magnetisation data for $\text{Cu}(\text{H}_2\text{O})_5(\text{VOF}_4)(\text{H}_2\text{O})$ in Fig. 3.5a. The PDODS data agree very well with the extraction susceptometer, successfully showing the sharp magnetic transition at low temperatures, as well as the more gradual change in magnetisation at higher temperatures.⁶ Further measurements were taken at several temperatures in between 0.5 K and 20 K, and they show similar agreement.

Similarly, the integrated magnetisation for $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$ is given in Fig. 3.5b. Once again the extraction susceptometer and the PDODS agree very well — we see a gradual concave rise in magnetisation typical of quasi-two-dimensional magnets, leading to a sharp transition at 18 T which has been rounded slightly because of the powdered average of the anisotropic g -factor [3].

⁶In Fig. 3.4, the small discrepancies at low fields between the PDODS and extraction magnetometer are due to imperfect background subtraction. Here, a separate coil was used to measure the background. For perfect results, the same coil should be used for measuring the sample and background.

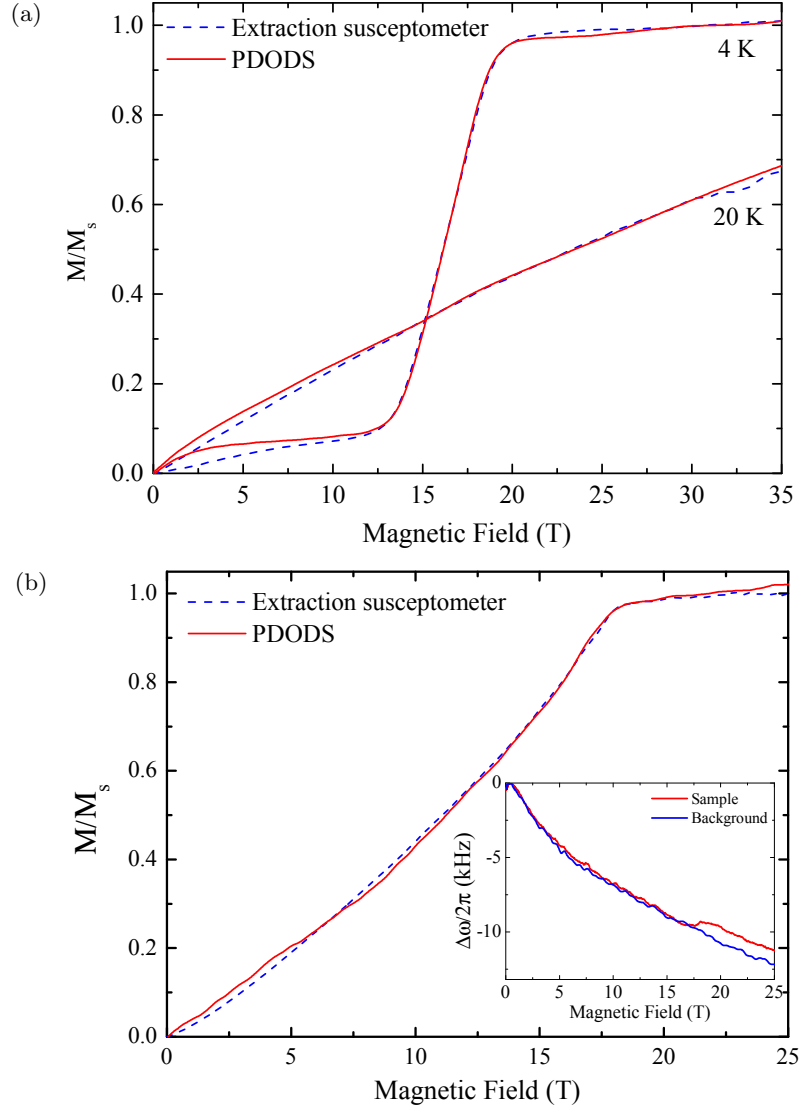


Figure 3.5: Comparison of the deduced magnetisation from the PDODS and the extraction susceptometer data, for (a) $\text{Cu}(\text{H}_2\text{O})_5(\text{VOF}_4)(\text{H}_2\text{O})$ and (b) $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$, *inset*: relative change in the PDODS resonant frequency during the pulse.

The absolute magnetisation can be found by comparing the PDODS results with respect to low temperature data from other magnetometers, such as a SQUID. Calibrating the PDODS in such ways is not a disadvantage, as all magnetometers, such as AC susceptometers, vibrating sample magnetometers and even modern SQUIDs, need to be similarly calibrated by using magnetic reference samples.

3.9 Conclusion

In this chapter I explained the resonant frequency behaviour of the proximity detector oscillator as a function of magnetic field when coupled inductively to a sensor coil containing an insulating sample. The frequency response consists of a magnetoresistive component, which was modelled for copper and aluminium coils, and an inductive component, which can be related to the coil filling factor and the dynamic magnetic susceptibility of the sample.

It was shown that for the two insulating samples $\text{Cu}(\text{H}_2\text{O})_5(\text{VOF}_4)(\text{H}_2\text{O})$ and $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{BF}_4$, the magnetic susceptibility dominates the inductance of the measurement coil, and that upon careful subtraction of the magnetoresistance background, the magnetic susceptibility and magnetisation can be determined — in agreement with data from a traditional extraction susceptometer.

In summary, I have proved that the proximity detector oscillator dynamic susceptometer (PDODS) is highly suitable for measurement of magnetisation and magnetic transitions in insulators. This, together with the small spatial footprint of the measurement coil, makes the PDODS highly adaptable for use in pressure cells for examination of materials with metallic-insulating phase transitions — allowing transport and magnetisation to be measured in the conducting and insulating phases respectively, and giving way for a full characterisation of the phase diagram as function of pressure, magnetic field and temperature.

The technique described in this chapter forms the basis of the experiments described in the rest of this thesis, where it was used for performing measurements

that could not have been done, or would have been extremely difficult to do, with more traditional techniques:

- In Chapter 4, the PDODS is used to measure the magnetisation of $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$ at high pressures and fields, which cannot be done with traditional techniques.
- In Chapter 5, the PDODS is used to measure the magnetisation of $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$, which shows a significant magnetocaloric effect in pulsed fields, and hence cannot be measured with a pulsed-field extraction susceptibility meter.
- In Chapter 6, the PDO is used to measure the upper critical field of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$, which is extremely air-sensitive, making the use of traditional four-contact resistivity measurements extremely challenging.

Chapter 4

Controlling magnetic interactions of Jahn-Teller active systems with pressure

“Man is born free, and everywhere he is in chains.”
– Jean-Jacques Rousseau (1712–1778)

Here I discuss the possibility of using applied pressures to control the magnetic exchange parameters and dimensionality of coordination polymers with Jahn-Teller active metal centres. I present the results of high-field magnetisation and muon-spin relaxation measurements on the coordination polymer $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyrazine})$ in pressures up to 22.5 kbar. I observe a transition from a quasi-two-dimensional to a quasi-one-dimensional antiferromagnetic phase at 9.1 kbar, driven by a rotation of the Jahn-Teller axis. Long-range antiferromagnetic ordering is seen in both regimes. The magnetic dimensionality switching as pressure is increased is accompanied by a significant reduction of the primary magnetic exchange energy J and a fivefold decrease in the ordering temperature T_N . This chapter is based on work published in Ref. [121].

4.1 Introduction

Pressure plays a central role in the exploration of physical phenomena, for example in metal-insulator transitions [122, 123] and superconductivity [124, 125]. This is because it allows a controlled adjustment of structural parameters, such that their influence on the electronic and magnetic properties can be determined. Pressure can also affect transition-metal coordination polymers. Often pressures of a few kbar¹ are enough to perturb the spin-orbit coupling and spin-exchange interactions in these materials [126–129], as opposed to the extreme ~ 200 kbar pressures needed to achieve similar effects in metal oxides [130]. A major selling point of coordination polymers is their tunability—the ability to use minor structural or chemical modifications to manipulate the magnetic behaviour, which allows for a systematic study of the magnetostructural properties [3]. Pressure allows for focusing on the magnetostructural properties of a single compound—in contrast to, for example, using different ligands to modify the bond lengths of the system. The ‘non-innocence’ of the ligands can obviously become a problem in the latter technique [131].

A number of coordination polymers are based on hetero-ligand Jahn-Teller (JT) [132, 133] active metal centres, where the transition metal ion sits in a position of octahedral symmetry, surrounded by an asymmetric ligand environment. In such systems each trans-coordinated ligand provides an additional degree of freedom on the JT-axis, meaning that small perturbations of the metal-ligand environment can be enough to rotate the JT-axis and radically modify the material properties. Pressure presents an ideal method of systematically achieving such perturbations, due to the relative softness and high compressibility of the organic framework.

In this chapter I will show that pressure can be used to operate a Jahn-Teller driven magnetic dimensionality switch between a two-dimensional and a one-dimensional antiferromagnetic phase in the extended Cu-based coordination network $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$ (pyz = pyrazine, $\text{C}_4\text{H}_4\text{N}_2$). In this compound, hydrogen-bonding interactions, a JT-active metal centre, and three different trans-coordinated ligands

¹Throughout this chapter I quote pressures in units of kbar. The relation to the S.I. unit of pressure (Pa) is 1 kbar = 0.1 GPa.

promote significant pressure-induced structural transitions. Together, these features enable pressure-induced perturbation of the magnetic exchange, allowing the modification of the system's magnetic dimensionality and providing the ability to tune the primary exchange energy J .

The work presented in this chapter is the result of a collective effort, and has been partially published in Ref. [121]. High pressure magnetisation measurements were performed by myself, with the assistance of P. A. Goddard, and J. A. Schlueter, and technical assistance from D. Graf and S. W. Tozer. All magnetisation and susceptibility data analysis were performed by myself. μ^+ SR measurements and analysis were performed by J. S. Möller, T. Lancaster, F. Xiao, and S. J. Blundell, with technical assistance from A. Maisuradze, and R. Khasanov. The samples were grown by J. A. Schlueter, who also performed the susceptibility measurements on $\text{Cu}(\text{NO}_3)_2(\text{pyz})$.

4.2 Previous work

$\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$ has a highly anisotropic structure, consisting of Cu-pyz-Cu chains along the crystallographic a -axis, with the Cu^{2+} metal centres also joined together via a two-dimensional hydrogen-bonding lattice in the bc -plane, as shown in Fig. 4.1. The spin-1/2 Cu atom sits at the centre of a distorted octahedron, surrounded by trans-pairs of Cu-O, Cu-F and Cu-N ligands. At ambient pressure the elongated JT-axis is oriented along the N-Cu-N bonds, implying that the $d_{x^2-y^2}$ orbitals and the directions of largest electronic overlap are directed perpendicular to this axis, and are within the bc -plane. This situation is confirmed by pulsed-field magnetisation, electron-spin resonance (ESR), muon-spin relaxation (μ^+ SR), and neutron scattering measurements [71, 134], showing that the compound displays highly two-dimensional antiferromagnetic behaviour with $J = 11.5$ K, secondary exchange energy $J_\perp \sim 10^{-4}J$, and long-range ordering temperature $T_N = 2.6$ K. The primary magnetic exchange is mediated via the Cu-OH $\cdots$ F-Cu spin exchange paths within

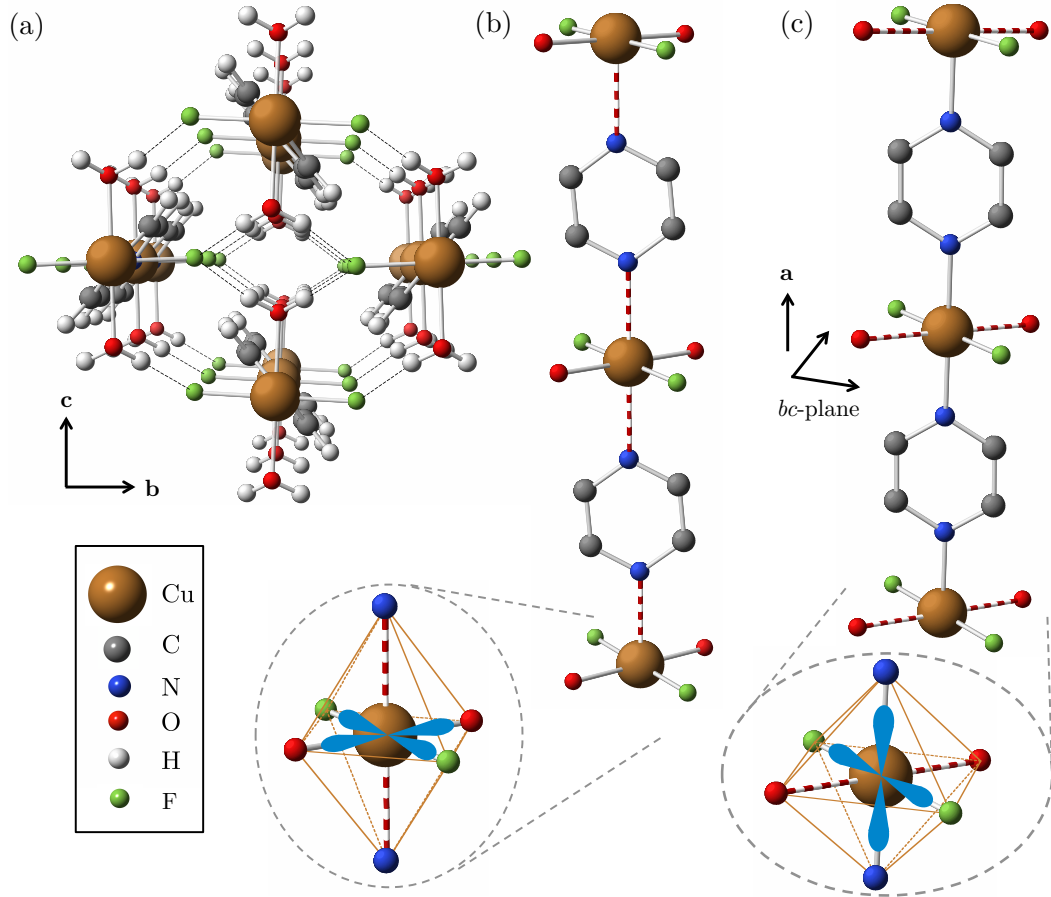


Figure 4.1: Crystal structure of $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$ [71, 136], showing (a) the 2D hydrogen bonding network at ambient pressure. Hydrogen positions are approximate. Also shown is an isolated Cu-pyz-Cu chain at (b) ambient pressure and (c) 13.9 kbar, on the same scale. The JT-axis is shown by the red striped bonds. The zoomed-in regions show the JT octahedron, together with a representation of the magnetic orbitals, which provide the dominant exchange pathways. The H atoms are not shown in the Cu-pyz-Cu chains for clarity.

the bc -planes, which is consistent with ambient-pressure density-functional theory calculations [71, 135].

Goddard *et al.* [136] carried out a detailed magnetisation study of the effect of selective isotopic substitution of hydrogen by deuterium. It was shown that deuterating the pyrazine molecules causes little change in the magnetic properties, while in contrast modifying the water molecules caused a 0.5 K drop in exchange energy J . This is due to the heavier mass of the deuterium atoms, leading to a smaller zero-point vibrational amplitude and a reduction in the overlap of the electronic wave functions [129, 137], thus reducing the exchange efficiency. This confirms the crucial role of the $\text{H} \cdots \text{F}$ bonds in mediating magnetic exchange in this material. Ambient pressure neutron scattering measurements by Wang *et al.* [134] show that the spins form a collinear structure along the b, c -axis at zero field, with a reduced magnetic moment of $0.60(3) \mu_{\text{B}}/\text{Cu}$ pointing in the $[0.7 \ 0 \ 1]$ real space direction. The magnetic lattice is doubled in the a -direction, while in the bc -plane the magnetic and structural lattices remain the same [134].

Recent synchrotron x-ray powder diffraction measurements by Halder *et al.* [136] have revealed that $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$ undergoes two structural phase transitions as a function of pressure, likely caused by a rotation of the JT-axis and orbital orientations. With the application of pressure, the elongated JT-axis was found to change from the Cu–N to the Cu–O bond direction at approximately 9 kbar. This shift was also detected in a single-crystal diffraction experiment, albeit at the higher pressure of 18 kbar [131]. The discrepancy between the two measurements is discussed at the end of Section 4.5. A further pressure induced change to the Cu–F direction was seen by Halder *et al.* [136] at approximately 31 kbar.

In this chapter I report a profound change in the magnetic properties occurring at 9.1 kbar in both single-crystal and powder samples. My interpretation of this result is consistent with the rotation of the JT-axis suggested by Halder *et al.* [136]. At this pressure the magnetic structure switches from quasi-two-dimensional (Q2D) to quasi-one-dimensional (Q1D) due to the reorientation of the $d_{x^2-y^2}$ orbitals, from

lying within the hydrogen-bonded bc -plane to the ac -plane — thus significantly decreasing the electronic overlap along the $\text{Cu-OH} \cdots \text{F-Cu}$ bonds, while simultaneously increasing the magnetic orbital overlap along the a -axis (see Fig. 4.1) [136]. This results in the primary exchange being mediated by pyrazine molecules via the Cu-pyz-Cu chain, therefore allowing Q1D antiferromagnetism to develop. To establish this pressure-induced dimensional switching, as well as to track the evolution of magnetic energies, the behaviour of $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$ as a function of pressure was explored using high-field magnetisation and muon-spin relaxation measurements.

4.3 Experimental details

The samples were formed by dissolving NH_4F and pyrazine in a teflon beaker, and then adding an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot y\text{H}_2\text{O}$ [71]. This results in a blue solution, in which pale blue crystal blocks begin to appear after a few minutes. After the crystals are grown to the appropriate size, they are collected via vacuum filtration and air-dried for a short time. In order to prevent desolvation over time, the crystals are immersed in solvent and stored in a freezer.

Single crystal magnetisation measurements in fields up to 35 T were performed at the National High Magnetic Field Laboratory (NHMFL), USA, using the proximity detector oscillator dynamic susceptometer. Measurements were performed up to 20 kbar using a piston-cylinder cell (PCC) at 1.4 K. Two measurements were performed in the low-pressure regime ($P < P_{c1}$), another at the critical pressure $P_{c1} \approx 9.1$ kbar, and a further four in the intermediate pressure region ($P_{c1} < P < P_{c2}$).

4.3.1 Piston cylinder cells

The experiment was performed using a Guertin piston-cylinder cell (PCC) designed and built at the NHMFL. A schematic diagram of the PCC is given in Fig 4.2. It essentially consists of a piston that pushes down on a sealed teflon cup, which contains the pressure medium and is placed over the sample holder. The PCC is

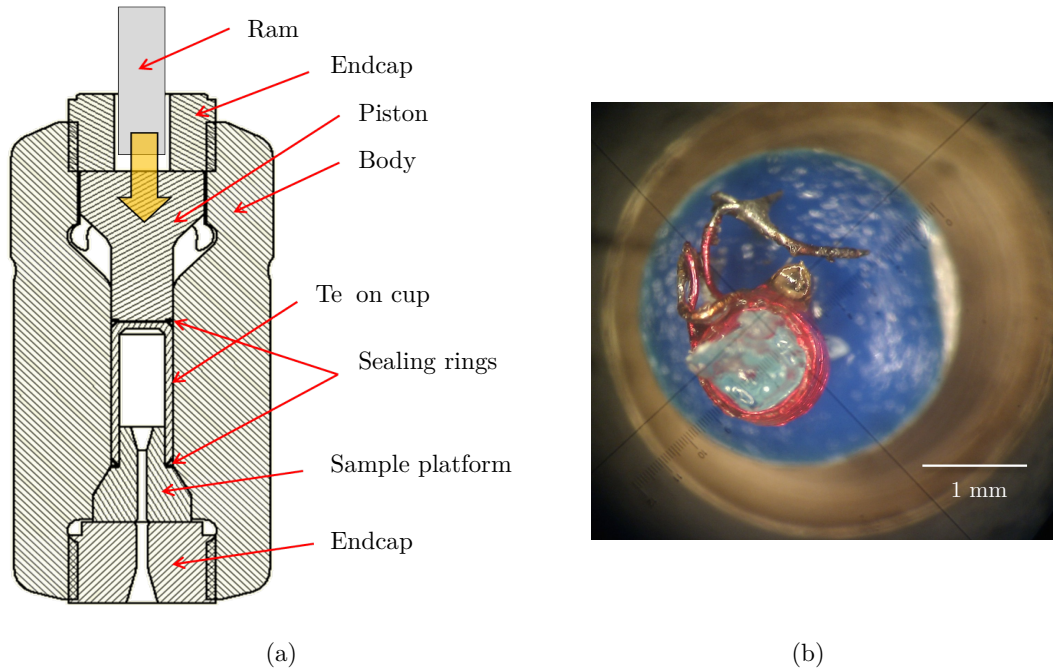


Figure 4.2: (a) Schematic diagram of a piston-cylinder cell, together with (b) an image of the sample holder with a sample mounted inside a PDO coil.

made of MP35N, a high-tensile non-magnetic nickel-cobalt-chromium-molybdenum alloy, and is manufactured to very exact engineering tolerances. As the piston is pushed down the teflon cup is constrained to compress vertically, reducing the sample volume. The pressure medium is sealed in the teflon cup, and so, being unable to escape, becomes pressurised. Thus the applied pressure is transferred to the sample via the pressure medium, and the piston never touches the sample directly.

The sample holder is prepared by feeding an aluminium-clad fibre optic cable and a pair of copper leads through the sample platform. The cables are firmly sealed in place using Stycast 2850 FT epoxy, which has been held under vacuum to remove any air bubbles. Air bubbles can collapse under pressure, leading to a failure of the pressure cell. The PDO coil is then soldered on to the feedthrough leads, and epoxied to end of the fibre optic cable using Stycast 1266 epoxy [see Fig. 4.2(b)].

After mounting the sample inside the PDO coil, a sealing ring is placed around the sample holder platform, and the sample holder is placed in an endcap and screwed securely into the bottom of the PCC. The pressure cell is then filled with an

appropriate pressure medium, and the teflon cup is placed on top. This is followed by another sealing ring, the piston, and finally another end-cap. The pressure cell is then placed inside a hydraulic press, and the required force is applied as measured by a calibrated transducer. As pressure is applied the sealing rings deform and the pressure medium becomes sealed in the teflon cup, unable to escape. The pressure is then ‘locked-in’ by turning in the threaded endcaps.

Once the desired pressure is reached, the pressure cell is removed from the hydraulic press, and placed on the measurement probe. The system is cooled at a rate of 1 K/min down to the measurement temperature. The slow rate of cooling is to prevent any thermal shock to the pressure cell, and to preserve hydrostatic conditions as the system goes past the freezing temperature of the pressure medium. Cooling from room temperature to liquid helium temperatures causes a pressure drop of approximately 2 kbar, due to the difference between the thermal expansion coefficients of the pressure medium and the cell itself.

The main advantage of piston-cylinder cells is the large sample space volume. This allows for use of large or multiple samples, and also makes the operation of the pressure cell easier. The large sample space also means that the pressure tends to be more hydrostatic (i.e. isotropic) than in the smaller diamond-anvil cells. However, the larger volume and mass means that a pressurised PCC holds a significant amount of energy, and the risk of damage or injury in the event of a structural failure is significant. The PCC used here has a maximum safe usage pressure of approximately 22 kbar under cryogenic conditions, although PCCs capable of reaching over 29 kbar exist [138].

4.3.2 Pressure calibration and hydrostaticity

The pressure was measured *in-situ* using the R₁-line fluorescence of small ruby crystals placed within the pressure cell, with the signal being brought out on a fibre-optic cable. In the PCC measurements small ruby chips were glued on top of the feedthrough fibre-optic cable next to the sample. Any applied pressure causes

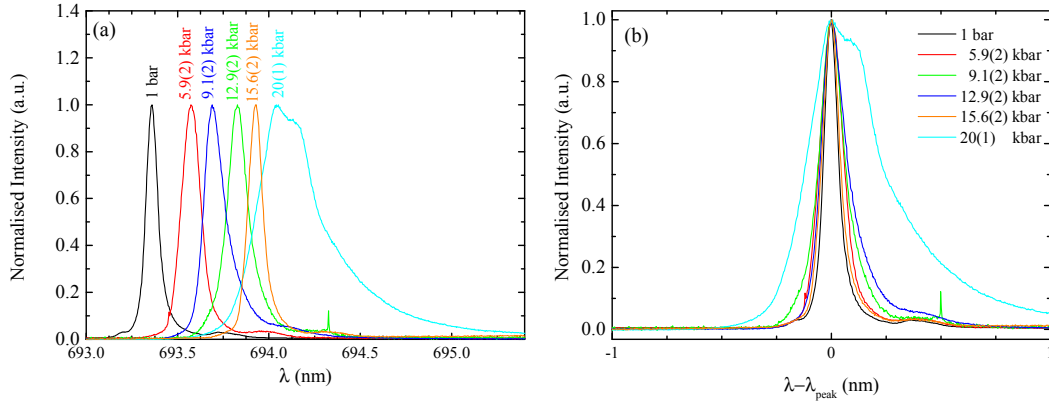


Figure 4.3: (a) R₁ laser fluorescence response of ruby crystals inside the piston-cylinder cell. Also shown in (b) are the normalised curves, showing the change in peak broadness as pressure is increased.

a linear wavelength shift (0.0365 nm/kbar) in the R₁ peak position, as shown in Fig. 4.3, which can be used to calibrate the pressure [139–141].

The choice of pressure medium can have a significant effect on the hydrostaticity, especially at high pressures. The hydrostaticity is affected by how much the pressure medium volume changes upon cooling, its freezing temperature, and the pressure at which it solidifies [142, 143]. The most hydrostatic pressure mediums are He or methanol/ethanol mixtures [142]. Helium is difficult to use due to being a gas at room temperature, and methanol/ethanol mixtures are not suitable as they may react with the sample. A 50:50 mix of Fluorinert 70:77 was used as the pressure medium for piston-cylinder cell measurements, except for a later measurement at 15.6 kbar in which I used Daphne 7474.

The hydrostaticity can be estimated through analysis of the fluorescence peak sharpness [144, 145]. Looking at the measurements in Fig. 4.3, there is no major increase in the peak width with applied pressures up to 15.6 kbar, an indication of good hydrostatic conditions. This is further supported by the fact that there is little difference between the Fluorinert and the Daphne 7474 measurements (Daphne 7474 is known to be hydrostatic up to ~ 37 kbar at room temperature [143]). However, a broadening of the peak at 20 kbar is seen, which can be an indication of a degree of non-hydrostaticity. We can place an upper limit on the non-hydrostaticity by looking

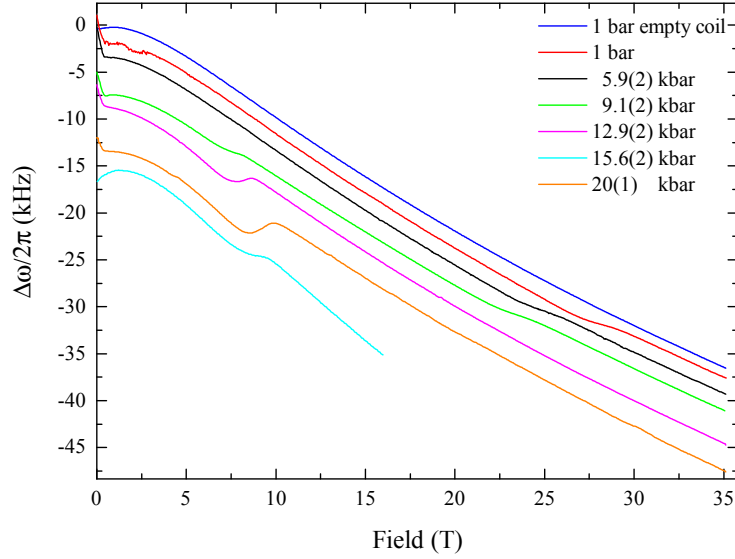


Figure 4.4: Change in the resonance frequency of the PDO susceptometer as a function of applied magnetic field parallel to the a -axis of $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$, at 1.4 K. The data have been shifted vertically for clarity. The 15.6 kbar data were taken in a 16 T superconducting magnet at a later time. The resonance frequency at zero field and ambient pressure was 29.2 MHz.

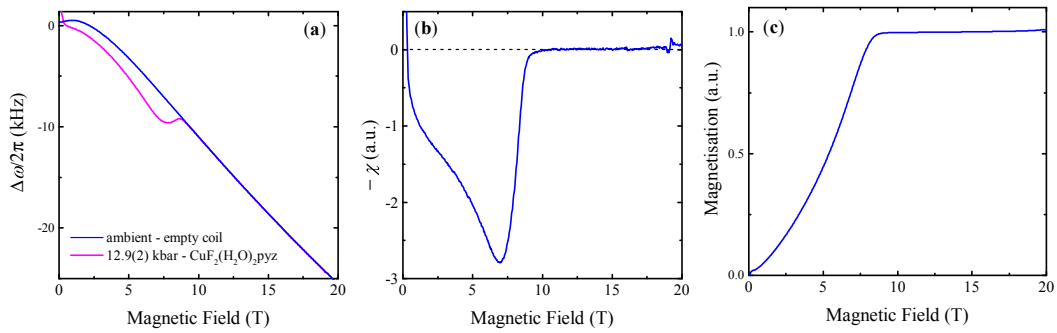


Figure 4.5: (a) PDODS resonance frequency for an empty resonator coil, and for one with $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$ single crystals at 12.9 kbar and $T = 1.4$ K. Also included is (b) the resulting magnetic susceptibility, which was integrated to give (c) the magnetisation.

at the increase in the peak width with respect to an ambient pressure measurement [142, 143], via

$$\Delta P = \frac{\text{FWHM}(P) - \text{FWHM}(\text{ambient})}{0.0365 \times 2.4}$$

where FWHM is the full-width at half-maximum as measured in nanometers, the factor of 0.0365 is to convert nanometer to kbar, and the factor of 2.4 is to convert the FWHM to the standard deviation, assuming the peak is Gaussian. This gives an upper bound of ± 0.7 kbar at $P_{c1} \approx 9.1$ kbar.

To prevent any crystal desolvation over time, fresh samples were grown shortly before the experiments, and were kept in solvent until needed. The crystals were examined upon release of pressure at the end of the experiment, and were found to be unaffected by the applied pressure, further indicating good hydrostatic conditions and absence of any major uniaxial stress in the PCC measurements.

4.3.3 PDO measurements

The relatively large sample space provided by the piston-cylinder cell allowed for a multi-turn coil of 8 turns of 75 μm -thick Cu wire, with a coil diameter of 1 mm. The samples were aligned with the applied magnetic field parallel to the crystal a -axis, and the coil filling factor was approximately 100%. In order to characterise any changes in the magnetoresistive background of the system as a function of pressure, empty-pressure cells were loaded and tested at various pressures in a 16 T superconducting magnet. It was found that, other than a slight rescaling, applied pressure induces no features in the magnetoresistance background.

The frequency response of the PCC measurements, for samples of $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$, is given in Fig. 4.4(a). Also shown is an empty coil background measurement at ambient pressure. Prompted by the form of the magnetisation at ambient pressures [11], the magnetoresistive background at each pressure was deduced by scaling the empty coil measurement until it matched the sample response above the saturation point, for example see Fig. 4.5. The magnetisation was then

found by subtraction of the scaled background data, and integration of the residual according to Eqn. 3.10.

4.4 Magnetisation

The magnetisation as measured across a range of pressures up to 20 kbar is given in Fig. 4.6(a). At ambient pressure the magnetisation rises monotonically with a curvature typical of Q2D antiferromagnetic systems [12], saturating at 28.1 T in agreement with previous measurements [71]. As pressure is applied, a steady reduction in the critical field B_c is observed, down to 23.4 T at 9.1 kbar [see Fig. 4.6(c)]. Further application of pressure leads to a dramatic drop in B_c to 8.3 T, after which any additional pressure serves to gradually increase the saturation field, in contrast to the behaviour seen at lower pressures.

The magnetism in $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$ can be described by the model

$$\mathcal{H} = J \sum_{\langle i,j \rangle_{\parallel}} \left(S_i^x S_j^x + S_i^y S_j^y + \gamma S_i^z S_j^z \right) + J_{\perp} \sum_{\langle i,j \rangle_{\perp}} \mathbf{S}_i \cdot \mathbf{S}_j + g\mu_B B \sum_i S_i^z, \quad (4.1)$$

where in a Q2D (Q1D) phase, J and $J_{\perp}$ are the magnetic exchange strengths within and normal to the planes (chains) respectively, γ is the spin-exchange anisotropy, and g is the g -factor. The first two summations are over the unique ligands through which the exchange couplings take place, and the last term is the Zeeman splitting term. Note that magnetic moments in this system are collinear and that a centre of inversion exists, thus prohibiting antisymmetric exchange Dzyaloshinskii-Moriya $\mathbf{D}_{ij}^{\text{DM}} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$ interactions in the Hamiltonian. Furthermore, the spin-1/2 Cu atoms should show no $D(S_z)^2$ single-ion anisotropy. Neutron scattering measurements give a spin-exchange anisotropy parameter of at least 0.99988 [134], proving the Heisenberg nature of the exchange interactions. Given Eqn. 4.1, the saturation field can be determined by the energy cost of flipping one of the spins from the fully

polarised state [12, 146], and is given via

$$g\mu_B B_c = nJ + n_\perp J_\perp, \quad (4.2)$$

for a spin-1/2 system, where n and $n_\perp$ are the number of nearest-neighbour exchange ligands of interaction strength J and $J_\perp$ respectively ($n = 4, n_\perp = 2$ for Q2D; $n = 2, n_\perp = 4$ for Q1D) [3].

For a Heisenberg spin-1/2 antiferromagnet (AFM) the form of the magnetisation up to saturation strongly reflects the magnetic dimensionality, and Quantum Monte-Carlo simulations have shown that the magnetisation becomes strongly concave as the dimensionality is reduced [3, 12, 147]. Indeed, looking at Fig. 4.6(b), the magnetisation becomes noticeably concave above 9.1 kbar, an indication of the reduction in the magnetic dimensionality. Moreover, looking at the 9.1 kbar data, we discover a noticeable change in the magnetisation gradient at a field (7.9 T) close to the critical field of the higher pressure phase. The curvature of the magnetisation below this field is similar to that of the higher pressure regime, while the curvature above it is closer to that seen at lower pressures [see Fig. 4.6(a)]. This implies a degree of phase separation, with coexisting volumes of the sample in the high- and low-pressure phases.

The fact that both the phase separation and the change in curvature occur at the same pressure as the JT-axis shift [136] leads us to conclude that the dramatic drop in B_c above 9.1 kbar is due to the proposed transition from the Q2D to a Q1D antiferromagnetic phase. In a strongly anisotropic system ($J_\perp \ll J$), we can approximate the saturation field as

$$B_c \approx nJ/g\mu_B.$$

The sudden change in B_c can thus be understood as a combination of the change in n from 4 to 2 (i.e. a Q2D to Q1D transition), and a simultaneous change in J .

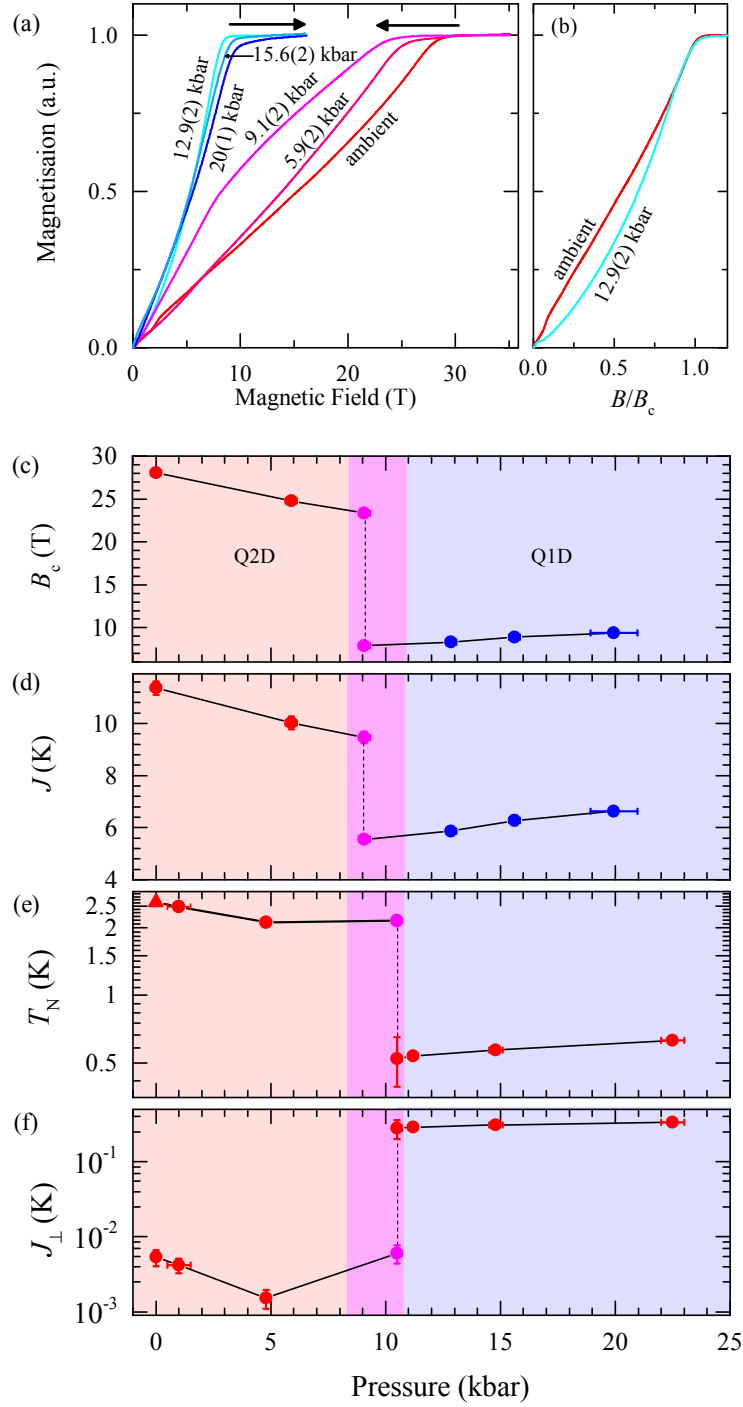


Figure 4.6: (a) Magnetisation of $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$ single crystals with $\mathbf{B} \parallel a$ -axis, at 1.4 K (2 K at 15.6 kbar). The arrows represent the change in the saturation field with increasing pressure. (b) M vs B/B_c at ambient pressure and 12.9 kbar, showing the change in curvature. Also shown is (c) the saturation field B_c , (d) the deduced primary exchange coupling energy J , (e) the ordering temperature T_N deduced from the μ^+ SR data (see Fig. 4.7), and (f) the secondary exchange $J_\perp$. To extract J , we have used values of g obtained from ESR measurements [131]. T_N at ambient pressure (triangle symbol) is from Ref. [71].

The extracted values of J are given in Fig. 4.6(d), where I have used the appropriate g -factor for the appropriate phase [131]. I find $J \approx 11.4$ K at ambient pressure, confirming previous pulsed-field measurements [71]. Under application of moderate pressures, J begins to decrease gradually at a rate of 0.21 ± 0.01 K/kbar, eventually reaching 9.5 K at 9.1 kbar. A further increase in pressure leads to a substantial reduction in J , down to 5.5 K, caused by the switching of the main exchange pathways to bonds with weaker effective nearest-neighbour interactions as the system undergoes a change in magnetic dimensionality. Within the high-pressure region, any further application of pressure results in a steady increase in J at the rate of 0.1 ± 0.01 K/kbar.

It is possible to compare the extracted J values to estimates from low-field susceptibility measurements. For a spin-1/2 Heisenberg AFM, a rough estimate of the exchange energy J can be deduced from the position of the short-range ordering peak in the low-field magnetic susceptibility, via

$$k_{\text{B}}T_{\chi}^{\text{max}} = aJ, \quad (4.3)$$

where $a = 0.641$ for a Q1D antiferromagnet [148], or $a = 0.94$ for a Q2D system [149]. From the work of Halder *et al.* [136], this gives $J \approx 10.6$ K at ambient pressure, and $J \approx 5.6$ K at 11.6 kbar, in good agreement with our findings. Note that this estimate is based on measurements made (a) over a wide range of temperatures, and (b) above the long-range ordering temperature T_{N} , whereas my magnetisation measurements are done at a set temperature which is below (Q2D phase), or in the vicinity of (Q1D phase), T_{N} , as detected from μ^+ SR data (see next Section).

Note that the magnetisation saturation field B_{c} is well resolved within the Q1D phase, despite the measurement temperature 1.4 K being above, but close to, T_{N} . This is due to short-range antiferromagnetic correlations, and the vicinity of the onset of long-range ordering at T_{N} .

4.5 Muon-spin relaxation

Further support for the dimensionality switch comes from μ^+ SR measurements which probe the magnetic ordering of a system and allow one to extract T_N [70]. Powder sample μ^+ SR measurements were carried out at the Swiss Muon Source, Paul Scherrer Institut, CH, with detailed temperature scans taken at six different pressures using a piston-cylinder cell, which showed good hydrostaticity [121]. Example μ^+ SR spectra are given in Figs. 4.7(a-c). The μ^+ SR data were fitted to

$$A(t) = \sum_i A_i e^{-\lambda_i t} \cos(2\pi\nu_i t + \phi_i) + \sum_i A_i e^{-\lambda_i t} + A_b(t),$$

where ν_i are the dominant oscillation frequencies due to long-range magnetic order of the sample, ϕ_i is a constant phase, the exponential terms account for residual magnetic dynamics in the sample, and the $A_b(t)$ term accounts for the background from the pressure cell. Full experimental details and detailed discussion of the muon technique can be found in Refs. [121, 135].

The evolution of the fitted oscillation frequencies is given in Figs. 4.7(d-f). Within the low-pressure regime, oscillations were observed at three frequencies below a critical temperature, which at approximately 1 kbar is 2.48(1) K. This is in agreement with previous ambient-pressure measurements which found oscillations at three frequencies below 2.59(1) K [71]. The onset of these oscillations implies long-range ordering within the system, and gives the ordering temperature T_N . In this regime, T_N is found to decrease with application of pressure [see Fig. 4.6(e)].

At 11.2 kbar and above there is no discontinuous change in the μ^+ SR spectra above 1 K. However, oscillations at a single frequency appear below 500 mK [Figs. 4.7(c,f)], providing evidence for long-range magnetic order in the high-pressure regime. T_N is found to increase with increasing pressure, in accordance with the behaviour of the dominant exchange J , and the change in T_N is found to be reversible upon reduction of pressure from 22.5 kbar to 11.2 kbar. Compared to a Q2D system, a Q1D system should be expected to have a much reduced long-range ordering

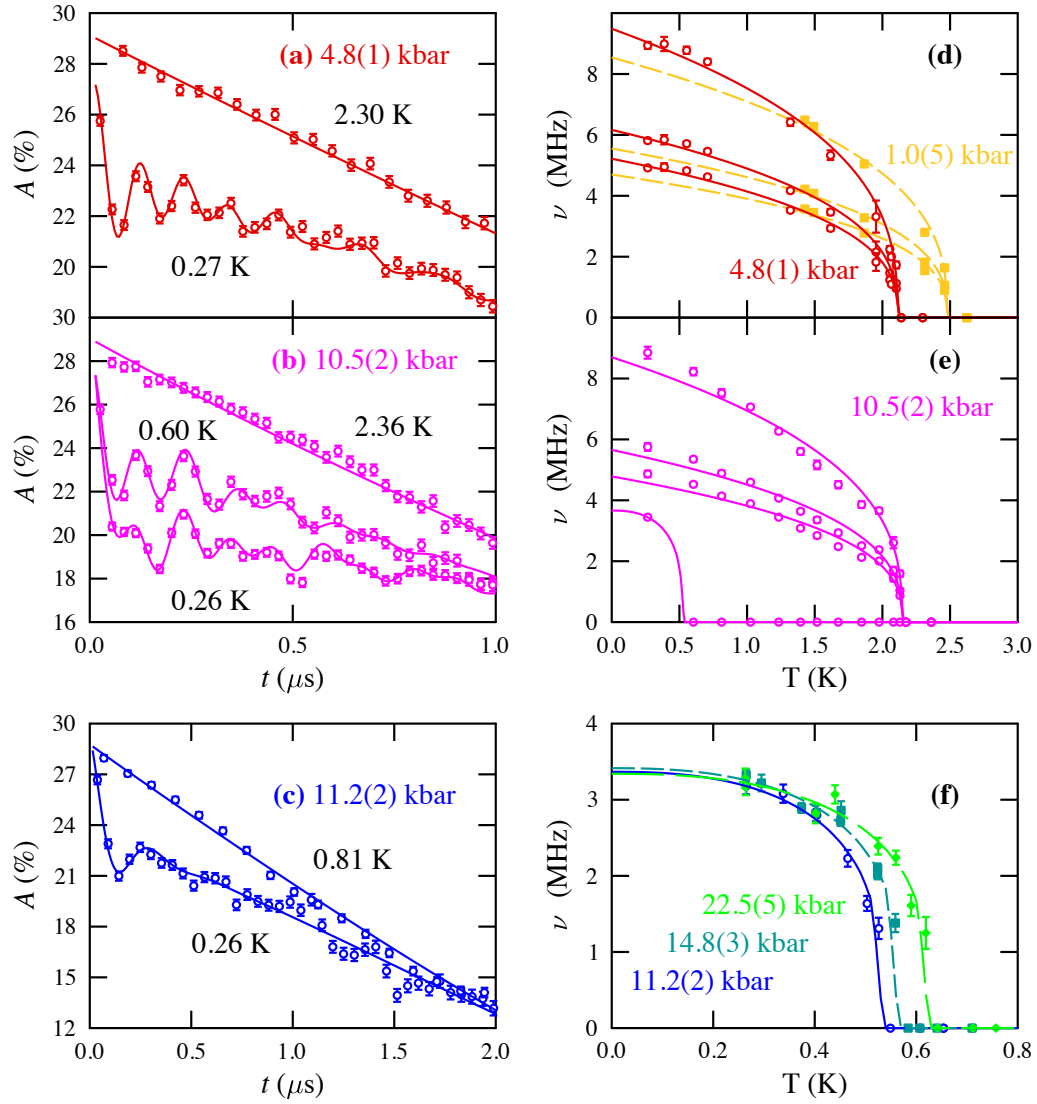


Figure 4.7: Time evolution of the μ^+ decay asymmetry $A(t)$ in (a-b) the low-pressure regime, and (c) the high-pressure phase. Also shown are (d-f) the fitted oscillation frequencies $\nu(T)$. Two frequencies were dominant in the low-pressure regime, while the higher pressure phase was well described by a single frequency.

temperature owing to the increased influence of fluctuations in one dimension [150]. Therefore, the large decrease in T_N that is observed in the critical pressure region [Fig. 4.6(e)] is consistent with a transition to Q1D magnetic behaviour at high pressures. Also note the different temperature dependence of the oscillation frequencies in the Q1D and Q2D phases.

The combination of a substantial change in the μ^+ SR frequencies and ordering temperature T_N , as well as a dramatic reduction in the critical field B_c , provides unambiguous evidence and direct confirmation of the proposed phase transition from Q2D to Q1D antiferromagnetism. I emphasize that the critical pressure region of 9.1 kbar is in agreement with the critical pressure of the JT-axis change seen in powder-sample structural measurements of Halder *et al.* [136], as well as infra-red spectroscopy measurements of Musfeldt *et al.* [151] which showed significant changes in the collective behaviour of the lattice vibrations at P_{c1} .

This dimensionality crossover is further supported by a single crystal ESR and structural study by Prescimone *et al.* [131], who observed a pressure-induced JT-axis shift accompanied by a rotation of the magnetic d -orbitals, albeit at a higher pressure of 18 kbar. Other than this difference in the critical pressure value, their structural measurements above and below the phase transition match that of Halder *et al.* [136]. As the g -factor is governed by the local environment of the Cu atoms, in this chapter I have used the appropriate g -factor for the appropriate structure from ESR, as given in Ref. [131]. The reason for the discrepancy between the critical pressure of our single-crystal magnetisation and powder-sample μ^+ SR measurements, as well as the structural and infrared measurements [136, 151] of others, and the work of Prescimone *et al.* [131] is not clear. One reason may be the effect of non-hydrostaticity, which is dependent on the pressure cell design, the cooling rate, the pressure medium, and the sample size, amongst other things. Furthermore, it is known that $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$ is sensitive to desolvation, and to prevent this my measurements were performed within 48 hours of the sample being grown. However,

the time length between the sample growth and measurements in Ref. [131] is not known.

4.6 Further discussion

Empirical formulae based on Quantum Monte Carlo simulations by Yasuda *et al.* [152] can be used to relate the secondary exchange $J_\perp$ to J and T_N , via

$$|J_\perp| = |J| \exp(2.43 - 0.88\lambda), \quad (4.4)$$

for a Q2D Heisenberg AFM, and

$$|J_\perp| = 1.073 T_N \frac{1}{\sqrt{\ln \lambda + 0.5 \ln \ln \lambda}}, \quad (4.5)$$

for a Q1D Heisenberg AFM, where $\lambda = 2.6 J/T_N$. The calculated values of $J_\perp$ are shown in Fig. 4.6(f). Within the low-pressure Q2D phase I find $J_\perp$ to be of the order of 1 mK. In the Q1D regime, $J_\perp$ is mediated by the portion of the $d_{x^2-y^2}$ orbitals that still lie within the bc -plane, and this leads to a jump in $J_\perp$ by two orders of magnitude to approximately 0.3 K as we move over to the Q1D phase.

Fluctuations reduce the size of the ordered moment in low-dimensional AFMs. Using a mean-field approximation, we can estimate the zero-field moment of a Q1D AFM from [153]

$$m_0 = \frac{28}{15} \sqrt{\frac{14}{15\pi}} g\mu_B \sqrt{\frac{J_\perp}{J}}.$$

The value of $J_\perp/J$ remains approximately constant within the Q1D phase, yielding a value of $m_0 = 0.46 \pm 0.01 \mu_B$. This compares with $0.5 \mu_B$ and $0.072 \mu_B$ in the Q1D AFMs KCuF_3 and Sr_2CuO_3 [153], and is smaller than $m_0 = 0.6 \mu_B$ estimated in the low-pressure Q2D phase from neutron data [134]. These values are noticeably smaller than that of a spin-1/2 free moment. Thus the effective moment is seen to decrease significantly with decreasing dimensionality. This is due to the increased significance of quantum and thermal fluctuations as the dimensionality is reduced [150].

The reduction in effective moment may also tentatively explain the increase in concavity of the magnetisation curve in low dimensional systems: as the dimensionality is reduced, the effective moment is lowered, and so the system has a lower magnetisation at a given field. However, the magnetisation of the fully polarised state is independent of the dimensionality,² and so both Q1D and Q2D phases must reach the same magnetisation value at the saturation field. Thus a low-dimensional system must ‘recover’ the reduced moment as the magnetic field approaches the saturation point, leading to a more concave magnetisation curve.

The trends in J [Fig. 4.6(d)] can be explained in terms of the effect of pressure on the crystal structure and the magnetic exchange ligands. The decrease seen in J within the Q2D phase is due to the increase in the β -angle between the a - and c -axes [136], which leads to a misalignment of Cu-pyz-Cu chains and causes them to begin to slide past each other [151]. This serves to severely disrupt the $\text{H}\cdots\text{F}$ bonded network, decreasing the efficiency of magnetic coupling along the $\text{Cu-OH}\cdots\text{F-Cu}$ exchange pathways and thus reducing J .

The steady increase in J with applied pressure within the Q1D regime is because unlike the soft $\text{H}\cdots\text{F}$ bonded layers, the Cu-N bonds and the pyrazine rings are relatively resilient, and so no major distortions are seen within the Cu-pyz-Cu chain in the Q1D regime [136, 151]. This resilience, together with the decrease in the chain length with applied pressure [136], enhances the magnetic d -orbital density overlap along the chain and results in the increase in J .

The μ^+ SR data provide evidence for phase separation at 10.5 kbar, where a fourth frequency appears at low temperatures and the other three frequencies remain present up to 2.15 K [see Fig. 4.7(e)]. The magnitude of the fourth frequency is consistent with those found for the Q1D ordering at 11.2 kbar and above, and the other three frequencies are consistent with those found for the Q2D ordering below 10 kbar. While I cannot completely rule out the effects of non-hydrostaticity,³ these observations in both powder μ^+ SR and single crystal magnetisation measurements,

²Note that this is not strictly true, as the g -factor may differ in different phases.

³The hydrostaticity is estimated to be ± 0.2 kbar for the 10.5 kbar μ^+ SR experiment [121]. We also estimate an upper limit of ± 0.7 kbar for the 9.1 kbar magnetisation measurement.

	Pressure (kbar)	ΔP (kbar)	B_c (K)	J (K)	Phase
Magnetisation	0.001	0	28.1(3)	11.4(3)	Q2D
	5.9(2)	0.5	24.8(3)	10.0(2)	Q2D
	9.1(2) ^a	0.7	23.4(3)	9.5(2)	Q2D
	9.1(2) ^a	0.7	7.9(1)	5.5(1)	Q1D
	12.9(2)	0.7	8.3(1)	5.9(1)	Q1D
	15.6(2)	0.2	8.9(1)	6.3(2)	Q1D
	20(1)	3.3	9.4(1)	6.6(2)	Q1D

Table 4.1: Summary of the magnetisation data on $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$. J was calculated using Eqn. 4.2, using the appropriate value of g . ΔP is the upper-limit of the non-hydrostaticity estimate.

^aAssuming phase separation.

	Pressure (kbar)	ΔP (kbar)	T_N (K)	$J_\perp$ (K)	Phase
$\mu^+\text{SR}$	0.001	0	2.59(1) ^a	5(1)	Q2D
	1.0(5)	0.5	2.48(1)	4.2(9)	Q2D
	4.8(1)	0.1	2.11(3)	1.5(4)	Q2D
	10.5(2) ^b	0.2	2.15(3)	6(2)	Q2D
	10.5(2) ^b	0.2	0.5(1)	280(80)	Q1D
	11.2(2)	0.2	0.535(5)	290(3)	Q1D
	14.8(3)	0.3	0.570(6)	308(4)	Q1D
	22.5(5)	0.5	0.628(8)	339(5)	Q1D

Table 4.2: Summary of the muon-spin relaxation measurements on $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$. $J_\perp$ was calculated from Equations 4.5 and 4.4, using values of J found from interpolation of the magnetisation data. ΔP is the non-hydrostaticity estimate.

^aFrom Manson *et al.* [71].

^bAssuming phase separation.

as well as in a separate ESR study [131], seem to point towards the presence of an intrinsic phase separation in the critical pressure region.

4.7 Another Jahn-Teller active material:

$\text{Cu}(\text{NO}_3)_2(\text{pyz})$

We observed that in $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$, the presence of three different ligands in the Cu-centered octahedra effectively introduced several degrees of freedom in the JT-axis orientation. This has allowed a sequential change in the direction of the JT-axis through structural perturbations, due to the different ligand strengths. It is interesting to compare this material to $\text{Cu}(\text{NO}_3)_2(\text{pyz})$, which is similarly based on a JT-active Cu atom sitting in a distorted octahedron, but only surrounded by two unique ligands.

$\text{Cu}(\text{NO}_3)_2(\text{pyz})$ has a structure very similar to that of $\text{Cu}_2(\text{H}_2\text{O})_2(\text{pyz})$, consisting of Cu-pyz-Cu chains along the a -axis, with the Cu-atoms joined together in the plane perpendicular to the chain direction by NO_3 bonds, as shown in Figs. 4.8(a,b). The Cu atoms sit within a distorted octahedral environment, surrounded by Cu-N and Cu-O ligands. This system is known to be a Q1D AFM at ambient pressure ($J = 10.6 \text{ K}$, $T_N = 0.107 \text{ K}$), with the magnetic orbitals lying within the Cu-pyz-Cu chain direction and the JT-axis along the Cu-O bonds [17].

Low-field (0.1 T) susceptibility measurements as a function of temperature were performed in a range of pressures up to 11.6 kbar, and are shown in Fig. 4.8(c). The broad peak in susceptibility is due to short-range antiferromagnetic ordering above T_N . The primary exchange energy J can be estimated via Eqn. 4.3, and is shown in Fig. 4.8(d). I observe no change in the exchange coupling J with applied pressure within this material, although a gradual increase in J with pressure may be present. Note the relatively large error bars in Fig. 4.8(c), which arise from the broadness of the susceptibility peaks. This highlights an advantage of magnetisation measurements, which can determine J to much better accuracy.

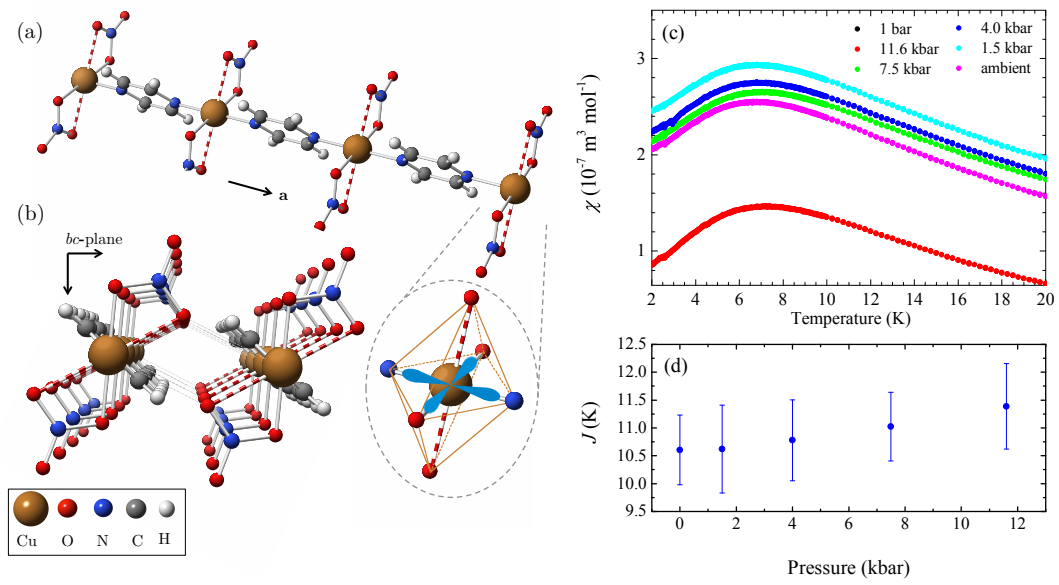


Figure 4.8: Crystal structure of $\text{Cu}(\text{NO}_3)_2(\text{py})_z$ at ambient pressure, along the (a) a -axis, and (b) the bc -plane. The red striped bonds represent the JT-axis. The zoomed-in region shows the JT-octahedron, together with one possible representation of the magnetic orbitals. (c) Low field (0.1 T) susceptibility measurement of $\text{Cu}(\text{NO}_3)_2(\text{py})_z$ across a range of pressure, with the field parallel to the a -axis. (d) A rough approximation of J , deduced from the position of the low-field susceptibility peaks.

However, unlike $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$, no JT-switching or orbital reorientation is seen upon application of pressure (up to 11.6 kbar) in this compound, likely due to the angle of the O–Cu–O bonds in the octahedra being significantly different from 90° . Such a mismatch with the symmetry of the $d_{x^2-y^2}$ orbitals would considerably increase the energy cost of an orbital reorientation. Furthermore, in $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$, the successive change in JT-axis from Cu–N to Cu–O, to Cu–F, is in accordance with the empirical ligand field strengths (*i.e.* spectrochemical series $\text{F}^- < \text{OH}^- < \text{pyrazine}$) [136, 154] and leads to a sequential decrease in the unit cell volume with increasing pressure. If the same JT-axis direction vs cell volume trend holds for $\text{Cu}(\text{NO}_3)_2(\text{pyz})$, then a rotation of JT distortion axis from Cu–O to Cu–N might lead to an increase in the unit cell volume, which would be energetically unfavourable.

4.8 Conclusion

Through high-pressure magnetisation and $\mu^+\text{SR}$ measurements, I have shown that pressure can be used to induce a Jahn-Teller driven magnetic phase transition in $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$. The system undergoes a phase transition from quasi-two-dimensional to quasi-one-dimensional antiferromagnetic behaviour at 9.1 kbar due to changes in the primary exchange pathways, leading to a dramatic change in the exchange coupling strength and ordering temperature. The exchange coupling J was found to decrease gradually with pressure in the two-dimensional phase, drop by more than a half at the phase transition, and then increase in the one-dimensional regime. I also related the changes in J to the effect of pressure on the crystal structure.

In this system the presence of different ligands in the Jahn-Teller octahedra has essentially induced several degrees of freedom on the Jahn-teller axis, whose direction can be sequentially changed due to the different ligand strengths. The chemistry of coordination polymers is well established, and so the possibility of designing similar systems with specific ligand strengths exists. This gives considerable control over

the Jahn-Teller axis behaviour when compared to other materials, such as Tutton salts [155, 156] or Na_3MnF_6 [157], where all the ligands are the same type, but a single pressure-driven Jahn-Teller axis switch is observed due to subtle differentiation of the ligands by second-order intermolecular interactions [136].

In conclusion, I have demonstrated that pressure can be used to adjust the magnetic properties of metal-polymeric systems, giving us the ability to tune the interaction strengths and select the magnetic dimensionality via external perturbation. This work emphasises the powerful role that pressure can play in exploring new materials and phases.

4.9 Further work: a second phase transition in $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$?

Structural measurements suggest that $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$ undergoes a second structural distortion at higher pressures [131, 136]. However, there is some controversy in literature with regards to (a) the critical pressure of this structural transition, and (b) the exact nature of the transition itself. Two new high-pressure structures have been proposed:

- Measurements by Halder *et al.* [136] show a structural phase transition at approximately 31 kbar, which they propose is consistent with switching of the JT-axis from the Cu–O to Cu–F bond direction.

Similarly to the previous phase transition at 9.1 kbar, this would cause a rotation of the $d_{x^2-y^2}$ orbitals from the *ac*- to *bc*-planes of the system, with the lobes of the orbital lying along the Cu–pyz–Cu and Cu–O bonds. Thus there would be little change in the overlap of the magnetic $d_{x^2-y^2}$ orbital and the Cu–pyz–Cu bonds across this phase transition, and the system remains Q1D. See Fig. 4.9(a).

- Measurements by Prescimone *et al.* [131] show a second phase transition at 21 kbar, a noticeably lower pressure than that of Halder *et al.* [136]. They

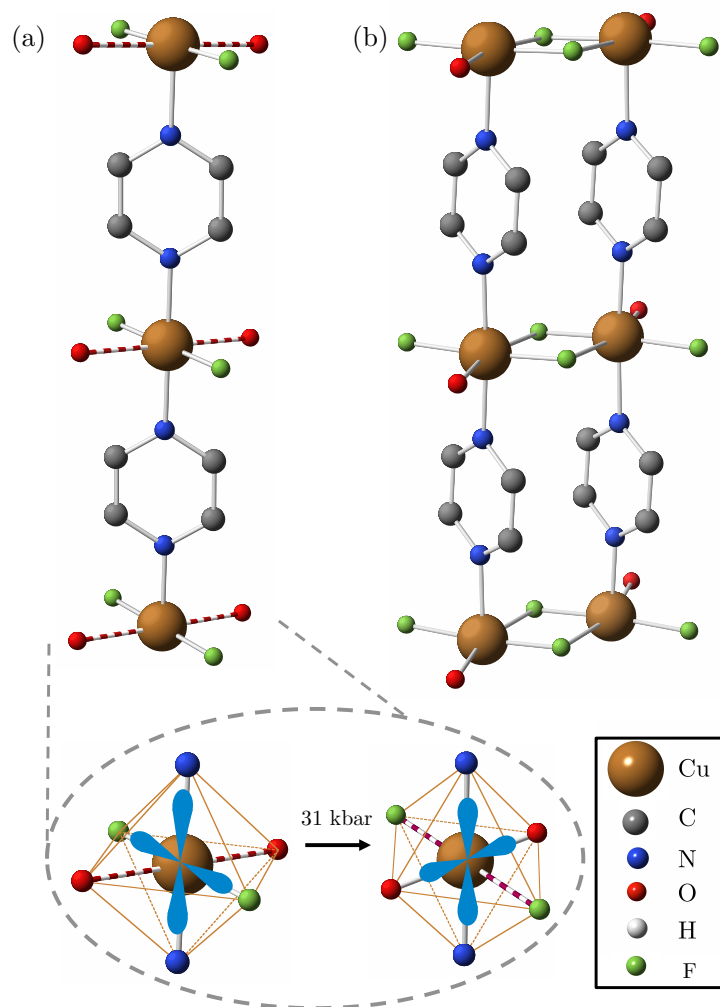


Figure 4.9: The proposed scenarios for a second structural transition in $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$: (a) a second JT-axis switch at 31 kbar [136], or (b) joining up of two chains via Cu-F bonds at 21 kbar [131], forming a spin-ladder. The hydrogen atoms are not shown for clarity. The JT-axis is shown by the red striped bonds. In (a) the zoomed-in region shows the proposed change in the JT-octahedron at 31 kbar. The blue lobes represent the magnetic orbitals, which provide the dominant exchange pathways. See Fig. 4.1 for comparison with phase transition at 9.1 kbar.

observe no JT-axis switching at this pressure, but instead propose that two-thirds of the chains begin to eject one water molecule per Cu atom, forcing the chains to join together via Cu–F–Cu bonds to fill the empty coordination position. The remaining one-third of the chains remain unaffected, with the ejected water molecules lying in-between the modified and unmodified chains. This situation is shown in Fig. 4.9(b).

This structural transition would lead to a second exchange coupling via the Cu–F–Cu bonds, forming a spin-ladder system, with J_{rung} and J_{leg} characterising the exchange along the Cu–F–Cu and Cu–pyz–Cu bonds, respectively. One might expect $J_{\text{rung}} > J_{\text{leg}}$ due to the shorter length of the Cu–F–Cu bonds. In this scenario the system would become dimerised, potentially exhibiting a spin-gap between a non-magnetic ground state and magnetic excited states (see Chapter 5).

In order to distinguish between the two proposed scenarios and to investigate this high-pressure phase, I performed a series of PDO measurements in diamond-anvil cells (DACs), reaching pressures of up to 56 kbar. The procedure for setting up DACs is given in Appendix A. Such experiments are extremely challenging. A great difficulty in DAC work is the very small dimensions that have to be worked with, which makes it significantly more demanding than piston-cylinder cells, and leads to a higher failure rate. For this experiment over ten DACs were prepared, using a wide variety of diamonds of different diameters, gasket thicknesses, gasket holes, and PDO coils. The most promising measurements were made using a cell with 0.8 mm cutlet diamonds and gasket thickness of 150 μm . A PDO coil with four turns of 15 μm Cu and coil diameter of 150 μm was used. The sample had a diameter of 80 μm and thickness of $\approx 40 \mu\text{m}$, giving a filling factor of less than 20%.

The experiment was performed using a 16 T superconducting magnet in a Quantum Design Physical Properties Measurement System at NHMFL, USA. The measurements were made at 22.0(4), 31.0(4), 39.9(4), and 56.3(6) kbar, at a temperature of 2 K. The results are given in Fig. 4.10(a). Features are difficult to see by eye in the

raw data, suggesting that the magnetoresistive background is higher than the sample signal. However, features in df/dB became apparent if several measurements were performed at the same pressure and the results averaged.

The df/dB curve for several pressures is given in Fig. 4.10(b). We observe a peak (labelled **a**) in the 22 kbar curve, which has a similar profile to the peaks seen at the sample saturation point in the piston-cylinder cell measurements presented earlier in this chapter. I suggest that this peak is also seen in the 31 kbar data at a slightly higher field, although it is less pronounced. The positions of these two peaks, once plotted with the sample saturation field at lower pressures, continue the trend followed by the saturation point of the Q1D phase as measured using piston-cylinder cells (see Fig. 4.11). Therefore, I tentatively suggest that the peaks labeled **a** represent the Q1D saturation point, implying that a portion of the sample remains in the Q1D phase up to 31 kbar. However, the origins of features **b** and **c** in df/dB remain unclear. It may be that **c** is part of a peak at fields just above 16 T.

It is clear that in these measurements the PDO is just at the edge of being sensitive to the sample magnetisation, with the magnetoresistive background dominating any signal from the sample. This is due to several factors, including,

- the low filling factor of the coil,
- the very small dimensions of the coil, which means that it has a low impedance, and
- the large fringe field of the superconducting magnet. This means that a considerable portion of the coaxial cable that connects the coil to the PDO is under a magnetic field, increasing the background.

The result that a portion of the sample remains in the Q1D phase up to 31 kbar is in agreement with the situation proposed by Halder *et al.* [136], who suggest that the critical pressure of the new phase would be at around 31 kbar. Alternatively, the features **a** could correspond to the portion of the Cu-pyz-Cu chains that remain Q1D and un-dimerised in the Prescimone *et al.* [131] proposal. Thus the data as

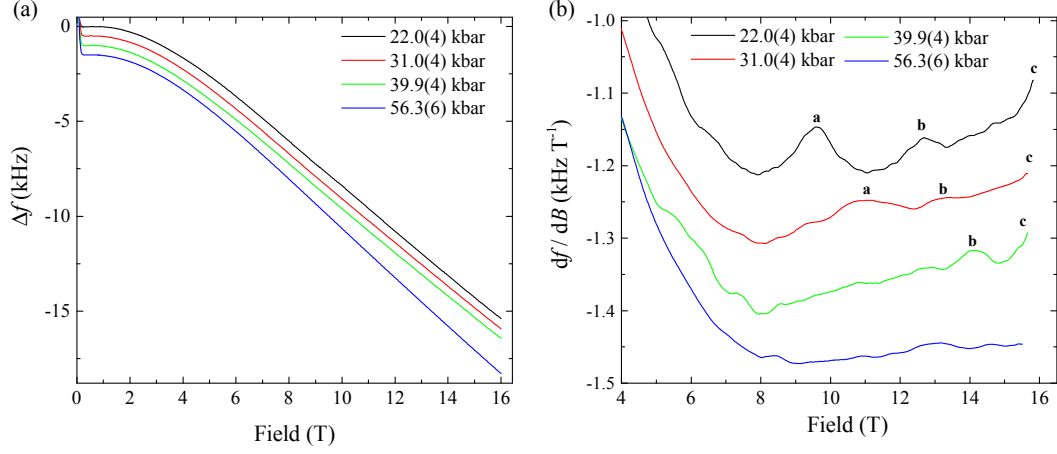


Figure 4.10: Results of $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$ PDO measurements, in a diamond-anvil cell at 2 K. (a) The evolution of the PDO resonant frequency as a function field, $f = \omega/2\pi$. The resonance frequency at zero field was 30.3 MHz. (b) Derivative of the frequency df/dB at several pressures, showing features **a**, **b**, and **c**. The reduction in df/dB at low fields is due to the magnetoresistive background. Note that the data are average of multiple measurements, and have been offset for clarity.

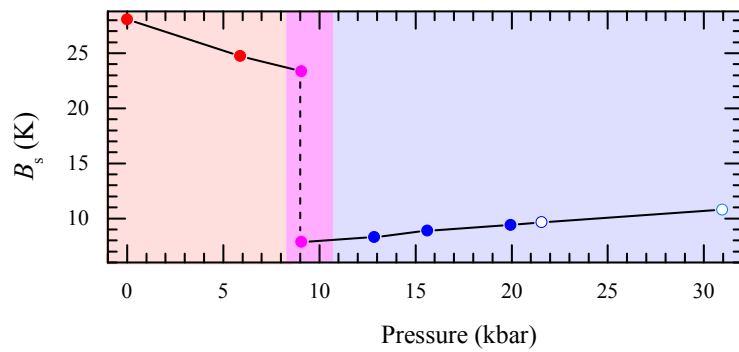


Figure 4.11: The evolution of the saturation field of $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$ with pressure. The filled points are from the piston-cylinder cell measurements. The open points are the positions of the features **a** seen in the data from the diamond-anvil cell measurements (see text).

presented here are compatible with both scenarios, and no firm conclusions can be made. In order to be able to distinguish between the two cases, data with a higher signal to background ratio and measured to higher fields are required.

One method of increasing the sample-signal to background ratio is to use pulsed magnetic fields. Pulsed-field magnets are notably smaller than steady-field magnets, and also have a significantly smaller fringe field. This would result in a considerable reduction in the magnetoresistive background. In fact, I have performed ambient pressure measurements in pulsed magnetic fields under the same sample conditions (coil size, sample size) as in a DAC, and my results show that even in these unfavourable conditions it is possible to extract the magnetisation curve. Note that pressure measurements in pulsed fields would require the use of plastic diamond-anvil cells, which have a lower maximum pressure limit than their metallic counterparts.

Chapter 5

Field-induced transitions in molecular magnets

“Quantum physics thus reveals a basic oneness of the universe.”
– Erwin Schrödinger (1887–1961)

In the previous chapter, it was shown how pressure-induced structural changes can cause a phase transition from two-dimensional to one-dimensional magnetism. In continuation, here I investigate the magnetic properties of two molecular compounds that are synthesised from the same starting building blocks, showing how a small chemical difference can lead to drastically different structural and magnetic behaviour in coordination polymers, leading to a change from one-dimensional to zero-dimensional magnetism at zero field. Through examination of the structural and magnetic behaviour, I demonstrate that $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$ is a quasi-one-dimensional Heisenberg antiferromagnet, while $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$ is a quasi-zero-dimensional system that is based on a lattice of spin-dimers, and remains disordered down to 0.03 K, but shows a field-temperature phase diagram that is reminiscent of that seen in materials showing Bose-Einstein condensation of triplons. This chapter is based on work published in Ref. [19].

5.1 Introduction

One of the goals of research in molecular magnetism is to achieve desirable magnetic properties in a material through control of the chemical components, hence ultimately making the design of bespoke magnetic materials a reality. This requires an extensive understanding of the relationship between the starting materials, the structure, and the magnetic properties of a system. Here I present a case where a synthesis route leads to realisation of two starting materials that are based on the same molecular building blocks. The different structural motifs of the materials promote contrasting exchange coupling pathways that lead to dramatically different magnetic behaviour. Through magnetisation, static and dynamic susceptibility, heat capacity, and muon-spin relaxation measurements, I show that $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$ shows highly one-dimensional Heisenberg antiferromagnetism, while the sister compound $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$ is a dimerised system with a non-magnetic singlet ground state, and so behaves as a zero-dimensional disordered magnet at zero field. Furthermore, $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$ is shown to undergo a field-induced phase transition through a quantum critical point (QCP) to an XY ordered phase, which is reminiscent of Bose-Einstein condensation of triplons [158–162]. Thus the two materials, although starting from the same chemical ingredients, show remarkably different behaviour, highlighting the importance of understanding the relationship between the magnetism and structure within these compounds.

This chapter is based on work published in Ref [19], and is the result of a collective effort. High-field magnetisation and dynamic susceptibility measurements, and relevant analysis, were performed by myself, with the assistance of F. R. Foronda and P. A. Goddard. The crystal orientation x-ray measurements were done by myself. μ^+ SR measurements and analysis were performed by T. Lancaster, J.S. Möller, P. J. Baker, F. L. Pratt, and S. J. Blundell. Heat capacity, static susceptibility, and the $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$ magnetisation measurements were performed by L. Huang and J. Wosnitza. Sample growth was done by J. L. Manson and students.

The materials were synthesised by slowly mixing aqueous solutions of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, glycine (=gly, $\text{C}_2\text{H}_5\text{NO}_2$), and pyrazine (=pyz, $\text{C}_4\text{H}_4\text{N}_2$) together to form a deep blue coloured solution. Purple blocks of $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$ typically form after about one week and are removed via suction filtration. Continuing evaporation of the mother liquid leads to blue rods of $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$. On several occasions, the two compounds grew simultaneously but were mechanically separated and their identities confirmed by infra-red spectroscopy and x-ray diffraction. Varying the relative ratios of the chemical reagents does not alter the outcome and the latter material is always obtained in higher yield.

5.2 A spin chain: $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$

The structure of $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$ is based on linear chains of $S = 1/2$ Cu^{2+} ions linked with pyrazine ligands as shown in Fig. 5.1. Glycine groups and H_2O molecules coordinate with the Cu^{2+} ions and these, with non-coordinating ClO_4 counter-ions, act to separate the chains. Pyrazine can be an effective mediator of magnetic exchange in coordination polymers, and so one would expect the chain-like structure to promote quasi-one-dimensional (Q1D) antiferromagnetism.

The magnetic behaviour of $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$ was characterised using magnetisation and static susceptibility measurements on polycrystalline samples, and was found to be well described by the predictions of a Heisenberg Q1D model. The model is defined by the Hamiltonian,

$$\mathcal{H} = J \sum_{\langle i,j \rangle_{\parallel}} \mathbf{S}_i \cdot \mathbf{S}_j + J_{\perp} \sum_{\langle i,j \rangle_{\perp}} \mathbf{S}_i \cdot \mathbf{S}_j + g\mu_{\text{B}}B \sum_i S_i^z, \quad (5.1)$$

where J is the strength of the exchange coupling within the magnetic chains, $J_{\perp}$ is the coupling between the chains, and the first and second summations refer to summing over unique pairs of nearest neighbours parallel and perpendicular to the chain, respectively. The third term is the Zeeman splitting term, scaled by the g -factor. The magnetic susceptibility was measured using a Quantum Design SQUID, and is

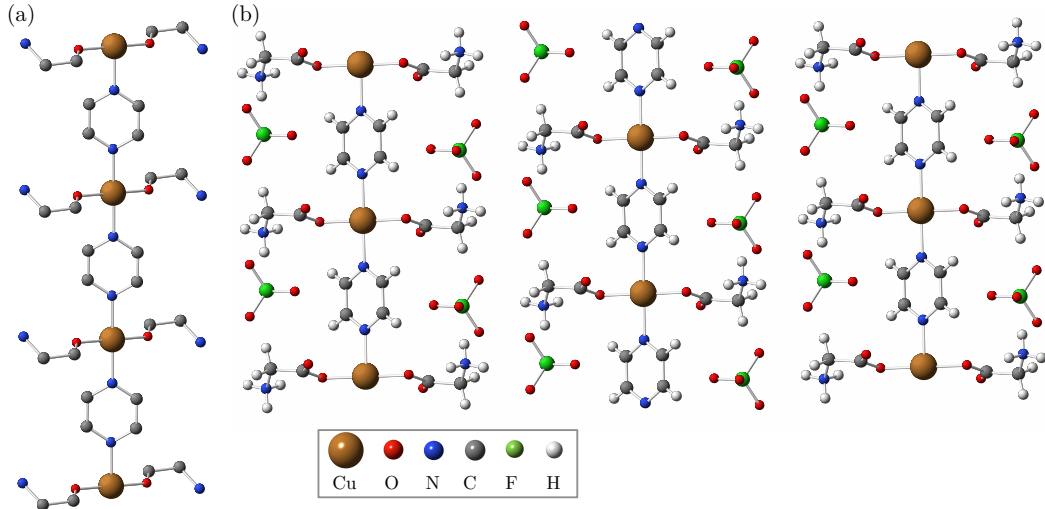


Figure 5.1: (a) The Cu-pyz-Cu chains on which $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$ is based, and (b) view of the material along the c -axis, showing the packing of the chains with non-coordinating ClO_4 groups, which occupy the empty spaces between the chains.

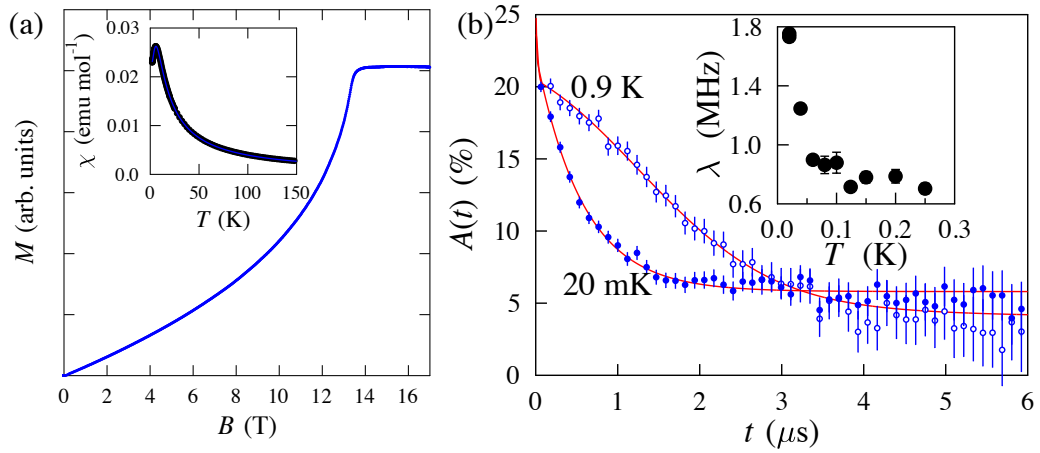


Figure 5.2: (a) Magnetisation of chain-like $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$ measured at 0.5 K. *Inset*: static magnetic susceptibility measured at 100 mT. (b) Zero-field μ^+ SR spectra at 0.9 K and 20 mK. *Inset*: relaxation rate as a function of temperature, showing the onset of the magnetic transition.

given in the inset of Fig. 5.2(a). It is well fitted by the susceptibility model for a Q1D Heisenberg antiferromagnet [148], and is consistent with an antiferromagnetic (AFM) intrachain exchange strength $J = 9.4(1)$ K and $g = 2.10(1)$. Magnetisation measurements are shown in Fig. 5.2(a), and have a concave curvature typical of a Q1D system [12]. The saturation field of the magnetisation, $B_s = 13.3(1)$ T, allows us to estimate the exchange coupling via $g\mu_B B_s = 2J + 4J_\perp$ (Eqn. 4.2). This, assuming $J_\perp \ll J$, suggests $J = 9.4(1)$ K in agreement with the susceptibility results above. Note that this value is typical of exchange through Cu-pyz-Cu bonds [3, 12].

In order to assess how well $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$ approximates a Q1D AFM, we can use the ratio of the magnetic ordering temperature T_N to J , which should be zero for a perfectly one-dimensional system and one for an isotropic AFM [163]. Many thermodynamic probes cannot resolve the ordering transition in low-dimensional systems, due to strong thermal and quantum fluctuations, which lower T_N . However, as was shown in Chapter 4 and elsewhere [12, 17], muons are often sensitive to long-range ordering that can be difficult to detect in Q1D systems with other techniques. Example μ^+ SR spectra are shown in Fig. 5.2(b). Although oscillations, which are usually characteristic of long-range ordering, are not seen, we do see a sudden change in behaviour at low temperatures. As the temperature is reduced there is a sharp increase in the relaxation rate λ , which has been observed in other chain-like materials of this type and is shown to be indicative of magnetic order [12]. Thus we estimate $T_N \leq 0.04(1)$ K for $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$.

Quantum Monte-Carlo simulations provide a means of estimating the effective interchain coupling $J_\perp$ of a spin-1/2 Q1D system via Eqn. 4.5. Using our values of T_N and J we obtain an estimate $|J_\perp/J| \leq 2 \times 10^{-3}$ which provides a measure of the degree to which $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$ realises a Q1D antiferromagnet ($|J_\perp/J| = 0$ for a perfect 1D system). It is therefore a better Q1D than the intermediate-pressure phase of $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyz})$ ($|J_\perp/J| \approx 0.05$) or $\text{Cu}(\text{pyz})(\text{NO}_3)_2$ ($|J_\perp/J| \approx 4.4 \times 10^{-3}$) as mentioned previously in Chapter 4, but is less well isolated

than the inorganic material Sr_2CuO_3 ($|J_\perp/J| \approx 7 \times 10^{-4}$) [164] or the organic salt DEOCC-TCNQF_4 ($|J_\perp/J| < 6 \times 10^{-5}$) [165].

5.3 Field-induced transitions in $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$

It is interesting to compare the magnetic behaviour and structure of $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$ with its sister compound $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$, which grows under identical conditions but has one less glycine and H_2O molecule per formula unit. This causes $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$ to develop a significantly different structure, where the Cu-pyz-Cu chains have been broken into individual Cu-pyz-Cu links, leading to a lattice of alternating Cu^{2+} dimers. This is shown in Fig. 5.3. The dimers are tethered with glycine bridges that connect them together to form corrugated sheets, with non-coordinating ClO_4 ions lying between these sheets. Due to efficiency of exchange coupling along pyrazine, we can expect the coupling between the Cu atoms to be strong. In contrast, the exchange along the glycine and ClO_4 ions can be expected to be relatively weak. This suggests that the physics of this material is due to Cu-Cu dimer units weakly coupled to their neighbours.

5.3.1 Results

The static magnetic susceptibility of a single crystal of $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$ was measured using a Quantum Design SQUID at a field of 5 mT, and the results are given in Fig. 5.4(a). The data is well described by the Bleaney-Bowers model [166], which gives the susceptibility of a system of isolated antiferromagnetic dimers. The model is based on a simple application of the Boltzmann distribution to the energy levels, giving

$$\chi_0 = \frac{2N_A\mu_0\mu_B^2g^2}{k_B T [3 + \exp(J_0/k_B T)]},$$

where J_0 is the intra-dimer exchange coupling and N_A is the Avogadro constant. This model predicts a peak in susceptibility at $T = |J_0/(1.599k_B)|$, and gives $J_0 = 7.5(1)$ K. The effect of a weak inter-dimer exchange J_1 can be thought of as

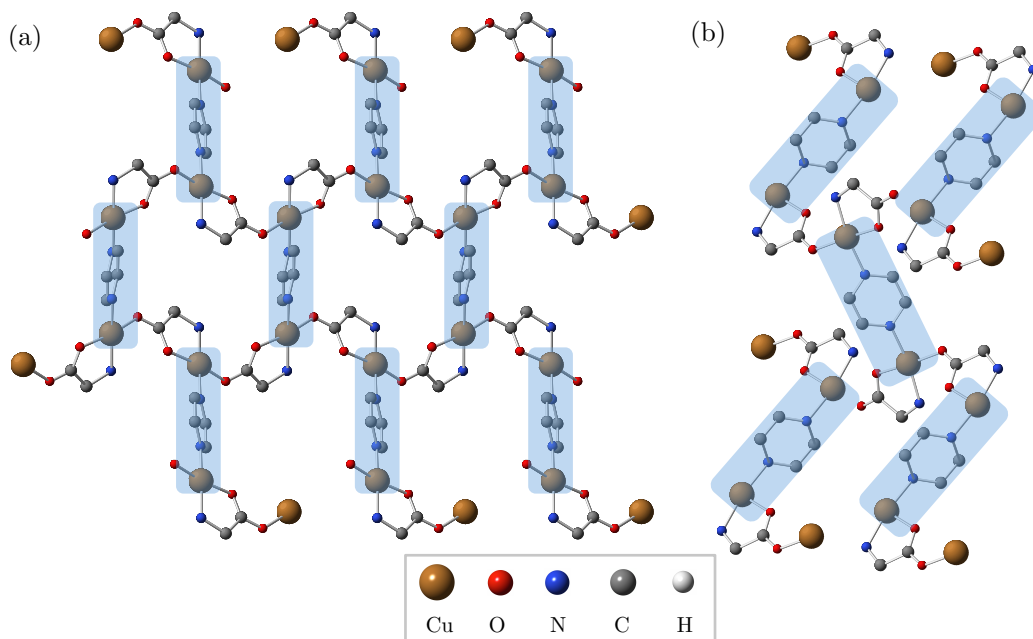


Figure 5.3: Structure of $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$ viewed along (a) the a -axis and (b) c -axis, showing the pairs of Cu atoms strongly coupled through pyrazine ligands to form alternating chains. Dimers are shaded, and the ClO_4 ions and H atoms have been omitted for clarity.

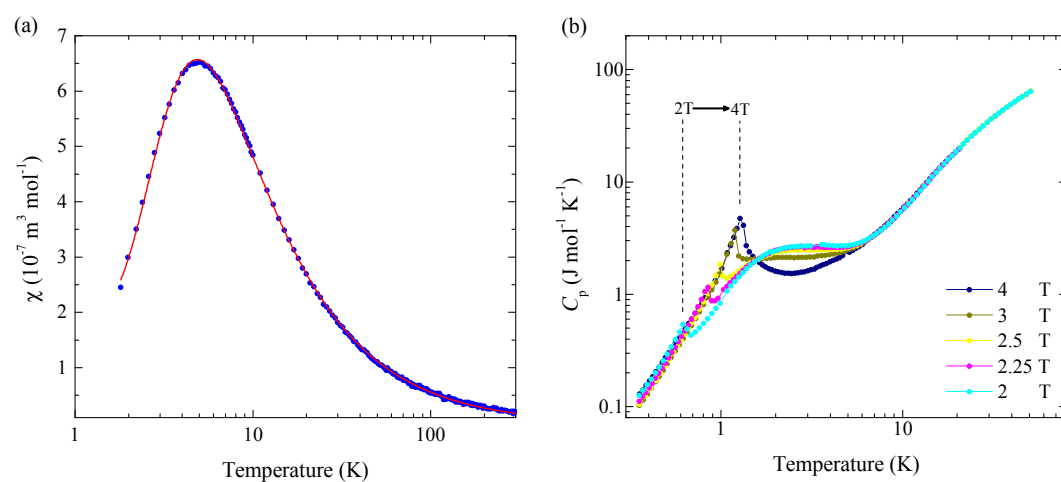


Figure 5.4: (a) The static magnetic susceptibility of $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$, at 5 mT. The fit is to the mean-field model of weakly interacting dimers. (b) Heat capacity of $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$ as a function of field, at steady magnetic fields of 2 – 4 T.

an additional field that competes with the applied magnetic field (i.e. a mean-field model) [60]. This has been shown to result in renormalisation of the Bleaney-Bowers model [60, 167], giving

$$\chi = (1 - \rho) \frac{\chi_0}{1 + \chi_0 J_1 / (\mu_0 \mu_B^2 g^2)} + \rho \frac{N_A \mu_0 \mu_B^2}{k_B T},$$

where I have also included a Curie-Weiss term for any spin-1/2 paramagnetic impurities, with ρ as the impurity percentage. ρ is found to be $\approx 1.8\%$, which is probably due to singly-occupied dimer sites [168]. This model gives a slightly better fit, resulting in a ferromagnetic (FM) coupling between the dimers of $J_1 = -2.1(1)$ K, and an AFM intra-dimer coupling of $J_0 = 8.13(2)$ K.

These results suggest that $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$ should be described by the Hamiltonian,

$$\mathcal{H} = J_0 \sum_i \mathbf{S}_{1,i} \cdot \mathbf{S}_{2,i} + \sum_{\langle mnij \rangle} J_{mnij} \mathbf{S}_{m,i} \cdot \mathbf{S}_{n,j} + g\mu_B B \sum_i S_i^z,$$

where i, j label dimers, m, n the magnetic sites within each dimer, and $\langle J_{mnij} \rangle = J_1$. The first two terms represent the intra-dimer and inter-dimer exchange couplings, respectively, and the third term is the usual Zeeman splitting term. Thus, it is clear that if J_{mnij} are weak compared to the AFM intra-dimer exchange J_0 , then the spin-1/2 Cu atoms within each dimer couple antiferromagnetically to form an $S = 0$ singlet, and the ground state is quantum disordered down to absolute zero. This is supported by zero-field μ^+ SR measurements, which see no signature of long-range magnetic order down to 32 mK.

Heat capacity measurements were performed using a Quantum Design PPMS (see Section 2.3). The heat capacity was measured as a function of temperature, in fixed magnetic fields up to 14 T, and the sample was oriented as in the static susceptibility measurements. Example heat capacity data are shown in Fig. 5.4(b). The application of a magnetic field is found to drive this material through a magnetic phase transition, resulting in a sharp peak in C_p . The phase transition occurs in the 2 – 6 T region in scans across the temperature range $0.4 \text{ K} < T < 1.4 \text{ K}$.

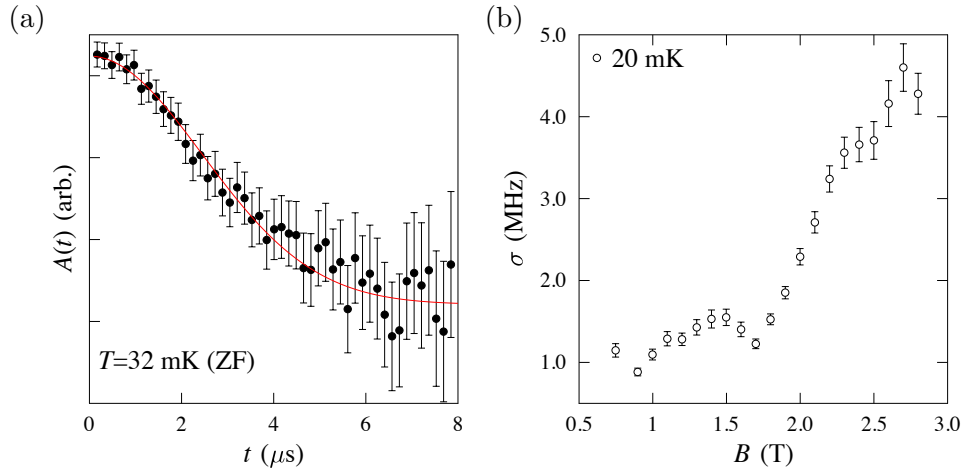


Figure 5.5: Example μ^+ SR data: (a) zero-field measurements at 32 mK, showing no change in the decay asymmetry, and (b) transverse field measurements at 20 mK, showing a transition at approximately 1.7 T.

Transitions were also seen in finite-field μ^+ SR measurements performed on unaligned polycrystalline samples. Measurements were performed using the Swiss Muon Source, Paul Scherrer Institut, CH, with the magnetic field in transverse field geometry (initial μ^+ spin normal to the field) and longitudinal field (initial μ^+ spin parallel to the field). The transition was seen in transverse field measurements as a dip in the relaxation rate, see Fig. 5.5(b). This was followed by a rapid rise in the μ^+ SR relaxation rate that is similar to that observed close to field-induced phase transitions in molecular magnets of this sort [152], and in the candidate BEC compound PbV_3O_9 [169]. See Refs. [19, 135] for full details of the μ^+ SR experiments.

Magnetisation measurements were performed in pulsed magnetic fields using the extraction susceptometer.¹ Sharp peaks indicative of field-induced transitions were observed in the dynamic susceptibility $\chi_d = dM/dB$, however they were found to be at a noticeably different region in the $B - T$ space when compared to the heat capacity and μ^+ SR data (see Fig. 5.7). In pulsed magnetic fields, the high rate of change of field and the short pulse-width means that often experiments are conducted under adiabatic conditions. Thus, the discrepancy in the pulsed field

¹Performed by myself, and also separately by J. Singleton and C. V. Topping. For brevity the pulsed field magnetisation curves are not shown.

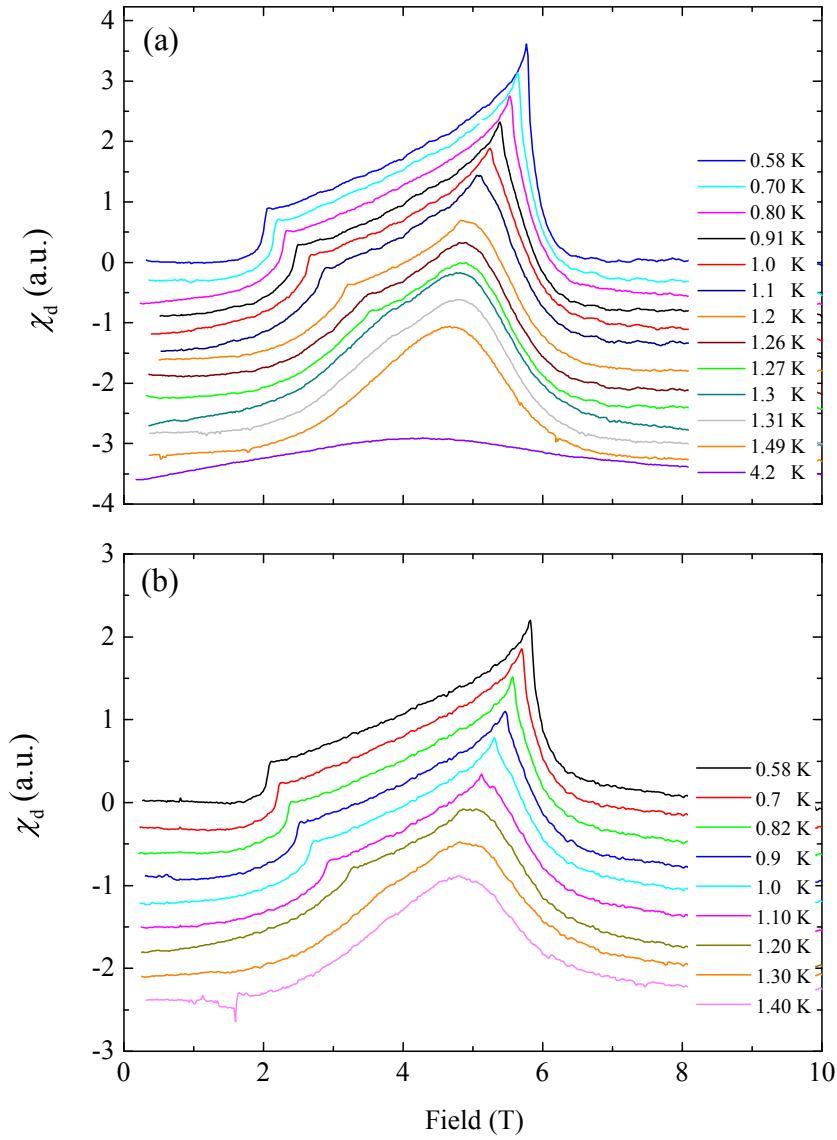


Figure 5.6: The dynamic susceptibility $\chi_d = dM/dB$ of $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$ at several temperatures, with the magnetic field normal to the (a) (110) and (b) (122) crystallographic planes, showing sharp features at the phase transitions. The data have been offset at each temperature for clarity. The resonant frequency at zero field was 29.8 MHz.

is due the magnetocaloric effect [170], where the sample temperature is reduced (by ~ 1 K) in the application of pulsed fields. The thermometry setup is unable to react within the millisecond timescale of the pulse, resulting in a discrepancy between the measured and actual sample temperature at the phase transition. The presence of a magnetocaloric effect is seen in other BEC candidate materials such as $\text{BaCuSi}_2\text{O}_6$ [171] and $\text{NiCl}_2\cdot 4\text{SC}(\text{NH}_2)_2$ [172], although it is not well-understood and is the subject of active research.

To ensure isothermal conditions, dynamic susceptibility measurements were performed using the proximity detector oscillator dynamic susceptometer, inside an Oxford Instruments 16 T superconducting magnet. The PDO coil was made out of 8 turns of $75\text{ }\mu\text{m}$ -thick Cu wire, and had a diameter of 0.8 mm. A custom-designed two-axis rotator was used, allowing measurements in two different orientations, with the magnetic field applied close to normal to the (110) or (122) crystallographic planes. The crystal directions were determined using a Oxford Diffraction SuperNova x-ray diffractometer. The field for the (110) orientation is parallel to the *ab*-plane, which contains the dimers. The PDODS magnetoresistive background was measured separately for each orientation, and was removed from the data as described in Chapter 3. The evolution of χ_d as a function of applied field and at various temperatures, is given in Fig. 5.6. The phase transitions can be seen as sharp features at ≈ 2 T and ≈ 6 T. Increasing temperature reduces the separation between these two features, such that they begin to merge together to form a broad hump at the maximum critical temperature of 1.4 K.

5.3.2 Discussion

The positions of the phase boundaries as determined from the different measurements show some degree of dependance on the crystal orientation, reflecting the effect of the *g*-factor anisotropy. Electron spin resonance measurements [19] have determined the *g*-factor for the dynamic susceptibility measurements with the field applied normal to the (110) plane as $g^{(110)} = 2.18$. The phase boundaries are found

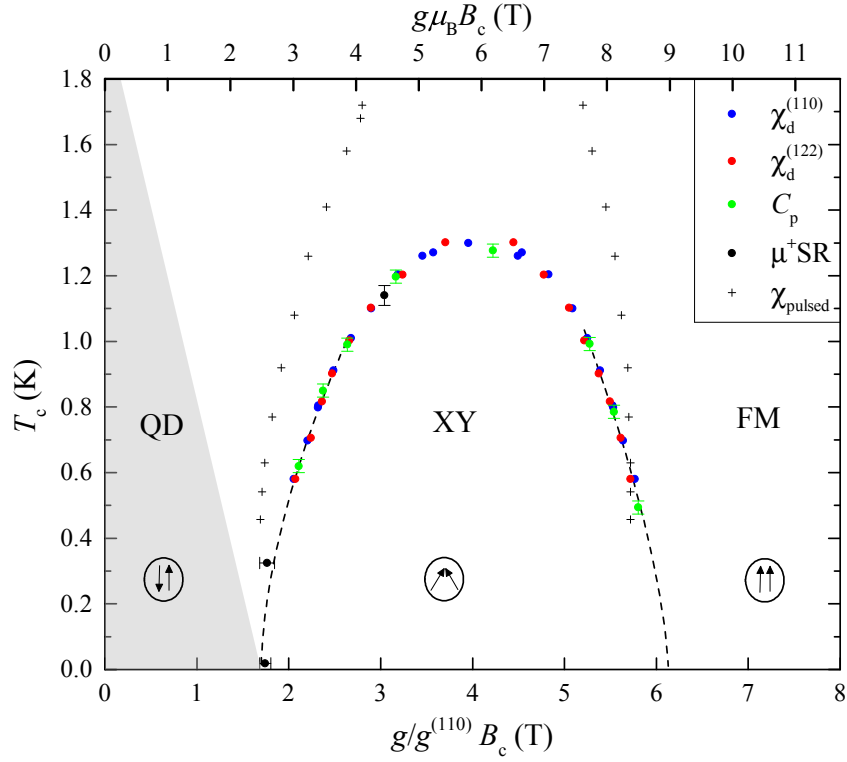


Figure 5.7: The B - T phase diagram of $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$, showing the quantum disordered, XY antiferromagnetic, and the polarised ferromagnetic phase. Quantum critical points can be seen at $g\mu_B B_c$ of 2.5(1) K and 9.0(2) K. The dashed lines show the expected behaviour of the phase boundaries with exponent $\phi = 2/3$, as predicted for the BEC of triplons. Arrows represent the state of the spins within each dimer, at different phases. Also shown (+) are the data from the pulsed field measurements, showing a large discrepancy with other measurements due to the magnetocaloric effect.

to coincide if one takes $g^{(122)} = 2.15$ for the χ_d measurement in the (122) crystal orientation, $g^{\mu\text{SR}} = 2.20$ for $\mu^+\text{SR}$, and $g^{\text{HC}} = 2.30$ for heat capacity measurements. I note that these g -factors fall within the range typically found in Cu-based coordination polymers [3, 12]. Scaling the critical field B_c at which the phase change occurs for each measurement by plotting $g\mu_B B_c$, I obtain the phase diagram shown in Fig. 5.7. The phase diagram shows the combined results of the dynamic susceptibility, heat capacity, and $\mu^+\text{SR}$ measurements, and as shown below, is consistent with that of a system of AFM dimers, coupled together with weak inter-dimer FM exchange interactions.

An isolated spin-1/2 dimer system with antiferromagnetic exchange forms an $S = 0$ singlet ground state, with a triply degenerate $S = 1$ excited state. In a weakly coupled system, these triplet excitations become mobile due to the inter-dimer coupling, and can ‘hop’ from one dimer to another. The triplet energy levels therefore become dispersive with a bandwidth D , as shown in the energy level diagram in Fig. 5.8(a) [173]. The phase diagram can be explained by considering the energy level diagram and the effect of an applied magnetic field on the $S^z = +1$ excited state. At temperatures well below J_0 , the ground state is a quantum-disordered paramagnet of singlets. The application of a magnetic field (say in the z direction) reduces the excitation energy of the $S^z = +1$ state due to the Zeeman energy.² Eventually the energy gap is closed at a quantum critical point (QCP) of $g\mu_B B_{c1}$, leading to a state of long-range magnetic ordering due to the exchange couplings J_0 and $J_1 = \langle J_{nmij} \rangle$ between the spins. Within this phase the system is an XY canted antiferromagnet, where further application of the magnetic field for $B > B_{c1}$ cants the spins along the z direction, and leads to a rise in the magnetisation [see Figs. 5.8(b)]. This continues until a second QCP at $g\mu_B B_{c2}$, where all the spins have become polarised along z , and the system is fully magnetised.

The situation described above will have a strong signature in the form of the magnetisation curve as a function of field and temperature [173, 174]. Example

²The energy of the $S^z = -1$ and $S^z = 0$ excited states increase, or remain unaffected upon the application of an applied magnetic field. Thus, provided that $T < J_0$ [9], they can be ignored as far as the low energy properties are concerned.

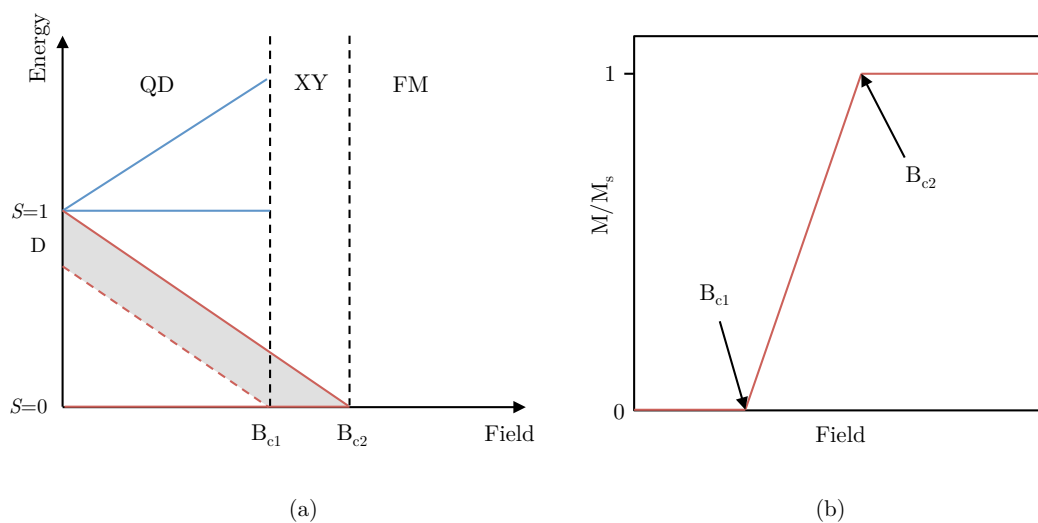


Figure 5.8: (a) Schematic energy level diagram of a weakly coupled spin-1/2 dimer system with FM inter-dimer couplings, showing the Zeeman splitting of the $S^z = +1$ triplet mode, with an energy bandwidth D . (b) Schematic of the resulting magnetisation curve at absolute zero, showing plateaus at zero and full magnetisation values.

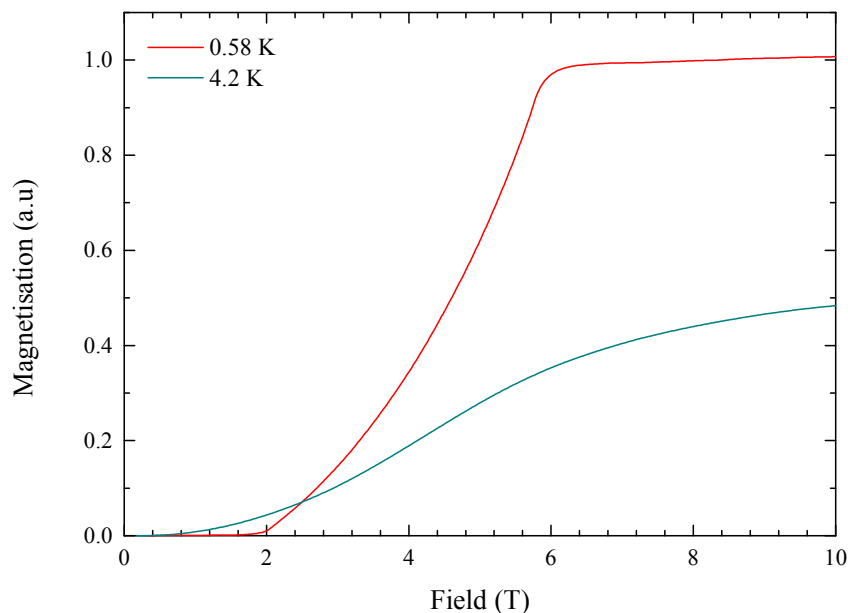


Figure 5.9: Magnetisation of $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$ at 4.2 K and 0.6 K, with the magnetic field normal to (110) crystallographic plane.

magnetisation curves of the sample in the (110) orientation, as found from integration of the dynamic susceptibility, are given in Fig. 5.9. The field-dependence of the magnetisation fully supports our description of the system as a weakly-coupled dimer, where at temperatures $T \ll J_0$ there is a non-magnetic plateau until B_{c1} , followed by an increase in magnetisation as the system enters the canted XY phase in $B_{c1} < B < B_{c2}$, with a final transition to the fully saturated phase at B_{c2} . At temperatures above the dome maximum, the magnetisation continuously evolves towards saturation, although the exact behaviour remains non-trivial [174].

In the mean-field approximation, the upper phase boundary for FM coupled dimers occurs at the inter-dimer exchange value $g\mu_B B_{c2} = J_0$ [159], which I estimate from the phase boundary to be 9.0(2) K, broadly consistent, but slightly larger than, the value derived from static field susceptibility. The value of J_0 is in excellent agreement with that seen for the AFM exchange along the pyrazine groups in the sister compound $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$. The mean-field model also predicts that $g\mu_B B_{c1} = J_0 - z|J_1|/2$, where z is the number of interacting nearest neighbours linked with a FM inter-dimer exchange J_1 [159]. I find $g\mu_B B_{c1} = 25(1)$ K, and so assuming $z = 4$, obtain $|J_1| \approx 3.3(1)$ K. If, instead, an AFM inter-dimer coupling is assumed then we would obtain $|J_1| \approx 4.5$ K [159], which is not compatible with the static susceptibility measurements.

5.3.3 Bose-Einstein condensation of triplons

It is convenient to discuss the triplet excited level as a triplon, a bosonic particle of $S = 1$, and the singlet state as the absence of a triplon. The bosonic nature of the triplon is confirmed by the fact that the spin-operators of two different triplons commute [173]. However, an added complication is that a dimer can only accommodate one triplon at a time, and so the bosonic picture requires the addition of a hard-core constraint to exclude states with more than one triplon per dimer [173]. This is often modelled through addition of a short-range repulsion between triplons.

The interpretation of the dimerised magnet as a system of triplet boson can be made more clear by rewriting the Hamiltonian as [160, 173, 175],

$$\mathcal{H} = -(h - J_0) \sum_i n_i + \sum_{ij} t_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{ij} U_{ij} a_i^\dagger a_j^\dagger a_j a_i,$$

where $a^\dagger$ and a are the triplon creation and annihilation operators, and $h = g\mu_B B$ is the magnetic energy. The hopping term t_{ij} is generated by the spin components $S_i^x S_j^x + S_i^y S_j^y$ and describes the hopping of the triplons from one dimer to another, U_{ij} is a repulsive term arising from when triplons occupy neighbouring dimers, and $n_i = a_i^\dagger a_i$ is the number of triplons at each dimer site. Looking at the form of the Hamiltonian, the term $(h - J_0)$ acts as a chemical potential, controlling the density of triplons.

Below B_{c1} , the ground state is a disordered set of singlets (i.e. vacuum of triplons). Once the spin-gap is closed, triplon formation becomes possible, and a linear increase in applied field causes a linear increase in the boson density.³ Within this phase the magnetisation is a direct measurement of the number of bosons. The wavefunction of each dimer can be given as a superposition of the singlet and triplet states, via $|\psi\rangle_i = \alpha_i |\text{singlet}\rangle + \beta_i |\text{triplon}\rangle$ [173], where the amplitudes α, β depend on the magnetic field, such that $\alpha = 1, \beta = 0$ at B_{c1} , and $\alpha = 0, \beta = 1$ at B_{c2} . Thus at B_{c2} all dimers are occupied by an $S^z = +1$ triplon, and the system is fully populated. In the spin picture, the onset of triplon formation at B_{c1} corresponds to the formation of the long-range ordering due to the $\langle S^x \rangle$ and $\langle S^y \rangle$ transverse spin components, which spontaneously breaks the rotational invariance symmetry in the plane normal to the magnetic field. Theoretically, this is analogous to breaking of charge conservation in the bosonic picture [173].

Systems such as this are often discussed in the context of Bose-Einstein condensation (BEC) of triplons, providing a description of the physics in terms of a transition from a vacuum to a Bose condensate of triplons at B_{c1} . Traditionally,

³The small deviation from linear behaviour between B_{c1} and B_{c2} in the magnetisation curve of Fig. 5.9 is due to the higher energy triplet states [176].

the proof of the BEC phase in dimerised antiferromagnetic systems has been the critical exponent of the phase boundaries [175]. The BEC picture expects the phase boundary to follow the power law $T_c \propto (B - B_{c1})^\phi$ near the quantum critical point B_{c1} , and by particle-hole symmetry $T_c \propto (B_{c2} - B)^\phi$ near B_{c2} , with the critical exponent $\phi = 2/d$, where d is the dimensionality of the BEC phase [173]. Our data is consistent with $\phi = 2/3$ as expected for a 3D BEC, although the paucity of the data points near the QCPs prevents this from being rigorously assessed (see Fig. 5.7). However, theoretically it has been shown that the BEC description requires an absence of any explicit symmetry breaking terms in the Hamiltonian [9, 171, 173, 176]. Within molecular magnets the symmetry can be broken by anisotropic interactions, such as spin-orbit coupling or dipolar interactions [173, 176]. In particular, presence of an antisymmetric exchange Dzyaloshinskii-Moriya (DM) interaction providing a term $\mathbf{D}_{ij}^{\text{DM}} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$ in the Hamiltonian can break the rotational invariance symmetry and cause mixing of the singlet-triplet spin levels [168, 177, 178]. Although an inversion centre exists between neighbouring dimer centres with the same orientation (see Fig. 5.3), neighbouring dimers of opposite orientation are symmetry related through a glide plane, and so a non-zero DM term is possible. This may affect the physics of the ordered phase, and could alter the critical exponents near the QCPs [9, 171, 173].

Thus the behaviour of the magnetisation, and the critical exponent of the phase diagram as deduced from the dynamic susceptibility, heat capacity and $\mu^+\text{SR}$, are shown to be consistent with that of a spin-1/2 dimerised system, whose physics may be approximated as a BEC of triplons. It was shown that the applied magnetic field acts as a chemical potential, and directly controls the number of triplons. As well as the spin-dimer system shown here, the physics of a variety of other magnetic systems, such as $S = 1$ quasi-one-dimensional spin chains [172, 179] and even field-induced frustrated antiferromagnets [180, 181], may be explained in terms of a BEC of magnetic excitations. However, in reality, very few materials have shown such behaviour [9, 173]. As a starting point for studying the physics of Bose-Einstein

condensation, such magnetic systems have several advantages over the traditional condensate of cold atoms in a Bose gas, including (a) the ability for the condensate to survive to high temperatures ($\sim$ K instead of $\sim$ nK), (b) the solid state of the magnetic system, which allows for a large variety of experimental measurements, and (c) the ability to continuously fine-tune the particle density through an applied magnetic field [173].

5.4 Conclusion

In summary, I have shown through magnetisation, susceptibility, heat capacity and μ^+ SR measurements, how a chemical synthesis route can lead to two separate phases of matter, whose structural difference allows them to develop two distinct models of quantum magnetism distinguished by their dimensionality. $[\text{Cu}(\text{pyz})\text{H}_2\text{O}(\text{gly})_2]\text{ClO}_4$ is an excellent realisation of a spin-1/2 quasi-one-dimensional system, which shows magnetic order at very low temperatures. In contrast $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$ is based on a lattice of magnetic dimers, giving rise to a quantum disordered ground state that is field-driven through a quantum critical point to an XY antiferromagnetic phase, which may approximate a Bose-Einstein condensate. Such mapping of magnetic systems opens up new ways of studying BEC phenomena.

This chapter shows the ability of polymeric magnets to form unusual quantum states, and highlights the importance of the quantum nature of such systems. This work also demonstrates the potential for creating novel magnetic ground states through chemical engineering, allowing coordination polymers to form a playground for realising exotic models. The magnetism within these systems may be finely tuned through the application of a magnetic field (as demonstrated in this chapter) and pressure (as shown in Chapter 4), leading to rich behaviour that may not be seen in more conventional systems.

Chapter 6

The upper critical field of NaFe_{1-x}Co_xAs superconductors

*“Absolute zero is colder than reality.
It would promote states of matter that break physicality:
Superconductivity is irresistible electrically,
Superfluidity is immeasurable in its viscosity.”*
– Anonymous poet

In this chapter, I discuss the upper critical field behaviour of NaFe_{1-x}Co_xAs superconductors. The critical field was measured across the whole of the superconducting dome ($x=0, \dots, 0.08$) and in pulsed magnetic fields up to 45 T, with the magnetic field applied parallel ($H_{c2}^{\parallel}$) or normal ($H_{c2}^{\perp}$) to the superconducting planes. The resulting data were fitted with one-band and two-band models. The orbital and paramagnetic components of the upper critical field were extracted for $H_{c2}^{\parallel}$, which I find to be strongly dominated by paramagnetic pair-breaking. Substitution of Fe by Co is found to enhance the paramagnetic limit above the BCS value by a factor of approximately 1.6. I also observe a significant convex curvature in the evolution of $H_{c2}^{\perp}$ with temperature, which I attribute to the multi-band nature of the superconductivity and the asymmetry between the two bands. Additionally, I discuss the behaviour of critical field anisotropy, coherence length ξ , and the penetration depth λ . This chapter is based on work published in Ref. [182].

6.1 Introduction

The discovery of the superconductor $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ [183, 184] and the extended Fe-pnictide superconductor family with critical temperatures of up to 56 K [185] has generated great interest and triggered huge efforts towards unmasking the underlying superconducting state. The upper critical field H_{c2} is a fundamental property of type-II superconductors, and its measurement is an important part of the experimental effort to verify or disprove the various theories [48, 186–188] for unconventional superconductivity. Studying the temperature dependence of H_{c2} and the interplay between the various pair-breaking mechanisms may hint towards the underlying pair-forming interaction. Furthermore, the critical field can be used to extract other fundamental properties such as the coherence length ξ and the London penetration depth λ . The upper critical field and its anisotropy can also shed light on the possible multi-band nature of the superconductivity, and are sensitive to the dimensionality and the underlying electronic structure of the system [189–191].

In this chapter, I discuss the upper critical field behaviour of the iron-based superconductor $\text{NaFe}_{1-x}\text{Co}_x\text{As}$, across the whole of the superconducting phase diagram. The crystal structure of NaFeAs is given in Fig. 6.1. At room temperature it forms a tetragonal structure with $a = b = 3.95 \text{ \AA}$, $c = 7.04 \text{ \AA}$. NaFeAs is based on layers of Fe_2As_2 formed out of edge-sharing FeAs tetrahedra, with the Na lying in between the planes in a square-based pyramidal site coordinated with four As atoms. The early work on stoichiometric NaFeAs was performed by Parker *et al.* [192] and Chu *et al.* [193], who showed that it becomes superconducting at a critical temperature T_c of approximately 11 K. The superconductivity was found to coexist with a long-range ordered antiferromagnetic (AFM) phase which is stabilised by the delocalised Fe d -band electrons. This makes NaFeAs one of the few iron-pnictide compounds that are superconducting without doping [186]. The coexistence of superconductivity and magnetism has been confirmed by further measurements [194, 195], which also showed that the AFM phase is preceded by a structural transition from tetragonal to orthorhombic structure at approximately 55 K, similar to the “1111”

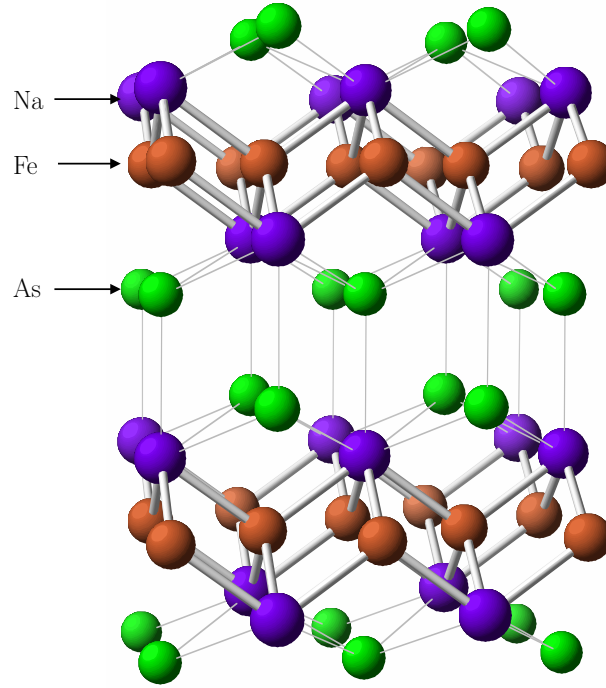
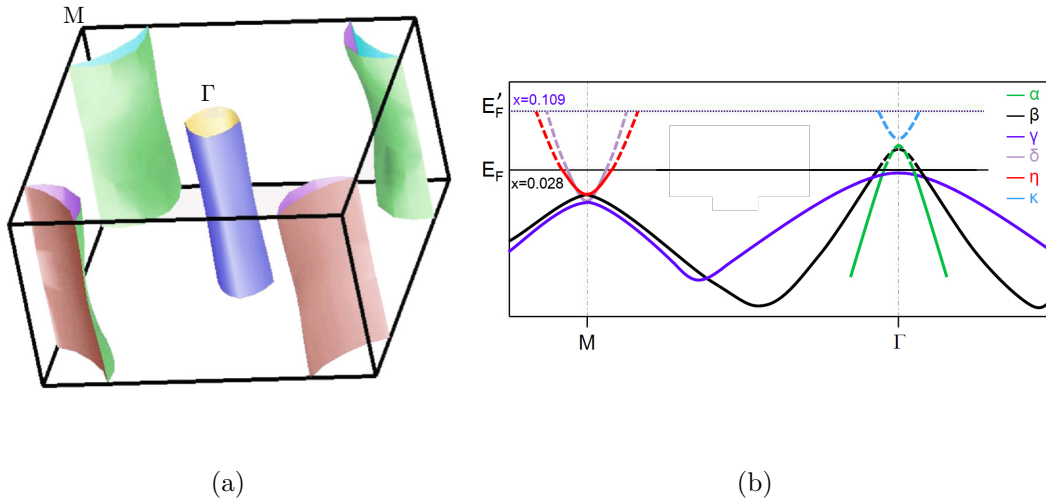
Figure 6.1: Crystal structure of NaFeAs , in the tetragonal phase.

Figure 6.2: (a) Fermi surface of NaFeAs as determined from band structure calculations [198], showing two hole columns and two electron columns at the Γ and M points of the Fermi surface, respectively. Copyright Physical Society of Japan. (b) Band structure of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$, as measured by angle-dependent photoemission spectroscopy measurements [199]. Doping by Co is seen to raise the Fermi energy. Copyright American Physical Society. Note that (a) and (b) have different colour schemes.

(ReFeAsO , Re = rare earth) and “122” (BaFe_2As_2) systems [42, 196]. Theoretically it has been proposed that whether the structural and magnetic transitions happen simultaneously or not depends on the coupling between the layers [197]. This suggests that the interlayer coupling in NaFeAs is weaker than the “122” family, where the transitions occur more closely together [42]. NaFeAs is found to have a relatively low superconducting volume fraction ($\sim 10\%$), and is highly air sensitive due to oxidative deintercalation of Na upon contact with O_2 or H_2O , which leads to a higher critical temperature [193].

The evolution of the magnetic and superconducting states with addition of Co has been explored through low-field susceptibility, neutron scattering and x-ray diffraction [200], as well as muon-spin relaxation [200, 201] and heat capacity [202] measurements. The addition of Co was shown to cause a rapid suppression of the magnetic phase, leading to the destruction of long-range ordering at $x \approx 0.02$ [200, 201]. The orthorhombic distortion is also reduced with increased doping, and disappears at a slightly higher doping of $x \approx 0.025$ [201]. The system reaches optimal doping upon the suppression of the AFM and structural transitions, and further doping leads to a reduction in T_c , and eventual destruction of superconductivity at $x \approx 0.1$. See Fig. 6.3(a).

Heat capacity measurements suggest that $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ is a multi-band superconductor [203], with two superconducting gaps of different magnitude. Angle-resolved photoemission spectroscopy (ARPES) measurements [199, 204–206] and band structure calculations [198, 207] have shown that in the normal state, the $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ Fermi surface consists of hole pockets at Γ and two electron pockets on the M points of the reciprocal space; with the electron Fermi surface being slightly warped, showing a small three-dimensional component. This is shown in Fig. 6.2. ARPES measurements show that doping with Co shifts the Fermi energy (*i.e.* electron doping), causing the electron pockets to widen and hole pockets to shrink with doping, until the hole pockets completely vanish at $x \approx 0.1$ [199]. Thus the Fermi surface is found to be highly sensitive to Co doping. However, the exact

effect of Co substitution on the electronic structure of iron-pnictides is under debate. In particular, it is unclear if it leads to electron doping and a rigid shift in the chemical-potential as for example suggested by the ARPES measurements [208, 209], or whether its primary effect is to introduce a random impurity potential leading to charge-carrier scattering [210–213], or a combination of both. I note that recent studies [210, 211] of $\text{Ca}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ suggest the effect of Co substitution to be beyond a simple band-shift. However, for consistency with literature, I shall use ‘doping’ nomenclature to refer to substitution of Fe by Co.

Until now there has been little exploration of the critical field behaviour of this system. Recently there has been a critical field measurement of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ with $x = 0.025$, limited to low fields and temperatures near the transition temperature T_c [214]. In the rest of this chapter, I investigate the upper critical field of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ up to 45 T, across the whole phase diagram from the under-doped to over-doped regime, including the parent compound. I find that a multi-band model is required to fully reproduce the critical field behaviour, with the fitted coupling values being insensitive to the pairing symmetry. Moreover, I find the in-plane critical field to be paramagnetically limited, being enhanced over the BCS value in doped samples by a combination of spin-orbit and strong-coupling effects.

This chapter is based on work published in Ref. [182]. The majority of measurements and analysis were done by myself. Sample growth, and a subset of the lower critical field measurements, was done by J. W. Wright at the University of Oxford.

6.2 Experimental details

Single crystals of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ were synthesised using the self-flux method. Freshly cut pieces of Na were mixed with ground As in a 1:1 molar ratio and heated in a 9 mm Nb tube (sealed under argon) to 300°C for 6 hours. The resulting black powder of overall composition NaAs was then ground with $\text{Fe}_{1-x}\text{Co}_x$ mixture in the ratio $\text{NaAs}:\text{Fe}_{1-x}\text{Co}_x = 2:1$. This was then placed into an 8 mm alumina crucible, itself then placed into a second sealed Nb tube and this in turn sealed in an

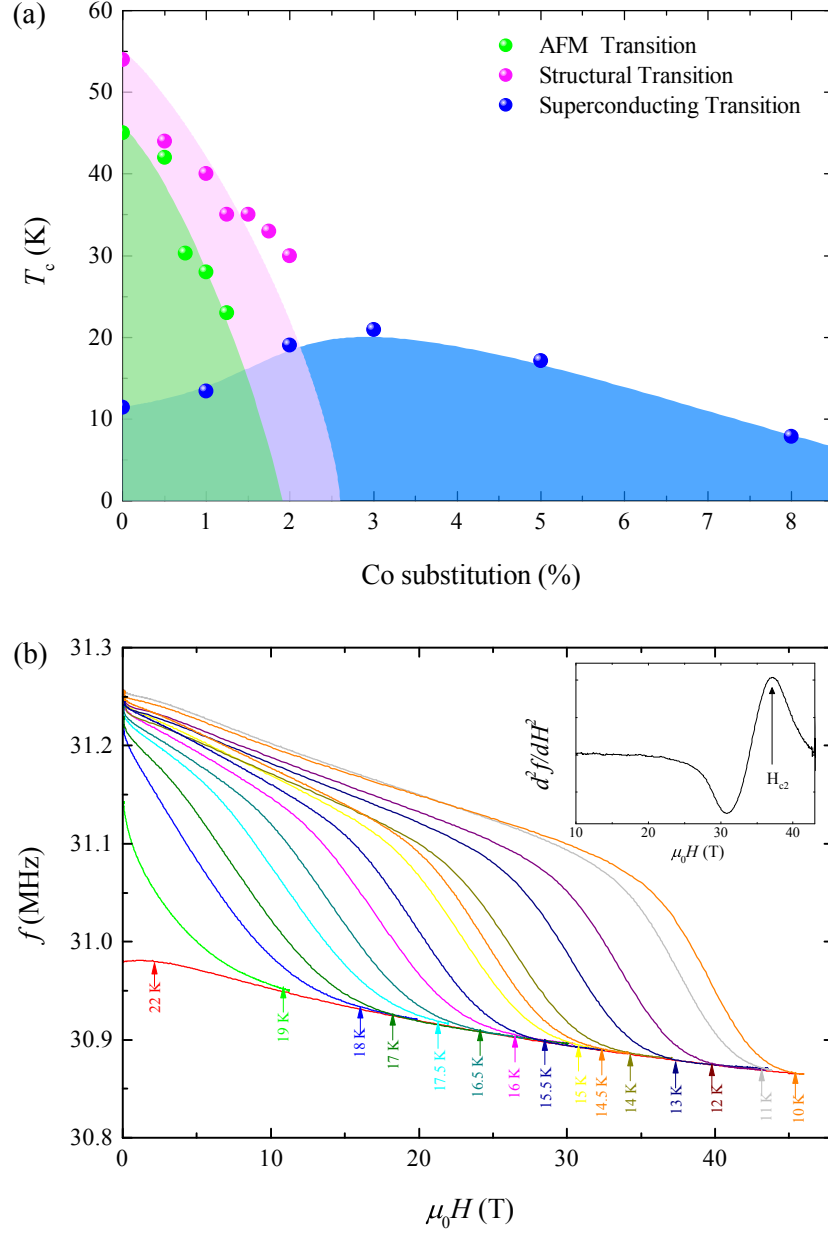


Figure 6.3: (a) Phase diagram of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$, showing the superconducting phase as measured in this chapter, together with the antiferromagnetic and the structural transitions [201]. (b) Evolution of the PDO frequency $f = \omega/2\pi$ with applied magnetic field, for an $x = 0.02$ sample at different temperatures, with the applied field parallel to the Fe-As planes. The arrowed numbers indicate the temperature. The superconducting transition is seen as a drop in frequency with increasing field (see main text). *Inset*: d^2f/dH^2 for the 12 K measurement.

evacuated silica ampoule to prevent the oxidation of Nb. The ampoule was then heated to 900°C at a rate of $\sim 1^\circ\text{C}/\text{min}$ before being slowly cooled to 400°C at a rate of $5^\circ\text{C}/\text{hr}$, at which point it was cooled rapidly to room temperature. The resulting crystals were around $1 \times 1 \times 0.1 \text{ mm}^3$ in dimension and could be easily removed from the flux mechanically. The growth procedure used here was found to be highly robust: the pre-reaction of Na and As minimised the reaction of Na with the alumina crucible, and sealing the crucible in Nb prevented any sublimed Na from attacking the silica ampoule. X-ray diffraction measurements carried out using an Oxford Diffraction SuperNova showed that no detectable impurity phases were present. Magnetic susceptibility data returned values of T_c in agreement with those previously published for each composition [200, 201]. The susceptibility data, and the critical field measurements described in this chapter, are consistent with a superconducting volume fraction of less than 20% in the parent compound, which increased to 100% at $x \geq 0.01$, as reported previously for powder samples [201].

H_{c2} was measured in pulsed magnetic fields at the Nicholas Kurti Magnetic Field Laboratory, Oxford, with magnetic fields of up to 45 T applied parallel ($H_{c2}^{\parallel}$) or normal ($H_{c2}^{\perp}$) to the Fe-As planes, and in temperatures down to 400 mK. The proximity detector oscillator technique was used, and the resonance frequency was monitored as a function of field and temperature. As explained in Chapter 3, for superconducting and metallic samples, the response of the PDO is strongly dominated by the depth to which the radio-frequency signal penetrates the sample. Using Equations 3.8 and 3.2, the change in PDO frequency upon a change in temperature or applied magnetic field is found to be proportional to the change in sample penetration/skin depth, with an additional smooth-changing component due to the coil resistance,

$$\Delta\omega = -a'\Delta\lambda - b\Delta R_0$$

where a' and b are constants, λ is the sample skin/penetration depth, and R_0 is the PDO coil resistance. Therefore, due to the large difference between the superconducting penetration depth and normal-state skin depth of a sample, the

superconducting–normal state phase transition can be seen as a large change in the resonant frequency at the critical temperature or field.

The measurements were performed using a 1 mm–diameter PDO coil made out of 4 turns of 21 μm –thick Cu wire, with samples cleaved to a diameter of approximately 0.9 mm. The samples were placed ‘flat’ in the coil, with the axis of the coil normal to the crystal planes. For $H_{c2}^\perp$ measurements the axis of the coil is parallel to the applied field, whilst for $H_{c2}^\parallel$ measurements the crystal/coil holder was rotated by 90. The superconducting–normal transition was seen as a drop in the PDO frequency of ~ 100 kHz, as shown for example in Fig. 6.3(b) for $x = 0.02$. As expected the transition moves to lower fields as the temperature is increased, and disappears at $T > T_c$. Above T_c only a smooth gradual change due to the $b\Delta R_0$ term is seen, which is observed to be significantly smaller than the sample response at the transition.

One challenge in critical field measurements is the presence of the irreversibility field H_{irr} , above which the pinning of the vortex flux lattice becomes ineffective due to thermal fluctuations, allowing the vortices to move and cause dissipation, and hence, finite resistance [26]. In resistivity and skin depth measurements this resistance can be mistakenly attributed to the onset of the superconducting–normal state transition, thus leading to a measurement of H_{irr} instead of H_{c2} . The thermal vortex fluctuations are parameterised by the Ginzburg parameter G_i [215], which is given as

$$G_i = \frac{1}{2} \left(k_B T_c \frac{8\pi^2 \lambda^2}{\xi \phi_0^2 \epsilon} \right)^2,$$

where ϕ_0 is the flux quantum, λ is the penetration depth, ξ is coherence length, and ϵ is a parameter that characterises the anisotropy. High G_i values imply strong vortex fluctuations and a significant difference between the irreversibility and true critical fields, and conversely, low G_i values indicate that H_{irr} and H_{c2} are similar [215, 216]. Iron-pnictide superconductors are known to have relatively small G_i values of $10^{-3} - 10^{-4}$ [216, 217], and so I expect $H_{\text{irr}} \approx H_{c2}$. Nevertheless, to ensure that H_{c2} is correctly measured, one can utilise the measurement at $T > T_c$, where the sample is completely normal. H_{c2} is then defined as the field at which the frequency

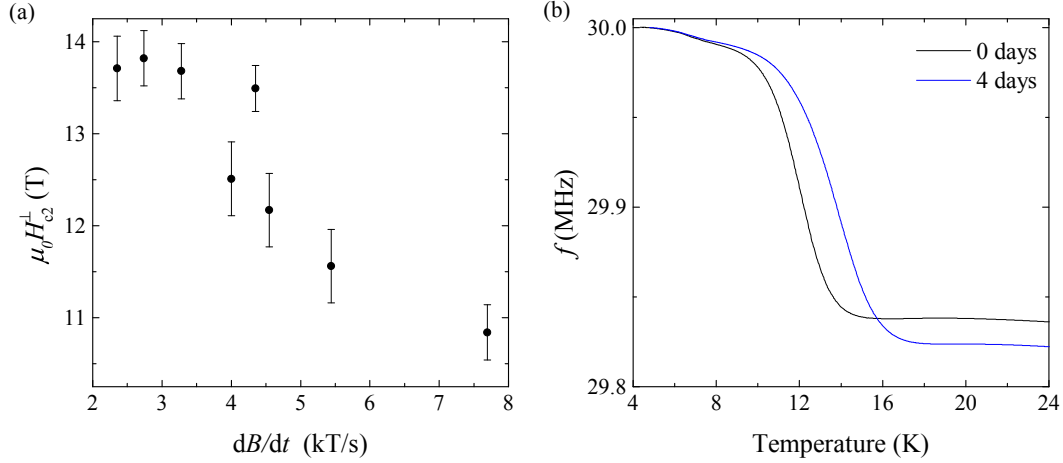


Figure 6.4: (a) Evolution of $H_{c2}^{\perp}$ as a function of dB/dt , for a sample of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ with $x = 0.05$, at 4.2 K. The decrease in $H_{c2}^{\perp}$ at high dB/dt is due to eddy current heating. (b) Evolution of PDO frequency $f = \omega/2\pi$ as a function of temperature for $x = 0.01$. A clear change in T_c is observed after four days, indicating that the sample has degraded.

response of the superconducting state maps on to that of the normal state. This is usually found by drawing a linear extrapolation of the transition curve, and seeing where it crosses the normal state line [92]. In order to be systematic, I deduce H_{c2} from the peak in d^2f/dH^2 [see inset of Fig. 6.3(b)]. Both methods give the same values for H_{c2} .

Heating can occur during pulsed field measurements due to the high value of dB/dt , which induces eddy currents within the sample and the PDO coil. I checked for sample heating by monitoring H_{c2} as the pulse width was changed, thus tracking H_{c2} as a function of the average dB/dt . This is shown in Fig. 6.4(a) for a sample of $x = 0.05$ at 4.2 K. It is clear that there is little or no heating below 3 kT/s. All samples were similarly checked for heating, and the measurements were performed at the minimum possible dB/dt for a given field. No heating was seen in data presented here.

As $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ is known to be highly air and moisture sensitive [37, 214], the samples were covered with generous amounts of vacuum-dried Apiezon N grease to arrest sample degradation. Even though covered with grease, it was found that samples may begin to degrade after a few days, with the parent compound NaFeAs

being the most sensitive. Sample degradation was found to lead to a noticeable change in T_c and a broadening of the transition, as shown for example in Fig. 6.4(b), and seen in other measurements [214]. During the measurements, T_c and the shape of transition was continuously and carefully monitored to detect sample degradation. If a sample was found to have degraded, all the data were discarded, and measurements repeated on a fresh sample. Sample degradation proved to be a problem for under-doped (0% – 2%) samples.

6.3 Results

The temperature dependence of the upper critical field for $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ was measured across the superconducting dome, from under-doped samples with $x = 0, 0.01, 0.02$, via the optimally-doped $x = 0.03$, to over-doped samples with $x = 0.05$ and 0.08 . The results are given in Fig. 6.5. For all dopings $H_{c2}^\perp$ and $H_{c2}^\parallel$ went to zero at T_c , and increased monotonically with decreasing temperature, with $H_{c2}^\perp < H_{c2}^\parallel$ at all temperatures. In the parent compound, I observe a critical temperature of 11.4(5) K and $\mu_0 H_{c2}^\perp$ ($\mu_0 H_{c2}^\parallel$) of 9.9(2) T (16.7(5) T) at $T \approx 0$. Doping slightly to 1% leads to a significant increase in H_{c2} for both directions. Upon doping to 2%, the behaviour of $H_{c2}^\perp$ as the temperature is decreased becomes almost linear, in contrast to the concave (positive curvature) temperature dependence of the parent compound. At 3% doping I find the highest T_c of 21 K, as well as the highest critical fields. Interestingly, at optimal doping $H_{c2}^\perp$ begins to rise upwards as the temperature is decreased and develops a convex (negative) curvature, in contrast to the behaviour of $H_{c2}^\parallel$. Further addition of Co moves the system to the over-doped regime, where any additional doping leads to a decrease in T_c and the upper critical fields, although $H_{c2}^\parallel$ and $H_{c2}^\perp$ retain their shape.

Therefore, there are two overall trends. One is the usual increase, and then decrease, of H_{c2} on moving from the under-doped to over-doped regime [see Fig. 6.7(a)]. The other is the gradual change in the behaviour of $H_{c2}^\perp$ from one extreme to another: from very concave at parent composition, to linear at 2% doping, to convex

at and above optimal doping. Note that the data agree well with the previous low-field resistivity study of 2.5% doped samples [214], and that the observed critical temperatures match published SQUID susceptibility measurements [200, 201].

6.4 Discussion

The upper critical field is determined by two independent mechanisms, one of which is the Clogston-Chandrasekhar spin paramagnetism [218, 219]. The spin paramagnetism polarises the normal state into spin-up and spin-down electron states due to the Zeeman effect, and leads to a reduction of the normal state free energy. In contrast the spin-singlet Cooper pairs are not affected. Thus, in effect the magnetic field reduces the energy gap between the superconducting and normal states. The paramagnetic effect can be thought of as the applied field breaking the Cooper pairs apart when the normal state paramagnetic energy $E_P = (1/2)\chi_N\mu_0^2H^2$ matches the superconducting condensation energy E_S , which in BCS theory is given as $(1/2)N\Delta^2$ [28]. Here $\chi_N = (1/2)g^2\mu_B^2N$ is the normal state susceptibility, g is the g -factor, Δ is the zero-temperature superconducting energy gap, and N is the density of states at the Fermi energy [220]. The paramagnetic (PM) limit is thus defined as

$$\mu_0 H_{c2}^{\text{pm}}(0) = \frac{\sqrt{2}\Delta}{g\mu_B}. \quad (6.1)$$

In the case of isotropic BCS s -wave pairing with $g = 2$, this reduces to $H_{\text{BCS}}^{\text{pm}}(0) \approx 1.84T_c$. However, this weak BCS coupling can underestimate the actual paramagnetic limit. The critical field can be enhanced by an increase in Δ , for example by strong electronic interactions giving

$$H_{c2}^{\text{pm}} = (1 + \lambda_{\text{sc}})H_{\text{BCS}}^{\text{pm}},$$

where λ_{sc} is the strong-coupling coefficient, or by spin-orbit coupling that may change g [221]. Additionally, spin-orbit interactions destroy spin as a good quantum number and allow for non-zero susceptibility in the superconducting state [222–

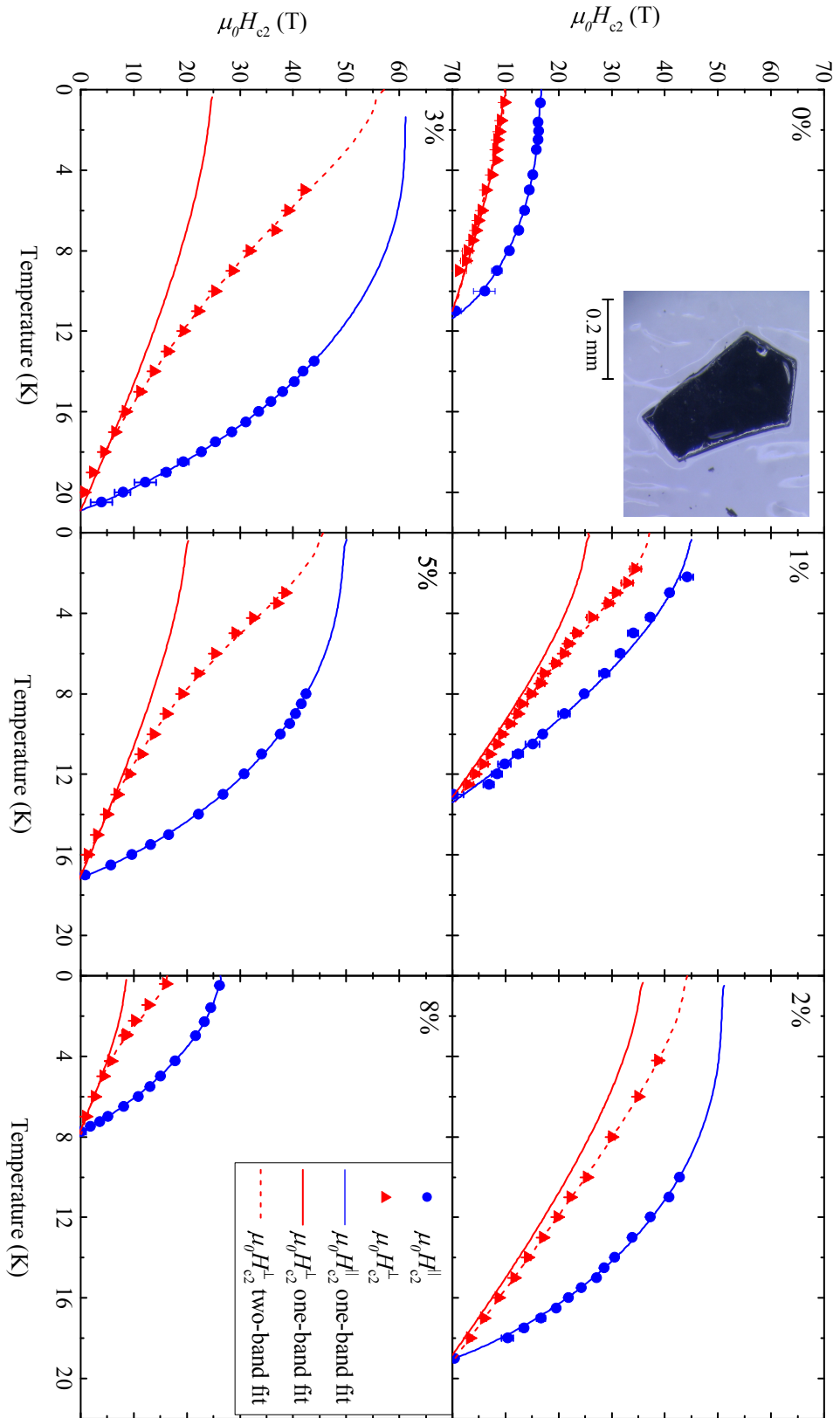


Figure 6.5: The upper critical field of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$, where the percentage denotes the amount of Co substitution. Blue circles and red triangles represent H_{c2} with the field applied parallel and normal to the Fe-As planes, respectively. The solid lines are fits using the one-band model, and the dashed lines are fits using the two-band model (see text) with $\lambda_{11} = \lambda_{22} = 1$, $\lambda_{11}\lambda_{22} - \lambda_{12}\lambda_{21} = 0.5$, and using diffusivity $D_1^\perp/D_2^\perp$ ratios as given in Table 6.2. Inset: picture of a NaFeAs sample.

226], thus bringing the spin-paramagnetism of the superconducting and normal states closer together, reducing the limiting effect of paramagnetism on the critical field [226–228]. Note that paramagnetic pair-breaking has no effect in triplet p -wave superconductivity, where the electrons within the Cooper pair already have their spins aligned together [229].

The second mechanism which limits the critical field is orbital pair-breaking, which is related to the creation of Abrikosov vortex lines and shielding superconducting currents around the vortex core, reducing the superconducting condensation energy [230]. This effect is dependent on the electronic properties of the material. See Fig. 6.6.

In general H_{c2} is influenced by both orbital and spin-paramagnetic effects, and thus is always less than both H_{c2}^{pm} and H_{c2}^{orb} . However, if there is a significant difference between H_{c2}^{pm} and H_{c2}^{orb} , then the smaller one dominates the critical field behaviour and sets the value of H_{c2} . Usually the critical field is limited by orbital pair-breaking in type-II superconductors, however the paramagnetic effect can become important when the orbital effect is suppressed, for example due to low-dimensional electronic structures which limit cyclotron motion of charge carriers out of the planes [220]. The relative importance of the orbital and paramagnetic limiting fields can be measured by the Maki parameter [226, 228]

$$\alpha = \sqrt{2} \frac{H_{c2}^{\text{orb}}}{H_{c2}^{\text{pm}}},$$

where H_{c2}^{orb} is the orbital critical field. If $\alpha > 1.85$, the superconductivity is considered to be paramagnetically limited [220].

As was shown in Fig. 6.2(a), $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ is a quasi-two-dimensional superconductor with a Fermi surface consisting of collinear warped columns. In such systems, application of magnetic field parallel to the superconducting planes causes the electrons to form open orbits along the cylinders [231], which significantly suppresses orbital motion, leading to a negligible orbital effect and significant enhancement of the orbital critical field above what would be expected for a more isotropic super-

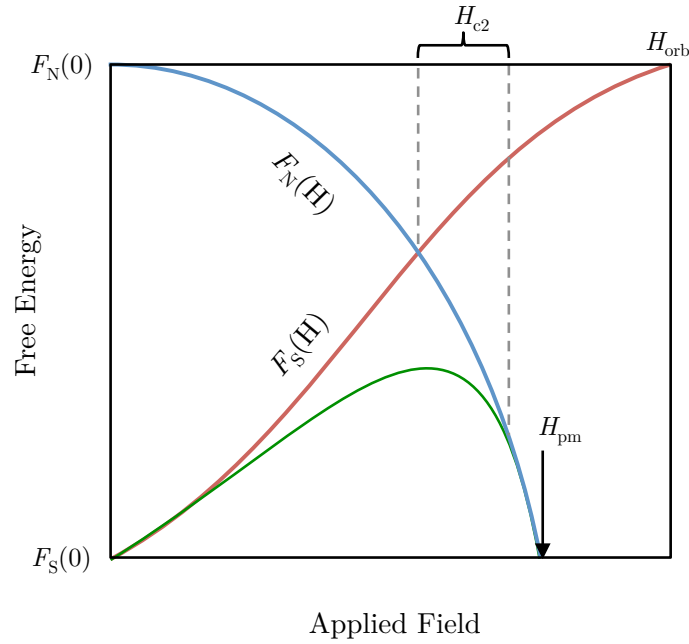


Figure 6.6: The evolution of the free energies with applied magnetic field. There is a parabolic reduction in the normal state free energy F_N due to the Zeeman effect (blue line), and a rise in the superconducting free energy F_S due to orbital effects (red line). The green line is a possible F_S when the spin-susceptibility in the superconducting state due to spin-orbit scattering is included [226]. H^{pm} (H^{orb}) is the field at which F_N (F_S) matches the zero-field superconducting (normal state) energy. H_{c2} is defined as the field at which $F_N(H) = F_S(H)$. Two possible upper critical fields are shown. See Ref. [226] for more details.

conductor. In contrast, application of field normal to the superconducting planes forms closed electron orbits within the Fermi sheets and leads to creation of vortices [232, 233], thus reducing the orbital limit [234]. Therefore in general $H_{c2}^{\parallel} > H_{c2}^{\perp}$, as is the case for $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ (see Fig. 6.5).

6.4.1 Dirty or clean?

In this chapter I assume that the samples are in the so-called dirty limit, where the mean free path $l \ll$ the coherence length ξ . This is justified by the low residual-resistivity ratio (as low as 4) [214], the low superconducting volume fraction ($< 20\%$) of the parent compound [201], and the tendency of pnictide superconductors to have a small l due to the low Fermi velocities [235] and high scattering rates [207, 236]. Published Hall effect data [40] on $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ show the Hall coefficient to be large and negative. Thus, assuming that the electrons are the major charge carriers in the normal state,¹ the mean free path can be estimated via

$$l = \frac{m^* v_F}{e \rho} |R_H|,$$

where R_H is the Hall coefficient, e is the electron charge, m^* is the effective electron mass, v_F is the Fermi velocity, and ρ is the resistivity [117]. Assuming $v_F \sim 10^5$ m/s and $m^* \sim m_e$, a comparison of the mean free path as estimated from published resistivity and Hall effect data [40], and the coherence length as calculated later in Section 6.4.7, gives values for $l_{\parallel}$ that are less than $\xi_{\parallel}$ at all dopings, but of similar order of magnitude. The under-doped samples are estimated to be dirtiest, for example $l_{\parallel} \approx 0.7$ nm and $\xi_{\parallel} \approx 3.4$ nm for the parent compound, while the optimally-doped and over-doped samples have slightly longer mean free paths, for example $l_{\parallel} \approx 1.8$ nm and $\xi_{\parallel} \approx 2.2$ nm at optimal doping. Values for $l_{\perp}$ ($\xi_{\perp}$) would be smaller (larger).

In this chapter, the data will be fitted with critical field models in the weakly coupled limit. However, as shown later, strong electronic interactions may be

¹So that $R_H = -1/ne$, where n is the charge carrier density.

present. I note that the author of Ref. [203] states that $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ heat capacity data [202, 203] might be understood using a highly modified Eliashberg theory in the strong-coupling limit.

6.4.2 Single-band model

One model for the upper critical field of a superconductor is the single-band Werthamer-Helfand-Hohenberg (WHH) model in the dirty limit [226]. This semi-classical model includes the effects of paramagnetism, orbital pair-breaking, and scattering that involves spin-orbit interactions. However it neglects any strong coupling, and is insensitive to Fermi surface anisotropy. H_{c2} is given implicitly via

$$\ln \frac{1}{t} = \sum_{v=-\infty}^{\infty} \left\{ \frac{1}{|2v+1|} - \left[|2v+1| + \frac{h}{t} + \frac{(\alpha h t)^2}{|2v+1| + (h + \lambda_{\text{so}})/t} \right]^{-1} \right\},$$

$$h = 4H_{c2} \left[\pi^2 T_c \left(\frac{dH_{c2}}{dT} \right)_{T=T_c} \right]^{-1},$$

where $t = T/T_c$, v is the summing index, and $\lambda_{\text{so}} = \hbar/(3\pi k_B T_c \tau_{\text{so}})$ accounts for the spin-orbit scattering with τ_{so} as the mean free scattering time [227]. The results of fits to the WHH model are shown in Fig. 6.5 (solid lines), and the fit values given in Table 6.2. $H_{c2}^{\parallel}$ is well-described by this model across all temperatures. However, in contrast $H_{c2}^{\perp}$ seems to be only well-fitted close to T_c —the WHH model is insufficient to reproduce the enhancement of these upper critical fields at low temperatures.

One explanation for such a convex curvature in $H_{c2}(T)$ is localisation of the electron wavefunctions as suggested by Lebed [237] and Dupuis *et al.* [238], where the application of high magnetic fields parallel to the superconducting planes and below a critical temperature $T^* < T_c$ leads to confinement of the electron motion to within the planes, causing a dimensionality crossover. This suppresses orbital pair-breaking, and in the absence of other pair-breaking effects leads to an increase in the critical field and the possibility of re-entrant superconductivity at high magnetic fields. However, this effect would imply that the convex curvature would be seen in $H_{c2}^{\parallel}$, whereas we have an upwards curvature in $H_{c2}^{\perp}$ instead. The second possibility,

x	T_c (K)	$\mu_0 H_{c2}^{\parallel}$ (T)	$\mu_0 H_{c2}^{\perp}$ (T)	$\mu_0 H_{c1}^{\perp}$ (mT)	$\mu_0 H_{\text{pm}}^{\parallel}$ (T)	$\mu_0 H_{\text{orb}}^{\parallel}$ (T)
0	11.4(5)	16.7(5)	9.9(2)	0.5(3)	16(2)	47(4)
0.01	13.4(3)	46.9(5)	40(2)	2.9(3)	50(9)	50(9)
0.02	19.0(3)	51(2)	45(3)	5.1(5)	55(5)	131(4)
0.03	20.9(1)	62(3)	56(6)	8.4(10)	61(3)	119(3)
0.05	17.1(1)	49.8(2)	47(5)	3.2(3)	51(3)	115(4)
0.08	7.8(2)	26.2(2)	16.5(5)	1.8(3)	22(4)	37(2)

Table 6.1: Results of the critical field measurements on $\text{NaFe}_{1-x}\text{Co}_x\text{As}$. All critical field values are given at $T = 0$. Where data close to 0 K was not available, the critical field was extrapolated to 0 K using the WHH model (see Section 6.4.2) for $H_{c2}^{\parallel}$, and the Gurevich model (see Section 6.4.3) for $H_{c2}^{\perp}$, and the extrapolation error included in the error values. $H_{c1}^{\perp}$ was measured using a SQUID susceptometer at 2 K (see Section 6.4.7). The orbital ($H_{\text{orb}}^{\parallel}$) and paramagnetic ($H_{\text{pm}}^{\parallel}$) components of $H_{c2}^{\parallel}$ were calculated using the Maki parameter extracted from the WHH fits.

x	α	λ_{so}	$\xi_{\parallel}$ (nm)	$\xi_{\perp}$ (nm)	$1/\lambda_{\parallel}^2$ (μm^{-2})	$D_1^{\perp}/D_2^{\perp}$
0	4.0(2)	0.55(8)	5.76(7)	3.4(1)	0.56(3)	2.5(3)
0.01	1.4(1)	3(2)	2.87(7)	2.50(7)	3.4(3)	4.7(4)
0.02	3.4(2)	0.3(2)	2.71(9)	2.4(1)	6.2(7)	2.4(1)
0.03	2.8(1)	0.19(9)	2.4(1)	2.2(2)	10.5(5)	6.6(3)
0.05	3.2(2)	0.4(1)	2.6(1)	2.5(1)	3.7(4)	8.8(5)
0.08	2.3(4)	1.8(8)	4.47(7)	2.81(5)	2.3(4)	10(1)

Table 6.2: The Maki parameter α and the spin-orbit scattering constant λ_{so} , as obtained from fits to $H_{c2}^{\parallel}$ using the one-band WHH model. Also given are the coherence lengths $\xi_{\parallel}$ and $\xi_{\perp}$, and the superfluid stiffness $\rho_s = 1/\lambda_{\parallel}^2$, all at 2 K. $D_1^{\perp}/D_2^{\perp}$ is the band anisotropy, extracted from fits to $H_{c2}^{\perp}$ using the two-band model with $\lambda_{11} = \lambda_{22} = 1$, $\lambda_{11}\lambda_{22} - \lambda_{12}\lambda_{21} = 0.5$ (see Section 6.4.3).

in the case of weak interlayer coupling, is the formation of a Josephson-coupled superconductor with flux lines trapped between the layers [239]. This causes a divergence in the orbital critical field and leads to a rapid increase of H_{c2} if the system is orbitally limited. However, this phenomenon can also be ruled out since (as shown later in Section 6.4.7) the superconducting coherence length is found to be larger than the interlayer separation.

6.4.3 Two-band model

It is likely that the upwards curvature in $H_{c2}^\perp$ is due to the multi-band nature of the superconductivity, as is thought to be the case for the rare-earth “1111” systems (ReFeAsO , Re = rare earth) [216, 234, 240], the “122” systems (BaFe_2As_2) [51], and the closely related “111” superconductor LiFeAs [216], amongst others. A two-band superconductor can be fitted using the model by Gurevich [190, 191], which is a generalisation of the one-band WHH model and is based on a weakly-coupled BCS system in the dirty limit. The model parameters are essentially the BCS coupling constants λ_{nm} (λ_{12} , λ_{21} inter-band; λ_{11} , λ_{22} intra-band) and the intra-band diffusivities D_1 and D_2 due to impurity scattering within each band. In the assumption of small inter-band scattering, the model relates the upper critical field and temperature via [190, 191]

$$a_0[\ln t + U(h)][\ln t + U(\eta h)] + ta_2[\ln t + U(\eta h)] + a_1[\ln t + U(h)] = 0, \quad (6.2)$$

$$U(x) = \psi\left(1/2 + x + i\frac{\mu_B H}{2\pi T}\right) - \psi(x),$$

where $\psi(x)$ is the digamma function, and,

$$\begin{aligned} \lambda_\pm &= \lambda_{11} \pm \lambda_{22}, & a_0 &= 2w/\lambda_0, & h &= H_{c2}D_1/2\phi_0T, \\ \lambda_0 &= \sqrt{\lambda_-^2 + 4\lambda_{12}\lambda_{21}}, & a_1 &= 1 + \lambda_-/\lambda_0, & \eta &= D_2/D_1, \\ w &= \lambda_{11}\lambda_{22} - \lambda_{12}\lambda_{21}, & a_2 &= 1 - \lambda_-/\lambda_0. \end{aligned}$$

The BCS coupling constants represent the pairing strength [27]. The band diffusivities D are related to the conductivity tensor σ_{ij} via [190]

$$\sigma_{ij} = e^2 \sum_m N_m D_m^{ij},$$

where e is the electron charge, N_m is the density of states of each band, and the sum is over all bands. Thus the diffusivity may be used as a handle on the band dirtiness—the smaller it is, the dirtier the band [190, 191].

Example fits of Eqn. 6.2 to $H_{c2}^\perp$ are shown in Fig. 6.5. This model accounts well for our $H_{c2}^\perp$, and attributes the convex curvature to a significant difference between the diffusivity of the two bands, $D_2^\perp/D_1^\perp < 1$ [190, 191]. This difference arises from the inequality of the two bands [191] and their Fermi velocities ($v_e \gg v_h$) [207], as well as scattering from impurities or strong magnetic excitations which might affect the bands differently [234, 240]. The use of the dirty-limit model does not matter in this case, since explaining the large negative curvature in the clean-limit also requires a significant band asymmetry [241]. Note that this argument depends on decoupling of the band scattering rates (*i.e.* small inter-band scattering), which would otherwise mix D_1 and D_2 . Interband scattering might be small due to the large separation between the electron and hole bands in k -space, and the difference in the orbital character of the bands as seen in ARPES measurements [205].

I note that in contrast to $H_{c2}^\perp$, the $H_{c2}^\parallel$ data can be fitted by setting $D_1^\parallel = D_2^\parallel$, which in essence reduces back to a one-band model and thus validates the previous $H_{c2}^\parallel$ one-band fit [190, 191]. This model was found to be strongly sensitive to the band diffusivities D_1 and D_2 , but significantly less dependent on the BCS couplings. Furthermore, due to the symmetry of the fitting functions the data can be fitted with attractive inter-band coupling $\lambda_{12}, \lambda_{21} > 0$ indicative of the conventional s -wave coupling scenario, as well as with repulsive inter-band coupling $\lambda_{12}, \lambda_{21} < 0$ which would indicate $s^\pm$ superconductivity. Thus the data can be used neither to rule out, nor confirm, the $s^\pm$ coupling suggested by a recent neutron study [242]. The data could be fitted with strong ($\lambda_{12}\lambda_{21} > \lambda_{11}\lambda_{22}$) or weak ($\lambda_{12}\lambda_{21} < \lambda_{11}\lambda_{22}$) inter-band

coupling. Therefore I find the two-band model to be over-parameterised in terms of λ_{nm} in our situation, and so shall not rely on this model for extracting values for λ_{nm} . Example fits shown in this chapter assume $\lambda_{11} = \lambda_{22} = 1, \lambda_{11}\lambda_{22} - \lambda_{12}\lambda_{21} = 0.5$. I suggest more generally that the number of parameters involved in the two-band model would make it difficult to draw strong conclusions regarding the nature of the underlying order from fitting this model to any H_{c2} data of this form.

There also exists the possibility of a Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) phase [243, 244], which would lead to a state of inhomogeneous superconductivity with a spatially varying gap function, and cause an increase in the experimentally measured critical field below $0.55T_c$ if the system is paramagnetically limited, hence accounting for the slope of $H_{c2}^{\parallel}$ [220]. The presence of an exotic FFLO phase cannot be ruled out, however it seems unlikely since (a) such a state is possible only in extremely clean materials ($l \gg \xi$), and (b) that the FFLO should lead to a second superconducting phase and appearance of additional features in thermodynamic measurements [220, 245], which have so far not been observed. However, I note that the possibility of a weak FFLO state has been raised for LiFeAs [83], where $l \approx \xi$ [246]. The proof of such a phase from upper critical field data requires the use of a modified two-band model [247]; however, this probably would not supply authoritative proof of an FFLO phase due to the over-parameterisation problem explained previously.

6.4.4 Enhancement of the paramagnetic limit

Given that in the case of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ the two-band model collapses into a one-band model when the applied field is parallel to the planes, I return to further analysis of the single-band fit of the WHH model to $H_{c2}^{\parallel}$, which allows one to separate the orbital and paramagnetic components of the critical field. The orbital limit is experimentally approximated as [190, 226]

$$H_{c2}^{\text{orb}}(0) = -0.69T_c \left(\frac{dH_{c2}^{\parallel}}{dT} \right)_{T=T_c} \quad (6.3)$$

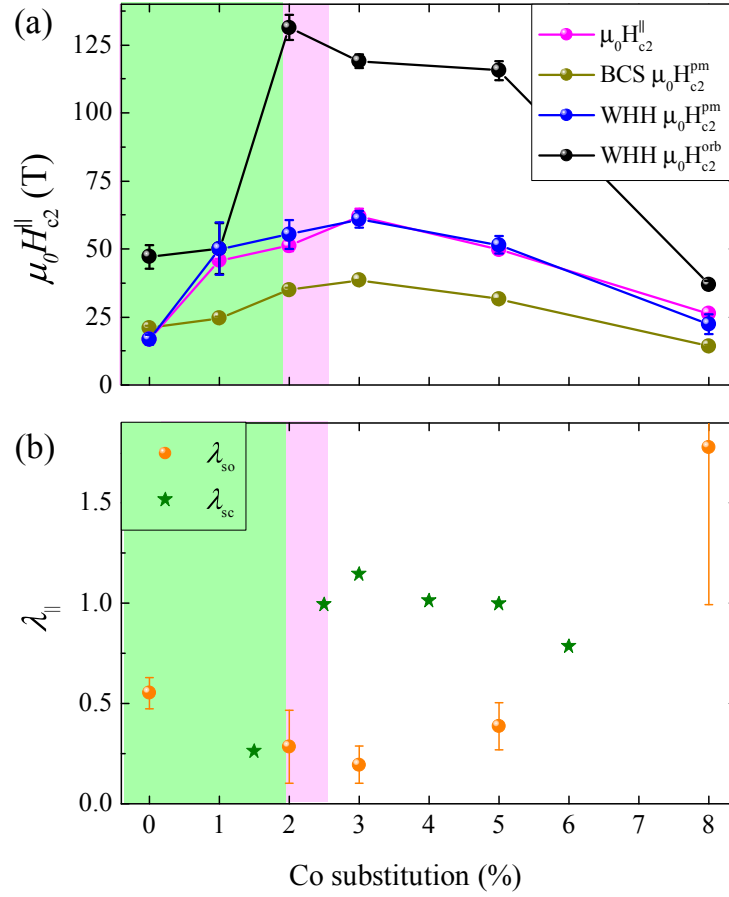


Figure 6.7: Evolution with Co doping of (a) $H_{c2}^||$ and the BCS paramagnetic limit $= 1.84T_c$, as well as the orbital and paramagnetic components deduced from fits to the WHH model, (b) the spin-orbit scattering constant λ_{so} for $H_{c2}^||$ (for 1% substitution, a reliable estimation is not possible) and the strong-coupling constant λ_{sc} (extracted from Ref. [203]). The green, purple and white areas represent the orthorhombic AFM phase, the non-magnetic orthorhombic phase, and the tetragonal phase, respectively.

in the dirty limit, and the paramagnetic component can be found from the Maki parameter via $H_{c2}^{\text{pm}}(0) = \sqrt{2}H_{c2}^{\text{orb}}(0)/\alpha$. The extracted orbital and paramagnetic components, the BCS paramagnetic limit $\mu_0 H_{\text{BCS}}^{\text{pm}}(0) \approx 1.84T_c$, and the experimental critical field $H_{c2}(0)$ (as extrapolated using the WHH model), are given in Fig. 6.7(b). I observe that at all dopings the extracted paramagnetic component matches $H_{c2}^{\parallel}(0)$ well, while the calculated orbital limit is noticeably higher than $H_{c2}^{\parallel}(0)$. This implies that the critical field behaviour is dominated by paramagnetic effects, and the Maki parameter is observed to be above 1.8 (see Table 6.2). The only exception is at 1% doping, where $H_{c2}^{\text{orb}}(0) \approx H_{c2}^{\text{pm}}(0)$ such that the effective critical field may be a function of both effects. This anomalous behaviour at 1% may also be a result of the paucity of data points near T_c for $H_{c2}^{\parallel}$, which increases the error in estimation of $(dH_{c2}^{\parallel}/dT)_{T=T_c}$ in Eqn. 6.3, and may significantly affect the accuracy of the $H_{c2}^{\text{orb}}(0)$ and $H_{c2}^{\text{pm}}(0)$ estimates at that doping. For the parent compound we observe the PM limit to be equal to that expected by BCS theory, however addition of Co leads to a significant enhancement of the PM limit above $H_{\text{BCS}}^{\text{PM}}$ by about 1.6. This enhancement of the PM limit is seen in all doped samples. Paramagnetic enhancement above the BCS limit seems to be a feature of Co-doped pnictides [248], and $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ can be compared with the more isotropic $(\text{Ba,Sr})\text{Fe}_{2-x}\text{Co}_x\text{As}_2$ [249, 250], which show paramagnetic enhancement by about $\sim 4 - 5$ and are thus likely to be orbitally limited instead.

The spin-orbit scattering constant λ_{so} , as extracted from the fit of the WHH model to $H_{c2}^{\parallel}$, is shown in Fig. 6.7(b). Starting from the parent compound, λ_{so} decreases upon doping, likely due to the reduction in scattering from magnetic excitations as the system moves away from the long-range ordered AFM phase. λ_{so} then reaches a minimum at optimal doping, but begins to increase in the over-doped region, possibly due to scattering from Co impurities. It is likely that the enhancement of the paramagnetic limit is due to a combination of the spin-orbit scattering and other strong electronic interactions; any increase in the g -factor or the effective mass caused by such interactions will enhance the paramagnetic limit by a further

$(m^*g)/(mg^*)$ [221, 251, 252]. I note that neither of the models considered so far include the Eliashberg strong-coupling renormalisation effects [253].

Heat capacity measurements by Tan *et al.* [203] suggest that $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ has two superconducting gaps, with larger gap $\Delta_L(0)$ being significantly above the BCS value $\Delta_{\text{BCS}}(0) = 3.5k_{\text{B}}T_c/2$. This allows us to extract the effective strong-coupling constant λ_{sc} via $\Delta_L(0) = (1 + \lambda_{\text{sc}})\Delta_{\text{BCS}}(0)$, as given in Fig. 6.7(b). This gives a maximum $\lambda_{\text{sc}} = 1.1$ at optimal doping,² implying the presence of significant strong electronic interactions, which are reduced on moving away from optimal doping. Therefore I conclude that the enhancement of the paramagnetic limit above the BCS value is a combination of both the spin-orbit and strong coupling effects. However, the reason for the absence of any PM enhancement in the parent compound, despite a finite λ_{so} , is not clear. Since $\lambda_{\text{sc}} \approx 0$ in the parent compound, this may indicate that strong coupling effects dominate the PM enhancement effect; but in such a case one wonders why there is a PM enhancement at 1% doping (which also has $\lambda_{\text{sc}} \approx 0$). Alternatively, the absence of PM enhancement in the parent compound may be caused by some underlying interaction between the magnetism and superconductivity, caused by the strong antiferromagnetism in the 0% doping region. It may also indicate that the PM limit is influenced by additional effects that are not encapsulated in λ_{so} or λ_{sc} .

As explained previously, application of magnetic fields parallel to the crystal planes leads to a significant H_{c2}^{orb} , thus allowing the paramagnetic effect to limit the observed critical field. It is this reduction in the importance of the orbital character which allows the one-band WHH model to describe the $H_{c2}^{\parallel}$ despite the underlying two-band nature of the system, and which sets the scene for the dominance of the paramagnetic limit. Within this regime I find the WHH model to be a better fit, as it includes the spin-orbit effects described previously. In contrast, application of field normal to the planes reduces the orbital critical field, and so the overall critical field now becomes an intricate combination of the two-band orbital and paramagnetic

²Note that there is an apparent disagreement in the reported value of $\Delta_L(0)$ at optimal doping between Refs. [203] and [202], giving $\lambda_{\text{sc}} = 1.1$ and $\lambda_{\text{sc}} = 0.8$, respectively.

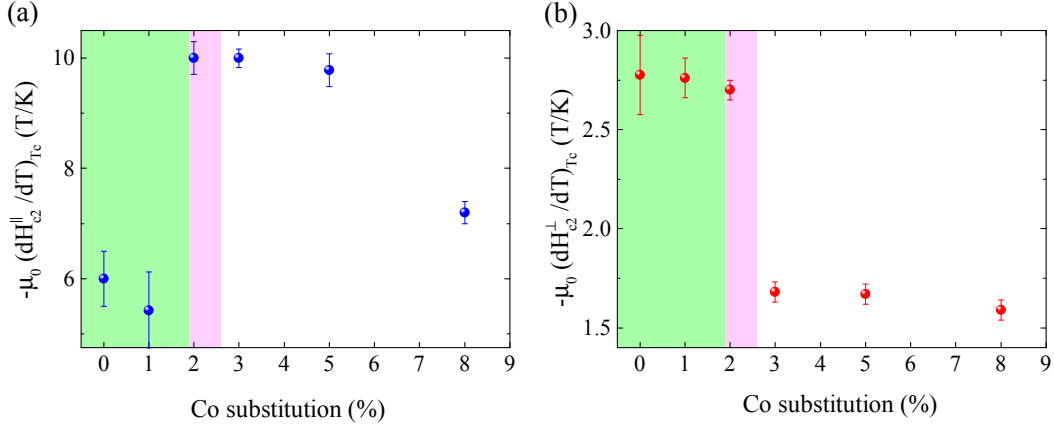


Figure 6.8: Differential with respect to temperature of (a) $\mu_0 H_{c2}^{\parallel}$ and (b) $\mu_0 H_{c2}^{\perp}$, at T_c and as a function of doping. The green, purple and white areas represent the orthorhombic AFM phase, the non-magnetic orthorhombic phase, and the tetragonal phase, respectively.

limits. This results in the one-band WHH model being no longer sufficient due to the increased sensitivity of the critical field to the underlying multi-band nature of the Fermi surface.

6.4.5 $(dH_{c2}/dT)_{T=T_c}$

Even though $H_{c2}^{\perp}$ cannot be fully described by a one-band model, $-\mu_0(dH_{c2}^{\perp}/dT)_{T=T_c}$ at T_c is still of interest as it should be proportional to the orbital critical field of the cleaner band [191]. The $-\mu_0(dH_{c2}/dT)_{T=T_c}$ for each sample orientation is plotted in Fig. 6.8, where we notice a sudden change at 2% – 3% doping for both. It is at this doping regime that the structural transition and the antiferromagnetism become suppressed, leading to the possible formation of a quantum critical point at absolute zero. The AFM structure is thought to form a columnar spin-stripe structure within the Fe-As planes, with simple columns of up/down spins along the c -direction [195, 254]. The coherence length is several times the relevant Fe-Fe separation distance d in both in-plane ($\xi_{\parallel} \sim 9d_{\parallel}$) and out-of-plane ($\xi_{\perp} \sim 4d_{\perp}$) directions, such that the Cooper pairs should feel a net internal field of zero. This implies that the sudden change in $(dH_{c2}/dT)_{T=T_c}$, and hence the corresponding effect on the orbital limit, is not simply due to internal

mean field effects. Thus it must be due to either a more inherent interaction between the superconductivity and antiferromagnetism, or due to the structural transition. I note that the sudden change in $(dH_{c2}^{\parallel}/dT)_{T=T_c}$ at 2% doping coincides with the suppression of antiferromagnetism, while the drop in $-(dH_{c2}^{\perp}/dT)_{T=T_c}$ coincides with the structural transition at $\approx 3\%$ doping. Furthermore, note that the sharp increase in λ_{sc} at 2% doping also coincides with the death of antiferromagnetism.

6.4.6 Anisotropy

Given the critical field in both directions, we can obtain the critical field anisotropy via $\gamma_H = H_{c2}^{\parallel}/H_{c2}^{\perp}$, as given in Fig 6.9(a). The anisotropy is highest just below T_c , and decreases with decreasing temperature. Such a temperature-dependent anisotropy is characteristic of pnictide superconductors, having been seen in $\text{Sr}_{1-x}\text{Eu}_x(\text{Fe}_{0.89}\text{Co}_{0.11})_2\text{As}_2$ [255], $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ [51], $\text{SmFeAsO}_{0.85}$ [234], and LiFeAs [256]. Temperature-dependent anisotropy arises from competition between the two bands and is a signature of the underlying multi-band nature of the system. In a single-band s -wave superconductor the anisotropy should be largely temperature independent, although note that it has been suggested that a single-band d -wave superconductor may also have a weakly temperature-dependent γ_H [189]. However, having measured the anisotropy up to $0.95T_c$ for most dopings, I do not see the γ_H peak at $T \sim 0.9T_c$ as seen in a number of other two-band materials [51, 234, 257]. This may be due to the increase in the γ_H error near T_c , or more likely because the peak occurs at $T \geq 0.95T_c$ in this material. The approach to unity at low temperatures can be explained in several ways [255]:

- (a) the upper critical field at absolute zero for both directions is the paramagnetic limit,
- (b) at low temperatures the band with lower diffusivity anisotropy dominates, or
- (c) the two bands have opposite anisotropy which compensate each other at low temperatures, for example $D_{\parallel}^1/D_{\perp}^1 < 1$, $D_{\parallel}^2/D_{\perp}^2 > 1$.

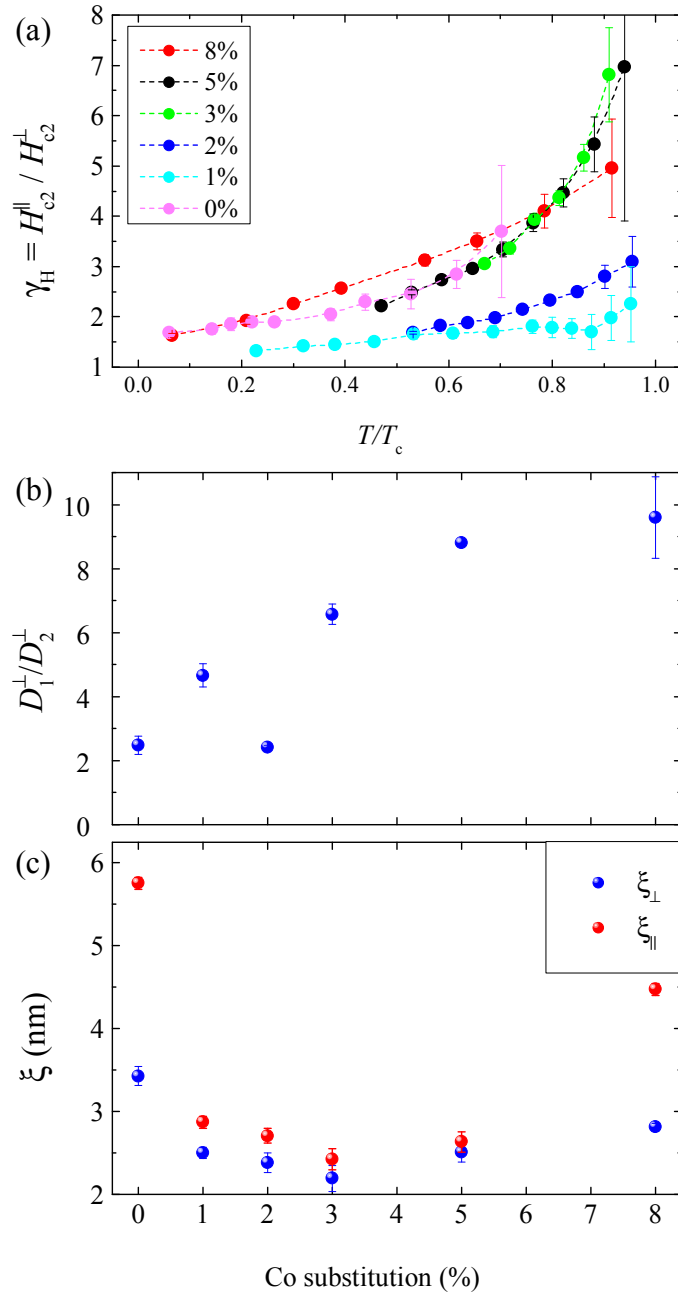


Figure 6.9: (a) The critical field anisotropy $\gamma_H = H_{c2}^{\parallel} / H_{c2}^{\perp}$ as a function of T/T_c ; (b) plot of the out-of-plane band diffusivity anisotropy $D_1^{\perp} / D_2^{\perp}$, from fits to the $H_{c2}^{\perp}$ with $\lambda_{11} = \lambda_{22} = 1, \lambda_{11}\lambda_{22} - \lambda_{12}\lambda_{21} = 0.5$. Also shown is (c) the coherence length at 0 K, found by extrapolating the critical field measurements to absolute zero using the WHH model for $H_{c2}^{\parallel}$ and the two-band model for $H_{c2}^{\perp}$. The uncertainty in extrapolation of the over-parametrised two-band model to 0 K has been included in error bars.

I note that the under-doped systems are relatively isotropic ($\gamma_{\text{H}} < 3$), whereas the optimally and over-doped systems become noticeably anisotropic near T_{c} ($\gamma_{\text{H}} \approx 7$). This is complemented by the fact that the positive curvature in $H_{\text{c}2}^{\perp}$ also becomes more pronounced as we move over from the under-doped to the over-doped regime (Fig. 6.5). Both observations could be accounted for by an increase in the band diffusivity anisotropy D_1/D_2 [see Fig. 6.9(b)], which magnifies the effect of the underlying multi-band nature on γ_{H} and $H_{\text{c}2}^{\perp}$. The Fermi surface is known to be highly sensitive to Co doping; causing the electron pockets to widen and hole pockets to shrink with doping (see Fig. 6.2). I tentatively suggest that it is this difference between the response of the hole and electron pockets (and the corresponding change in the Fermi velocity v_{F}), as well as the increase in scattering from impurities with additional doping, which leads to an increase in D_1/D_2 .

6.4.7 Coherence length and the superfluid stiffness

The Ginzburg-Landau coherence lengths can be estimated using [26]

$$\xi_{\parallel} = \sqrt{\frac{\phi_0}{2\pi\mu_0 H_{\text{c}2}^{\perp}}}, \quad (6.4)$$

$$\xi_{\perp} = \frac{\phi_0}{2\pi\mu_0 H_{\text{c}2}^{\parallel} \xi_{\parallel}}. \quad (6.5)$$

Extrapolating the critical field measurements to absolute zero using the WHH model for $H_{\text{c}2}^{\parallel}$ and the two-band model for $H_{\text{c}2}^{\perp}$, we can calculate the coherence lengths as given in Fig. 6.9(c), showing a minimum at optimal doping. The superconducting layer thickness δ can be estimated as $\delta = \sqrt{12}\xi_{\parallel} H_{\text{c}2}^{\perp}/H_{\text{c}2}^{\parallel}$ [258], which gives us a minimum superconducting layer thickness of 7.25 nm, an order of magnitude longer than the lattice c -axis parameter. This rules out the possibility of a dimensional crossover, or the formation of a Josephson-coupled superconductor, as discussed in Section 6.4.2.

The lower critical field $H_{\text{c}1}$, which denotes the onset of Abrikosov vortex formation, was measured using a Quantum Design SQUID magnetometer. Due to the very

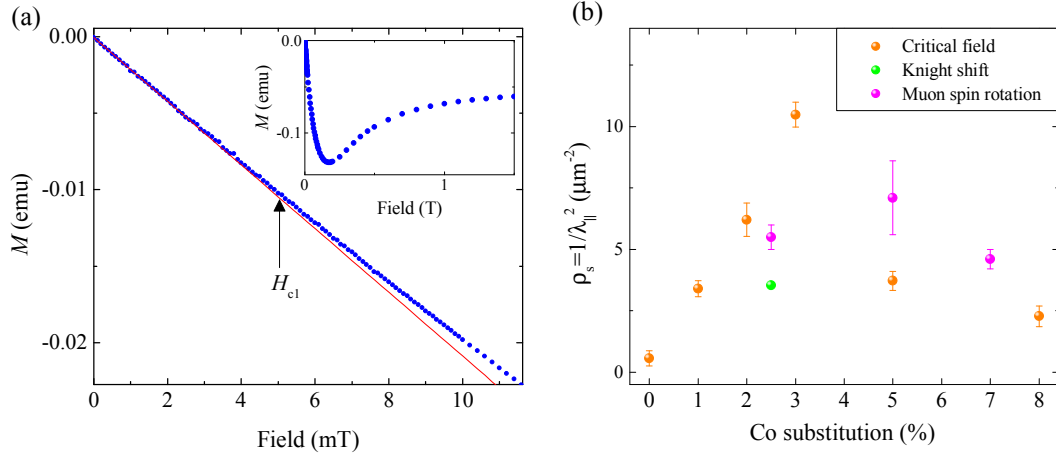


Figure 6.10: (a) The magnetic moment of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$, $x = 0.02$, taken at 2 K after zero-field cooling. The lower critical field H_{c1} is defined as the field at which the moment deviates from the straight line. Also shown in (b) is the evolution of the superfluid stiffness $\rho_s = 1/\lambda_{||}$ at 2 K with doping, where I have also included data from Knight shift [260] and muon-spin relaxation [201] measurements.

small values of H_{c1} , any trapped remanent flux in the superconducting coil windings may cause anomalous readings [259]. To remove this remnant field, the magnet was quenched by heating the magnet coil above its critical temperature before the measurements. The samples were zero-field cooled from 300 K down to 2 K, and then their magnetic moment was recorded upon slowly increasing the field from 0 T. H_{c1} was determined, in a consistent manner, as the point at which the magnetisation deviates from the straight line representing the Meissner condition $\chi = -1$ [26], see Fig. 6.10(a). The values for $H_{c1}^\perp$ are presented in Table. 6.1. Having obtained the lower critical field, the London penetration depth can then be calculated via

$$\mu_0 H_{c1}^\perp = \frac{\phi_0}{4\pi\lambda_{||}^2} \ln \frac{\lambda_{||}}{\xi_{||}}, \quad (6.6)$$

$$\mu_0 H_{c1}^\parallel = \frac{\phi_0}{4\pi\lambda_{||}\lambda_\perp} \ln \sqrt{\frac{\lambda_{||}\lambda_\perp}{\xi_{||}\xi_\perp}}. \quad (6.7)$$

The penetration depth is related to the superfluid stiffness ρ_s and the superconducting density of states n_i via $\lambda_{||}^{-2} \equiv \rho_s \propto \sum n_i$ [261]. The evolution of the superfluid stiffness at 2 K was calculated and is given in Fig. 6.10(b), where we observe a maximum at optimal doping, with ρ_s decreasing almost linearly in the under-doped

region. Such a rapid fall could be due to (a) the competition between superconductivity and antiferromagnetism which removes a portion of charge carriers that might otherwise join the condensate [262, 263], and/or (b) strengthening of the AFM phase and increased magnetic fluctuations in the coexistence region [204], which increase pair-breaking scattering as the system moves into the magnetic region [264]. The slower decrease within the over-doped regime may be a result of the reduction in the carrier density as the hole pockets begin to shrink, although it has been noted by authors of Refs. [264, 265] that an anisotropic reduction in the pairing strength in the $s^\pm$ scenario can also lead to such an effect. Finally, I emphasise that the $1/\lambda_{\parallel}^2$ values given here are approximate as I have neglected any geometric factors or demagnetisation effects at sharp corners of the sample [266], however I note that the data is in relatively good agreement with previous Knight shift [260] and muon-spin relaxation [201] measurements.

6.5 Conclusion

In summary, I have measured the upper critical field of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ across the superconducting phase, with the magnetic field applied normal and parallel to the superconducting planes. I find that the in-plane critical field is paramagnetically limited across the phase diagram, with the critical field matching the BCS limit in the parent compound. Doping leads to an enhancement of the critical field above the BCS paramagnetic limit due to a combination of spin-orbit and strong electronic interactions. I note that a multi-band model is necessary to fully describe the critical field behaviour, in particular the upwards curvature in $H_{c2}^\perp$ at low temperatures, and is further confirmed by the critical field anisotropy. I also discovered a sudden change in $(dH_{c2}/dT)_{T=T_c}$ at optimal doping, which I related to the death of the antiferromagnetic order and/or the structural transition near optimal doping. Furthermore, I discussed the penetration depth ξ and discovered a peak in the superfluid stiffness at optimal doping.

6.6 Further work

Focusing on the high-field measurements of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$, and on the data presented in this chapter, there is room for further work to be done. Note that the measurements were performed only up to 45 T, while the critical field extrapolations down to absolute zero reach values of ≈ 60 T or more, effectively limiting the upper critical field measurements of optimally-doped samples to the high temperature region around T_c . Therefore the measurements would greatly benefit from access to higher fields. The pulsed magnetic field facility at Oxford is currently in the process of being upgraded with new magnets that can reach 70 T, facilitating further in-house critical field measurements.

There have been a number of ARPES studies on $\text{NaFe}_{1-x}\text{Co}_x\text{As}$. However, ARPES is essentially a surface measurement, and as such it is highly sensitive to surface effects. In particular surface charge redistribution on a number of pnictide superconductors, in particular the “1111” family, prohibits ARPES measurements, although this is not a significant problem in $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ due to the non-polar surface [204]. Deintercalation of the mobile Na atoms at the surface can lead to a different surface Na concentration when compared to bulk [206]. The most established method for measuring Fermi surfaces is quantum oscillations in resistivity (Shubnikov–de Haas effect) or magnetisation (de Haas–van Alphen effect) [2, 117]. The proximity detector oscillator is an excellent technique for observing Shubnikov–de Haas oscillations, due to its contactless nature and high sensitivity to the sample penetration depth, and hence, resistivity. Additionally, pulsed field extraction magnetometry is a proven technique for observing de Haas–van Alphen oscillations due to the high dB/dT which amplifies the sample signal. However, despite the best efforts of myself, and others, no quantum oscillations have yet been observed in $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ or a range of other Co-doped superconductors, probably due to presence of defects within the samples, which dampen the oscillations [2, 117]. Higher fields increase the magnitude of quantum oscillations, and so the upgrade of the Oxford pulsed field facility will provide further opportunity to search for quantum

oscillations in $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ and a variety of other iron-pnictide superconductors. Measurements at other high-field facilities, for example the pulsed-field facility at Los Alamos, USA, also remain an option.

It would also be useful to further investigate the multi-band nature of the superconductivity. The original theory by Gurevich [191] was developed for the quintessential two-band superconductor MgB_2 , where the critical field behaviour could be qualitatively described by considering the system as a bilayer of two different superconductors, with the superconductivity in each layer arising from one of the bands [191]. It would be interesting to see if this analogy can be carried further, and in particular to see if the critical field of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$ could be described by a combination of two or more one-band models.

Chapter 7

Conclusion and outlook

In this thesis, a number of transition-metal coordination polymers and iron-pnictide superconductors were investigated under extreme conditions, such as high magnetic fields, high pressures, and low temperatures. This chapter summarises the results, and presents a brief outlook of future experiments.

In Chapter 4, I discussed the effect of pressure on the magnetic properties of the coordination polymer $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyrazine})$. It was shown that pressure could be used to modify the magnetic parameters of the system, giving us the ability to control the exchange couplings and the ordering temperature. Specifically, the presence of a Jahn-Teller active metal centre within a hetero-ligand environment meant that pressure could be used to induce a phase transition from quasi-two-dimensional to quasi-one-dimensional magnetism at 9 kbar. This was shown to lead to a significant reduction of the primary exchange coupling and a five-fold decrease in the ordering temperature.

This work has been published in Ref. [121], and presents a notable contribution to the field of coordination magnetism, showing that it is possible to directly control the magnetic parameters and dimensionality via external perturbation, giving us the ability to fine-tune the exchange couplings to desired values. This work also emphasises the role that pressure can play in exploring new materials and phases,

and provides a path for further high-pressure magnetometry measurements on coordination polymers and other magnetic insulators.

In Chapter 5, I showed how a chemical synthesis route can lead to two separate phases of matter which, although made from the same molecular building blocks, show drastically different magnetic properties. It was shown that the coordination polymer $[\text{Cu}(\text{pyrazine})\text{H}_2\text{O}(\text{glycine})_2]\text{ClO}_4$ is an excellent realisation of a quasi-one-dimensional antiferromagnet. However, the removal of a glycine molecule from this compound at the synthesis stage leads to a radical change in the structural and magnetic properties. It was demonstrated that $[\text{Cu}(\text{pyrazine})(\text{glycine})]\text{ClO}_4$ becomes a zero-dimensional spin-dimer system, and remains disordered down to absolute zero, but undergoes a field-induced phase transition to an XY ordered phase. This work has been published in Ref. [19], and highlights the fact that even very small changes at the synthesis stage can lead to significant modification of a material's structure, and hence, magnetic properties. Furthermore, this chapter shows that applied magnetic fields, as well as enabling measurement of the material's magnetic properties, can be used to modify the energy levels of a system and induce phase transitions.

I briefly discussed the physics of $[\text{Cu}(\text{pyrazine})(\text{glycine})]\text{ClO}_4$ in terms of formation of $S = 1$ quasiparticles upon the application of a magnetic field, showing that the bosonic interpretation can be more intuitive than the original spin-picture of the system. Such a connection between spins and bosons has been exploited since the discovery of quantum mechanics [173]. This work demonstrates and gives weight to the idea of using coordination polymers as ‘quantum simulators’ of phenomena that may occur in quantum mechanical systems [267], such as Bose-Einstein condensation.

Overall, my work on coordination polymers highlights the quantum nature of the magnetism in these systems, and the potential for creating novel magnetic ground states. There exists the possibility of using polymeric magnets as a playground for realising exotic magnetic phenomena, enabling one to investigate rich behaviour that may rarely be seen in more conventional materials. The combination of my

work in Chapters 5 and 4 suggests a route for achieving this aim: by (a) using chemical synthesis to grow materials with structures that might lead to interesting magnetic behaviour; and then (b) using the external perturbations such as pressure or magnetic field to control the magnetic parameters and the dimensionality, thus fine-tuning the system towards the desired magnetic ground state. Phenomena of interest might include magnetic frustration, and the formation of a Haldane gap or a spin-Peierls instability in spin-chains, amongst others.

There is room for significant further experimentation and research in the field of coordination polymers. I have already begun investigating several materials of interest along the route suggested above. Such materials include (a) $[\text{Ni}(\text{H}_3\text{F}_4)(4\text{-Fpy})_4]\text{SbF}_6$ (py=pyridine, $\text{C}_5\text{H}_5\text{N}$), a coordination polymer with a kagome structure which could give rise to geometrical frustration, (b) $\text{Cu}(\text{H}_2\text{O})_5\text{VOF}_4$, a material which has a spin-gap consistent with formation of Cu-V spin-dimers, and (c) a number of weakly-coupled Cu-based tetramers, amongst others.

In Chapter 6, I presented a high-field study of the iron-based superconductor $\text{NaFe}_{1-x}\text{Co}_x\text{As}$. Specifically, I measured the upper critical field of this material across the whole of the doping phase diagram, from the parent to over-doped compounds. I assessed the ability of various models to describe the upper critical field behaviour, and found that a multi-band model is required to explain the unusual upwards curvature seen in the critical field vs temperature curve of the optimally-doped and over-doped compounds. Furthermore, I showed that with the magnetic field parallel to the Fe-As planes, the critical field is strongly limited by paramagnetic pair-breaking effects. Doping by cobalt was shown to lead to a significant enhancement of the paramagnetic limit. Additionally, I extracted and discussed the behaviour of the critical field anisotropy, the penetration depth, the coherence length, and the superfluid stiffness.

The results of Chapter 6 have been published in Ref. [182], and presents a comprehensive study of the effect of doping on the upper critical field of $\text{NaFe}_{1-x}\text{Co}_x\text{As}$,

which is a highly topical superconductor. Thus this work represents an advance in the study of the high-field behaviour of this class of compounds. Unconventional superconductivity is one of the major intellectual problems in current condensed matter physics, and the intense interest in this phenomena means that there is an almost continuous discovery of new materials. In this context, my work in Chapter 6 presents some insights and provides a path for future studies of other iron-based superconductors. For example, my group in Oxford has already begun performing similar experiments on FeSe, a superconductor which shows an increase in the critical temperature when intercalated with molecular spacer layers [39].

Returning to the beginning of this thesis, in Chapter 3 I described my development of the proximity detector oscillator dynamic susceptometer, a new radio-frequency based technique which can be used for both magnetometry and transport measurements. This system has no dependence on dB/dt and can operate at extremely high fields, making it suitable for use in both steady and pulsed magnetic fields. Furthermore, the small spatial footprint and absence of moving parts in this system makes it ideal for use in pressure cells or sample rotators. Such magnetometry measurements would have previously been extremely challenging or impossible. Thus the development of this technique has made a significant contribution to the field of high-pressure and high-field magnetometry, making new experiments possible. The results of Chapter 3 have been published in Ref. [72].

This conclusion is essentially supported by the rest of the thesis, where the proximity detector oscillator (PDO) was used to perform measurements that would have been very difficult to do otherwise: measuring the magnetisation of $\text{CuF}_2(\text{H}_2\text{O})_2(\text{pyrazine})$ as a function of pressure, (b) measuring the magnetisation of $[\text{Cu}(\text{pyz})(\text{gly})]\text{ClO}_4$, a sample which had a large magnetocaloric effect and could not be measured using traditional pulsed-field techniques, and (c) performing upper critical field measurements on $\text{NaFe}_{1-x}\text{Co}_x\text{As}$, a highly air-sensitive sample. One unique property of the PDO that hasn't been explored so far is the unique ability to observe transport and magnetic properties in the same experiment. The PDO, in

combination with a pressure cell and high magnetic fields, would be ideal for exploring materials that show metal-insulator phase transitions [268]. This would enable characterisation of the magnetic properties in the insulating phase, and transport properties in the metallic phase, providing a path for gaining new insights into the physics of these materials.

The discipline of high magnetic fields is continuously evolving, with new technologies and concepts being used to achieve ever-increasing fields. This means that there is an on-going need to develop new measurement techniques and instrumentation that can operate within these extreme conditions. One current challenge is the operation of transport and magnetometry experiments in the 300 T single-turn explosive magnets, which have an extremely short pulse width (microseconds). Several new technologies that address this challenge are currently in development, including a modified version of the PDO that will operate at much higher frequencies (~ 100 MHz) and uses fibre-optics as part of its circuitry [269].

The PDO has a bright future as a multi-purpose tool in the hands of the high-field experimentalist, widening the range of experiments that can be performed and the number of samples that can be investigated. A recent report by the US National Research Council has confirmed the important part that high magnetic fields play in both basic and applied scientific research, and has recommended development of new 60 T steady-field and 150 T pulsed-field magnets [5]. The PDO, due to its unique advantages and versatility, is bound to be one of the measurement techniques of choice in these new systems.

Appendix A

Diamond anvil cell measurements

This appendix describes the procedure for setting up turnbuckle diamond-anvil cells for the experiment described in Section 4.9.

The diamond-anvil cells (DACs) were designed and made at the National High Magnetic Fields Facility, USA. The schematic diagram of a DAC is given in Fig. A.1. The pressure cell consists of a pair of natural diamonds, each with a highly polished flat surface. Each diamond is set into a high-tensile BeCu alloy endcap. A thin gasket, reinforced by a Zylon outer ring, is placed on the flat surface of the bottom diamond. A small hole at the centre of the gasket acts as the sample space, which is filled with an appropriate pressure medium. The DAC uses a turnbuckle design, where the endcaps have threads of the opposite sense. The two diamonds are then placed in the turnbuckle body using a specially designed load-cell assembly [see Figs. A.1(a,b)], and each turn of the turnbuckle brings the diamonds closer together. As the diamonds are brought together, the gasket becomes compressed, sealing the pressure medium in. Further application of force compresses the gasket even more, causing a pressure buildup within the pressure medium.

The gasket is reinforced by an outer ring of epoxy-impregnated Zylon fibre, and is made by mixing a powder made of 5–10 μm diamond particles with Stycast 1266

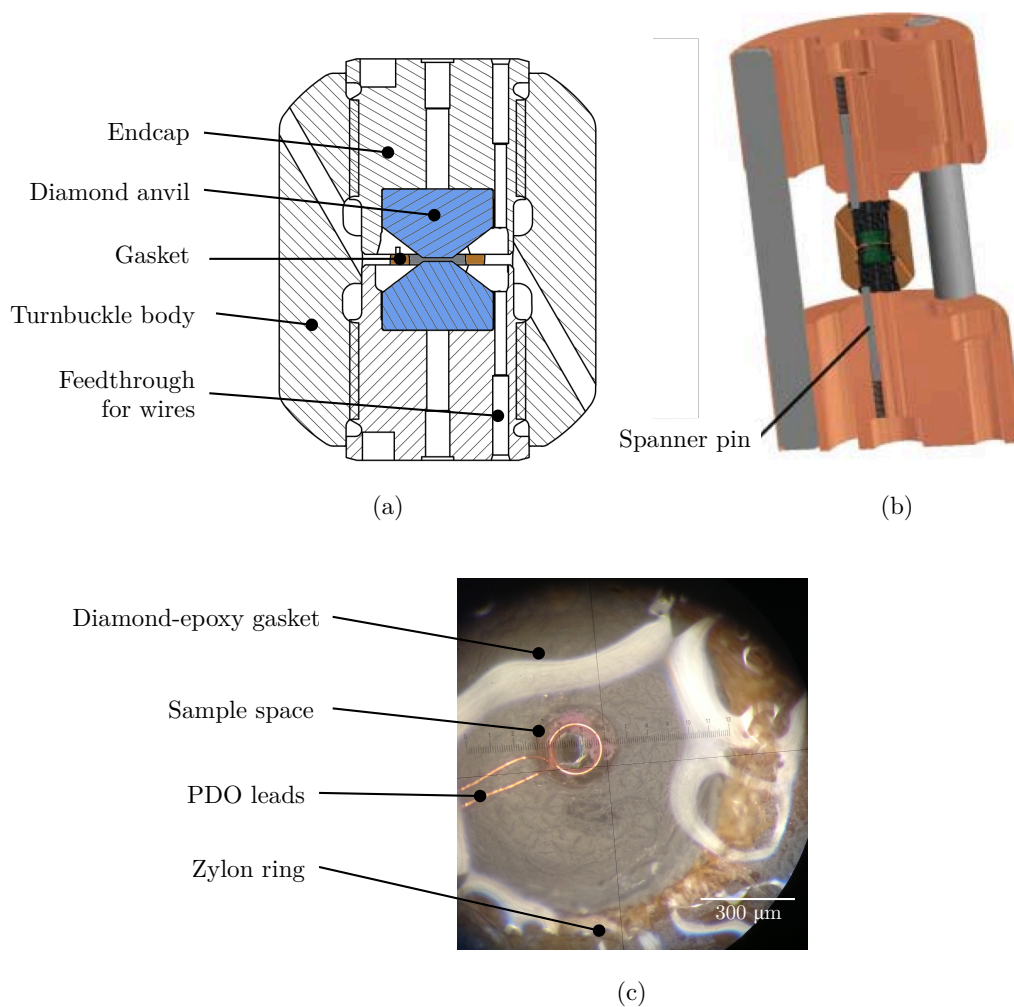


Figure A.1: Schematic diagram of (a) a turnbuckle diamond-anvil cell and (b) the spanner system for tightening the turnbuckle [270]. Also shown is an image of a DAC gasket loaded with a PDO coil and a sample. The pink dots next to the sample are the ruby spheres used for pressure calibration.

epoxy. The smallest amount of epoxy is used, as higher diamond content leads to a stronger (but more fragile) gasket. The gasket is prepared as follows: firstly a Zylon ring is fixed to the sides of the diamond surface using Araldite 5-minute epoxy, and once dry, the Zylon ring is filled with the gasket mixture. The second diamond is coated using a thin film of PTFE lubricant, and both diamond stones are then placed in the turnbuckle body, and are brought together in a controlled manner, compressing the gasket material. The gasket is compressed until the desired thickness is reached, after which the DAC assembly is placed inside an oven for the gasket to cure. The top diamond can then be easily removed due to the added lubricant, giving access to the newly made gasket.

The sample space is created by making a hole of the appropriate size at the centre of gasket, the walls of which are covered with a thin layer of epoxy for added strength. Two channels are made in the gasket and the Zylon ring, for feeding through the PDO coil leads. The PDO coil is placed inside the gasket hole, and the wires are positioned inside the channels and fixed in place with epoxy. These channels are needed to prevent the wires from being completely crushed or disconnected as the DAC is pressurised. Finally, the sample and some ruby spheres (used for pressure calibration) are placed inside the coil, and the gasket hole filled with the pressure medium. The bottom and top diamonds are then placed inside the turnbuckle assembly, and brought together by turning the turnbuckle. As the diamonds are brought together the applied pressure is continuously monitored using the luminescence of ruby, as discussed in the next section.

Similar to piston-cylinder cells, the DAC is slowly cooled at a rate of 0.5 K/min during the experiment, to prevent thermal shocks and reduce non-hydrostaticity. However, in contrast to PCCs, cryogenic cooling increases the pressure by a factor of 2–3. This is due to the low thermal expansion coefficient of diamond when compared to the cell body. All pressures quoted here are taken *in-situ* at the measurement temperature, using the R_1 fluorescence line of the ruby spheres (see Section 4.3.2).

Diamond anvil cells are used for their ability to reach higher pressures than other pressure cells. In this thesis (see Section 4.9) a maximum pressure of 56 kbar was achieved, although pressures in excess of 500 kbar are possible in DACs. The maximum pressure that can be achieved in the DAC setup explained here depends on the diamond cutlet (diameter), as well as the gasket thickness, material, and hole diameter. Using smaller diamonds or thinner gaskets allows higher pressures to be achieved, as a smaller amount of force is required to reach a particular pressure, although at the obvious cost of a smaller sample space. Typically turnbuckle DACs of this design fail by either (a) developing a leak at the lead channels, or (b) an expansion of the gasket hole. In the latter case the gasket becomes unable to support the pressure—the application of further force simply serves to deform the gasket hole, and the pressure remains constant or is reduced. Finally, DAC experiments can also fail when the gasket compresses so much that both diamonds begin to touch the sample directly, crushing it in the process.

For the experiment described in Section 4.9, over ten DACs were prepared, using a wide variety of diamond cutlets (0.6–1.2 mm), gasket thicknesses (50 – 150 μm), gasket holes (0.2 – 0.4 mm diameter) and PDO coils (100 – 300 μm diameter). Successful measurements up to 56 kbar were made using a 0.8 mm cutlet diamond with a gasket of thickness 150 μm and gasket hole of 300 μm diameter.

Bibliography

- [1] S. E. Sebastian, N. Harrison, M. M. Altarawneh, C. H. Mielke, R. Liang, D. A. Bonn, and G. G. Lonzarich, PNAS **107**, 6175 (2010).
- [2] D. Shoenberg, *Magnetic oscillations in metals* (Cambridge University Press, 1984).
- [3] 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, New. J. Phys. **10**, 083025 (2008).
- [4] S. E. Sebastian, N. Harrison, C. D. Batista, L. Balicas, M. Jaime, P. A. Sharma, N. Kawashima, and I. R. Fisher, Nature **441**, 617 (2006).
- [5] *High Magnetic Field Science and Its Application in the United States: Current Status and Future Directions* (The National Academies Press, 2013).
- [6] H. Arnold and G. Elmen, Bell System Technical Journal **2**, 101 (1923).
- [7] S. J. Blundell and F. L. Pratt, J. Phys.: Condens. Matter **16**, R771 (2004).
- [8] M. Julliere, Physics Letters A **54**, 225 (1975).
- [9] A. Zheludev and T. Roscilde, C. R. Physique **14**, 740 (2013).
- [10] N. D. Mermin and H. Wagner, Phys. Rev. Lett. **17**, 1133 (1966).
- [11] P. A. Goddard, J. Singleton, C. Maitland, S. J. Blundell, T. Lancaster, P. J. Baker, R. D. McDonald, S. Cox, P. Sengupta, J. L. Manson, K. A. Funk, and J. A. Schlueter, Phys. Rev. B **78**, 052408 (2008).
- [12] 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. E. Ayala-Valenzuela, J. F. Corbey, H. I. Southerland, P. Sengupta, and J. A. Schlueter, Phys. Rev. Lett. **108**, 077208 (2012).
- [13] T. Yankova, D. Hvonon, S. Mhlbauer, D. Schmidiger, E. Wulf, S. Zhao, A. Zheludev, T. Hong, V. Garlea, R. Custelcean, and G. Ehlers, Philosophical Magazine **92**, 2629 (2012).
- [14] J. L. Manson, K. E. Carreiro, S. H. Lapidus, P. W. Stephens, P. A. Goddard, R. E. Del Sesto, J. Bendix, S. Ghannadzadeh, I. Franke, J. Singleton, T. Lancaster, J. S. Moller, P. J. Baker, F. L. Pratt, S. J. Blundell, J. Kang, C. Lee, and M.-H. Whangbo, Dalton Trans. **41**, 7235 (2012).

- [15] J. L. Manson, J. G. Lecher, J. Gu, U. Geiser, J. A. Schlueter, R. Henning, X. Wang, A. J. Schultz, H.-J. Koo, and M.-H. Whangbo, *Dalton Trans.*, 2905 (2003).
- [16] S. H. Lapidus, J. L. Manson, H. Park, A. J. Clement, S. Ghannadzadeh, P. Goddard, T. Lancaster, J. S. Moller, S. J. Blundell, M. T. F. Telling, J. Kang, M.-H. Whangbo, and J. A. Schlueter, *Chemical Communications* **49**, 499 (2013).
- [17] T. Lancaster, S. J. Blundell, M. L. Brooks, P. J. Baker, F. L. Pratt, J. L. Manson, C. P. Landee, and C. Baines, *Phys. Rev. B* **73**, 020410 (2006).
- [18] J. L. Manson, A. G. Baldwin, B. L. Scott, J. Bendix, R. E. Del Sesto, P. A. Goddard, Y. Kohama, H. E. Tran, S. Ghannadzadeh, J. Singleton, T. Lancaster, J. S. Miller, S. J. Blundell, F. L. Pratt, V. S. Zapf, J. Kang, C. Lee, M.-H. Whangbo, and C. Baines, *Inorganic Chemistry* **51** (2012).
- [19] T. Lancaster, P. A. Goddard, S. J. Blundell, F. R. Foronda, S. Ghannadzadeh, J. S. Möller, P. J. Baker, F. L. Pratt, C. Baines, L. Huang, J. Wosnitza, R. D. McDonald, K. A. Modic, J. Singleton, C. V. Topping, T. A. W. Beale, F. Xiao, J. A. Schlueter, R. D. Cabrera, K. E. Carreiro, H. E. Tran, and J. L. Manson, *Phys. Rev. Lett.* **112**, 207201 (2014).
- [20] B. C. Watson, V. N. Kotov, M. W. Meisel, D. W. Hall, G. E. Granroth, W. T. Montfrooij, S. E. Nagler, D. A. Jensen, R. Backov, M. A. Petruska, G. E. Fanucci, and D. R. Talham, *Phys. Rev. Lett.* **86**, 5168 (2001).
- [21] T. Masuda, A. Zheludev, H. Manaka, L.-P. Regnault, J.-H. Chung, and Y. Qiu, *Phys. Rev. Lett.* **96**, 047210 (2006).
- [22] V. O. Garlea, A. Zheludev, L.-P. Regnault, J.-H. Chung, Y. Qiu, M. Boehm, K. Habicht, and M. Meissner, *Phys. Rev. Lett.* **100**, 037206 (2008).
- [23] H. K. Onnes, Nobel Lecture **4** (1913).
- [24] W. Meissner and R. Ochsenfeld, *Naturwissenschaften* **21**, 787 (1933).
- [25] F. London and H. London, *Proc. R. Soc. Lond. A* **149**, 71 (1935).
- [26] J. Annett, *Superconductivity, superfluids, and condensates* (Oxford University Press, 2004).
- [27] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).
- [28] M. Tinkham, *Introduction to superconductivity* (McGraw Hill (New York), 1996).
- [29] J. Bednorz and K. Müller, *Zeitschrift für Physik B Condensed Matter* **64**, 189 (1986).
- [30] R. Hott, R. Kleiner, T. Wolf, and G. Zwicknagl, “Superconducting materials: A topical overview,” in *Frontiers in Superconducting Materials*, edited by A. V. Narlikar (2005).

- [31] A. Schilling, M. Cantoni, J. D. Guo, and H. R. Ott, *Nature* **363**, 56 (1993).
- [32] H. Takahashi, K. Igawa, K. Arii, Y. Kamihara, M. Hirano, and H. Hosono, *Nature* **453**, 376 (2008).
- [33] D. C. Johnston, *Advances in Physics* **59**, 803 (2010).
- [34] G. R. Stewart, *Rev. Mod. Phys.* **83**, 1589 (2011).
- [35] P. J. Hirschfeld, M. M. Korshunov, and I. I. Mazin, *Rep. Prog. Phys.* **74**, 124508 (2011).
- [36] J. Paglione and R. L. Greene, *Nat Phys* **6**, 645 (2010).
- [37] J. Wright, *Magnetism and superconductivity in iron pnictides and iron chalcogenides*, Ph.D. thesis, University of Oxford (2013).
- [38] X. Zhu, F. Han, G. Mu, B. Zeng, P. Cheng, B. Shen, and H.-H. Wen, *Phys. Rev. B* **79**, 024516 (2009).
- [39] M. Burrard-Lucas, D. G. Free, S. J. Sedlmaier, J. D. Wright, S. J. Cassidy, Y. Hara, A. J. Corkett, T. Lancaster, P. J. Baker, S. J. Blundell, and S. J. Clarke, *Nat Mater* **12**, 15 (2013).
- [40] A. F. Wang, J. J. Ying, X. G. Luo, Y. J. Yan, D. Y. Liu, Z. J. Xiang, P. Cheng, G. J. Ye, L. J. Zou, Z. Sun, and X. H. Chen, *New J. Phys.* **15**, 043048 (2013).
- [41] D. N. Basov and A. V. Chubukov, *Nat Phys* **7**, 272 (2011).
- [42] J.-H. Chu, J. G. Analytis, C. Kucharczyk, and I. R. Fisher, *Phys. Rev. B* **79**, 014506 (2009).
- [43] K. Ishida, Y. Nakai, and H. Hosono, *J. Phys. Soc. Jpn.* **78**, 062001 (2009).
- [44] P. C. Canfield, S. L. Bud'ko, N. Ni, J. Q. Yan, and A. Kracher, *Phys. Rev. B* **80**, 060501 (2009).
- [45] T. Park, E. Park, H. Lee, T. Klimczuk, E. D. Bauer, F. Ronning, and J. D. Thompson, *Journal of Physics: Condensed Matter* **20**, 322204 (2008).
- [46] C.-H. Lee, A. Iyo, H. Eisaki, H. Kito, M. Teresa Fernandez-Diaz, T. Ito, K. Kihou, H. Matsuhata, M. Braden, and K. Yamada, *Journal of the Physical Society of Japan* **77**, 083704 (2008).
- [47] J. R. Kirtley, C. C. Tsuei, Ariando, C. J. M. Verwijs, S. Harkema, and H. Hilgenkamp, *Nat Phys* **2**, 190 (2006).
- [48] I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, *Phys. Rev. Lett.* **101**, 057003 (2008).
- [49] J. Chang, N. Doiron-Leyraud, O. Cyr-Choiniere, G. Grissonnanche, F. Laliberte, E. Hassinger, J.-P. Reid, R. Daou, S. Pyon, T. Takayama, H. Takagi, and L. Taillefer, *Nat Phys* **8**, 751 (2012).

- [50] H. Shishido, A. F. Bangura, A. I. Coldea, S. Tonegawa, K. Hashimoto, S. Kasahara, P. M. C. Rourke, H. Ikeda, T. Terashima, R. Settai, Y. Ōnuki, D. Vignolles, C. Proust, B. Vignolle, A. McCollam, Y. Matsuda, T. Shibauchi, and A. Carrington, *Phys. Rev. Lett.* **104**, 057008 (2010).
- [51] M. Kano, Y. Kohama, D. Graf, F. Balakirev, A. S. Sefat, M. A. McGuire, B. C. Sales, D. Mandrus, and S. W. Tozer, *J. Phys. Soc. Jpn.* **78**, 084719 (2009).
- [52] D. Larbalestier, A. Gurevich, D. M. Feldmann, and A. Polyanskii, *Nature* **414**, 368 (2001).
- [53] H. Schneider-Muntau, J. Toth, and H. Weijers, *Applied Superconductivity, IEEE Transactions on* **14**, 1245 (2004).
- [54] *Opportunities in high magnetic field science* (The National Academies Press, 2005).
- [55] H. Witte and H. Jones, *Physica B: Condensed Matter* **346-347**, 663 (2004), proceedings of the 7th International Symposium on Research in High Magnetic Fields.
- [56] K. A. G. Jr, V. K. Pecharsky, and A. O. Tsokol, *Rep. Prog. Phys.* **68**, 1479 (2005).
- [57] H. Witte, *Magnet design using finite element analysis*, Ph.D. thesis, University of Oxford (2007).
- [58] ZYLON (PBO fibre) Technical Information, Toyobo Co., Ltd., www.toyobo-global.com.
- [59] B. J. Gao, H. Schneider-Muntau, Y. Eyssa, and M. Bird, *Magnetics, IEEE Transactions on* **32**, 2503 (1996).
- [60] S. E. Sebastian, *Bose-Einstein condensation in spin dimer compounds*, Ph.D. thesis, Stanford University (2006).
- [61] A. Mari and L. Brossard, *Rev. Sci. Instrum.* **64**, 1364 (1993).
- [62] Quantum Design USA, www.qdusa.com.
- [63] L. H. Lewis and K. M. Bussmann, *Rev. Sci. Instrum.* **67**, 3537 (1996).
- [64] B. H. Blott and G. J. Daniell, *Measurement Science and Technology* **4**, 462 (1993).
- [65] N. Casa-Pastor, P. Gomez-Romero, and L. C. Baker, *Journal of Applied Physics* **69**, 5088 (1991).
- [66] S. Blundell and K. Blundell, *Concepts in thermal physics* (Oxford University Press, 2006).
- [67] *Physical Property Measurement System: Heat Capacity Option User's Manual*, Quantum Design USA, 11th ed. (2014).

- [68] J. Lashley, M. Hundley, A. Migliori, J. Sarrao, P. Pagliuso, T. Darling, M. Jaime, J. Cooley, W. Hults, L. Morales, D. Thoma, J. Smith, J. Boerio-Goates, B. Woodfield, G. Stewart, R. Fisher, and N. Phillips, *Cryogenics* **43**, 369 (2003).
- [69] J. S. Hwang, K. J. Lin, and C. Tien, *Rev. Sci. Instrum.* **68**, 94 (1997).
- [70] S. J. Blundell, *Contemporary Physics* **40**, 175 (1999).
- [71] J. L. Manson *et al.*, *Chem. Mater.* **20**, 7408 (2008).
- [72] S. Ghannadzadeh, M. Coak, I. Franke, P. A. Goddard, J. Singleton, and J. L. Manson, *Rev. Sci. Instrum.* **82**, 113902 (2011).
- [73] J. D. Fletcher, A. Carrington, P. Diener, P. Rodière, J. P. Brison, R. Prozorov, T. Olheiser, and R. W. Giannetta, *Phys. Rev. Lett.* **98**, 057003 (2007).
- [74] J. D. Fletcher, A. Carrington, O. J. Taylor, S. M. Kazakov, and J. Karpinski, *Phys. Rev. Lett.* **95**, 097005 (2005).
- [75] F. Manzano, A. Carrington, N. E. Hussey, S. Lee, A. Yamamoto, and S. Tajima, *Phys. Rev. Lett.* **88**, 047002 (2002).
- [76] S. E. Sebastian, J. Gillett, N. Harrison, P. H. C. Lau, D. J. Singh, C. H. Mielke, and G. G. Lonzarich, *J. Phys.: Condens. Matter* **20**, 422203 (2008).
- [77] E. A. Yelland, J. Singleton, C. H. Mielke, N. Harrison, F. F. Balakirev, B. Dabrowski, and J. R. Cooper, *Phys. Rev. Lett.* **100**, 047003 (2008).
- [78] T. A. Olheiser, Z. Shi, D. D. Lawrie, R. W. Giannetta, and J. A. Schlueter, *Phys. Rev. B* **80**, 054519 (2009).
- [79] R. Prozorov, M. D. Vannette, G. D. Samolyuk, S. A. Law, S. L. Bud'ko, and P. C. Canfield, *Phys. Rev. B* **75**, 014413 (2007).
- [80] S. E. Sebastian, N. Harrison, C. H. Mielke, R. Liang, D. A. Bonn, W. N. Hardy, and G. G. Lonzarich, *Phys. Rev. Lett.* **103**, 256405 (2009).
- [81] E. Ohmichi, E. Komatsu, and T. Osada, *Rev. Sci. Instrum.* **75**, 2094 (2004).
- [82] W. A. Coniglio, L. E. Winter, K. Cho, C. C. Agosta, B. Fravel, and L. K. Montgomery, *Phys. Rev. B* **83**, 224507 (2011).
- [83] K. Cho, H. Kim, M. A. Tanatar, Y. J. Song, Y. S. Kwon, W. A. Coniglio, C. C. Agosta, A. Gurevich, and R. Prozorov, *Phys. Rev. B* **83**, 060502 (2011).
- [84] A. Carrington, R. W. Giannetta, J. T. Kim, and J. Giapintzakis, *Phys. Rev. B* **59**, R14173 (1999).
- [85] C. Mielke, J. Singleton, M.-S. Nam, N. Harrison, C. C. Agosta, B. Fravel, and L. K. Montgomery, *J. Phys.: Condens. Matter* **13**, 8325 (2001).
- [86] J. Singleton, C. de la Cruz, R. D. McDonald, S. Li, M. Altarawneh, P. Goddard, I. Franke, D. Rickel, C. H. Mielke, X. Yao, and P. Dai, *Phys. Rev. Lett.* **104**, 086403 (2010).

- [87] C. Boghosian, H. Meyer, and J. E. Rives, Phys. Rev. **146**, 110 (1966).
- [88] T. Coffey, Z. Bayindir, J. F. DeCarolis, M. Bennett, G. Esper, and C. C. Agosta, Rev. Sci. Instrum. **71**, 4600 (2000).
- [89] C. T. V. Degrift and D. P. Love, Rev. Sci. Instrum. **52**, 712 (1981).
- [90] M. M. Altarawneh, C. H. Mielke, and J. S. Brooks, Rev. Sci. Instrum. **80**, 066104 (2009).
- [91] F. Nasreen, K. Kothapalli, M. M. Altarawneh, H. Nakotte, N. Harrison, and E. Brck, J. Phys.: Conf. Ser. **273**, 012154 (2011).
- [92] M. M. Altarawneh, K. Collar, C. H. Mielke, N. Ni, S. L. Bud'ko, and P. C. Canfield, Phys. Rev. B **78**, 220505 (2008).
- [93] S. E. Sebastian, N. Harrison, P. A. Goddard, M. M. Altarawneh, C. H. Mielke, R. Liang, D. A. Bonn, W. N. Hardy, O. K. Andersen, and G. G. Lonzarich, Phys. Rev. B **81**, 214524 (2010).
- [94] S. E. Sebastian, N. Harrison, M. M. Altarawneh, R. Liang, D. A. Bonn, W. N. Hardy, and G. G. Lonzarich, Phys. Rev. B **81**, 140505 (2010).
- [95] T. Coffey, *Novel Metals, Magnets, and Measurements: The Critical Magnetic Field Phase Diagram of an Organic Conductor*, Ph.D. thesis, Clark University (2003).
- [96] B. Bleaney and B. Bleaney, *Electricity and Magnetism* (Oxford University Press, 1976).
- [97] J. Singleton, Rep. Prog. Phys. **63**, 1111 (2000).
- [98] G. J. Athas, J. S. Brooks, S. J. Klepper, S. Uji, and M. Tokumoto, Rev. Sci. Instrum. **64**, 3248 (1993).
- [99] M.-S. Nam, J. Singleton, A.-K. Klehe, W. Hayes, M. Kurmoo, and P. Day, Synth. Met. **103**, 2259 (1999), international Conference on Science and Technology of Synthetic Metals.
- [100] D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature **452**, 970 (2008).
- [101] M. Z. Hasan and C. L. Kane, Rev. Mod. Phys. **82**, 3045 (2010).
- [102] J. Orenstein and A. J. Millis, Science **288**, 468 (2000).
- [103] M.-H. Fang, H.-D. Wang, C.-H. Dong, Z.-J. Li, C.-M. Feng, J. Chen, and H. Q. Yuan, EPL (Europhysics Letters) **94**, 27009 (2011).
- [104] J. Singleton, C. Mielke, A. Migliori, G. Boebinger, and A. Lacerda, Physica B: Condensed Matter **346-347**, 614 (2004), proceedings of the 7th International Symposium on Research in High Magnetic Fields.
- [105] N. Suresh and J. L. Tallon, J. Phys.: Conf. Ser. **121**, 052004 (2008).

- [106] K. M. Purcell, D. Graf, M. Kano, J. Bourg, E. C. Palm, T. Murphy, R. McDonald, C. H. Mielke, M. M. Altarawneh, C. Petrovic, R. Hu, T. Ebihara, J. Cooley, P. Schlottmann, and S. W. Tozer, *Phys. Rev. B* **79**, 214428 (2009).
- [107] J. G. Analytis, R. D. McDonald, J.-H. Chu, S. C. Riggs, A. F. Bangura, C. Kucharczyk, M. Johannes, and I. R. Fisher, *Phys. Rev. B* **80**, 064507 (2009).
- [108] P. A. Goddard, J. Singleton, A. L. Lima Sharma, E. Morosan, S. J. Blundell, S. L. Bud'ko, and P. C. Canfield, *Phys. Rev. B* **75**, 094426 (2007).
- [109] J. G. Analytis, C. M. J. Andrew, A. I. Coldea, A. McCollam, J.-H. Chu, R. D. McDonald, I. R. Fisher, and A. Carrington, *Phys. Rev. Lett.* **103**, 076401 (2009).
- [110] J. Sims, A. Baca, G. Boebinger, H. Boenig, H. Coe, K. Kihara, M. Manzo, C. Mielke, J. Schillig, Y. Eyssa, B. Lesch, L. Li, and H. Schneider-Muntau, *IEEE T. Appl. Supercon.* **10**, 510 (2000).
- [111] C. Mielke and R. McDonald, 2006 IEEE international conference on Megagauss magnetic field generation and related topics , 227 (2006).
- [112] J. B. Hagen, *Radio-frequency Electronics: Circuits and Applications* (Cambridge University Press, 2009).
- [113] ST Microelectronics, *TDA0161 proximity detectoe specification*.
- [114] L. Drigo, F. Durantel, A. Audouard, and G. Ballon, *Eur. Phys. J. Appl. Phys.* **52** (2010).
- [115] W. Duffin, *Electricity and magnetism* (McGraw-Hill College, 1990).
- [116] J. Ekin, *Experimental techniques for low-temperature measurements: cryostat design, material properties, and superconductor critical-current testing* (Oxford University Press, USA, 2006).
- [117] J. Singleton, *Band theory and electronic properties of solids* (Oxford University Press, 2001).
- [118] J. de Launay, R. Dolecek, and R. Webber, *J. Phys. Chem. Solids* **11**, 37 (1959).
- [119] P. Kapitza, *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **123**, 292 (1929).
- [120] F. Fickett, *Proceedings of the Fourth International Conference on Magnet Technology*, Brookhaven National Laboratory, Upton, NY **539**, 539 (1972).
- [121] S. Ghannadzadeh, J. S. Möller, P. A. Goddard, T. Lancaster, F. Xiao, S. J. Blundell, A. Maisuradze, R. Khasanov, J. L. Manson, S. W. Tozer, D. Graf, and J. A. Schlueter, *Phys. Rev. B* **87**, 241102 (2013).
- [122] H. Okabe, N. Takeshita, M. Isobe, E. Takayama-Muromachi, T. Muranaka, and J. Akimitsu, *Phys. Rev. B* **84**, 115127 (2011).

- [123] A. Irizawa, S. Suga, G. Isoyama, K. Shimai, K. Sato, K. Iizuka, T. Nanba, A. Higashiya, S. Niitaka, and H. Takagi, Phys. Rev. B **84**, 235116 (2011).
- [124] D. Graf, R. Stillwell, T. P. Murphy, J.-H. Park, E. C. Palm, P. Schlottmann, R. D. McDonald, J. G. Analytis, I. R. Fisher, and S. W. Tozer, Phys. Rev. B **85**, 134503 (2012).
- [125] T. Park, F. Ronning, H. Q. Yuan, M. B. Salamon, R. Movshovich, J. L. Sarrao, and J. D. Thompson, Nature **440**, 65 (2006).
- [126] M. Mito, H. Deguchi, T. Tajiri, S. Takagi, M. Yamashita, and H. Miyasaka, Phys. Rev. B **72**, 144421 (2005).
- [127] A. Sieber, R. Bircher, O. Waldmann, G. Carver, G. Chaboussant, H. Mutka, and H.-U. Gdel, Angewandte Chemie **117**, 4311 (2005).
- [128] W. Fujita and K. Awaga, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals **341**, 389 (2000).
- [129] S. Scheiner and M. Cuma, J. Am. Chem. Soc. **118**, 1511 (1996).
- [130] Y. Ding, D. Haskel, Y.-C. Tseng, E. Kaneshita, M. van Veenendaal, J. F. Mitchell, S. V. Sinogeikin, V. Prakapenka, and H.-k. Mao, Phys. Rev. Lett. **102**, 237201 (2009).
- [131] A. Prescimone, C. Morien, D. Allan, J. A. Schlueter, S. W. Tozer, J. L. Manson, S. Parsons, E. K. Brechin, and S. Hill, Angew. Chem. Int. Ed. **51**, 7490 (2012).
- [132] H. A. Jahn and E. Teller, Proc. R. Soc. Lond. **161**, 220 (1937).
- [133] L. R. Falvello, J. Chem. Soc., Dalton Trans. **23**, 4463 (1997).
- [134] C. H. Wang, M. D. Lumsden, R. S. Fishman, G. Ehlers, T. Hong, W. Tian, H. Cao, A. Podlesnyak, C. Dunmars, J. A. Schlueter, J. L. Manson, and A. D. Christianson, Phys. Rev. B **86**, 064439 (2012).
- [135] J. Möller, *Muon-spin relaxation and its application in the study of molecular quantum magnets*, Ph.D. thesis, University of Oxford (2013).
- [136] G. J. Halder, K. W. Chapman, J. A. Schlueter, and J. L. Manson, Angew. Chem. Int. Ed. **50**, 419 (2011).
- [137] J. Dunitz and R. Ibberson, Angewandte Chemie International Edition **47**, 4208 (2008).
- [138] I. R. Walker, Rev. Sci. Instrum. **70**, 3402 (1999).
- [139] G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. **46**, 2774 (1975).
- [140] F. Datchi, A. Dewaele, P. Loubeyre, R. Letoullec, Y. Le Godec, and B. Canny, High Pressure Research **27**, 447 (2007).

- [141] J. C. Chervin, B. Canny, and M. Mancinelli, *High Pressure Research* **21**, 305 (2001).
- [142] N. Tateiwa and Y. Haga, *Review of Scientific Instruments* **80**, 123901 (2009).
- [143] K. Murata, K. Yokogawa, H. Yoshino, S. Klotz, P. Munsch, A. Irizawa, M. Nishiyama, K. Iizuka, T. Nanba, T. Okada, Y. Shiraga, and S. Aoyama, *Rev. Sci. Instrum.* **79**, 085101 (2008).
- [144] Y. Shu-Jie, C. Liang-Chen, and J. Chang-Qing, *Chin. Phys. Lett.* **26**, 096202 (2009).
- [145] G. J. Piermarini, S. Block, and J. Barnett, *J. Appl. Phys.* **44**, 5377 (1973).
- [146] K. Wierschem and P. Sengupta, *Journal of Physics: Conference Series* **400**, 032112 (2012).
- [147] J. C. Bonner and M. E. Fisher, *Phys. Rev.* **135**, A640 (1964).
- [148] D. C. Johnston, R. K. Kremer, M. Troyer, X. Wang, A. Klümper, S. L. Bud'ko, A. F. Panchula, and P. C. Canfield, *Phys. Rev. B* **61**, 9558 (2000).
- [149] M. Lines, *J. Phys. Chem. Solids* **31**, 101 (1970).
- [150] T. Giamarchi, *Quantum physics in one dimension* (Oxford University Press, 2004).
- [151] J. L. Musfeldt, Z. Liu, S. Li, J. Kang, C. Lee, P. Jena, J. L. Manson, J. A. Schlueter, G. L. Carr, and M.-H. Whangbo, *Inorg. Chem.* **50**, 6347 (2011).
- [152] C. Yasuda, S. Todo, K. Hukushima, F. Alet, M. Keller, M. Troyer, and H. Takayama, *Phys. Rev. Lett.* **94**, 217201 (2005).
- [153] H. J. Schulz, *Phys. Rev. Lett.* **77**, 2790 (1996).
- [154] P. Atkins, T. Overton, J. Rourke, M. Weller, and F. Armstrong, *Shriver and Atkins' Inorganic Chemistry*, 5th ed. (Oxford University Press, 2010) p. 475.
- [155] C. Dobe, T. Strässle, F. Juranyi, and P. L. W. Tregenna-Piggott, *Inorg. Chem.* **45**, 5066 (2006).
- [156] C. J. Simmons, M. A. Hitchman, H. Stratemeier, and A. J. Schultz, *J. Am. Chem. Soc.* **115**, 11304 (1993).
- [157] S. Carlson, Y. Xu, U. Hlenius, and R. Norrestam, *Inorganic Chemistry* **37**, 1486 (1998).
- [158] J. Rogiers and M. Tachiki, *Physica A: Statistical Mechanics and its Applications* **87**, 614 (1977).
- [159] M. Tachiki and T. Yamada, *J. Phys. Soc. Jpn.* **28**, 1413 (1970).
- [160] T. Giamarchi and A. M. Tsvelik, *Phys. Rev. B* **59**, 11398 (1999).

- [161] C. Ruegg, N. Cavadini, A. Furrer, H.-U. Gudel, K. Kramer, H. Mutka, A. Wildes, K. Habicht, and P. Vorderwisch, *Nature* **423**, 62 (2003).
- [162] T. M. Rice, *Science* **298**, 760 (2002).
- [163] S. Blundell, *Magnetism in Condensed Matter* (Oxford University Press, 2001).
- [164] A. Keren, L. P. Le, G. M. Luke, B. J. Sternlieb, W. D. Wu, Y. J. Uemura, S. Tajima, and S. Uchida, *Phys. Rev. B* **48**, 12926 (1993).
- [165] F. L. Pratt, S. J. Blundell, T. Lancaster, C. Baines, and S. Takagi, *Phys. Rev. Lett.* **96**, 247203 (2006).
- [166] B. Bleaney and K. D. Bowers, *Proc. R. Soc. Lond. A* **214**, 451 (1952).
- [167] O. Kahn, *Molecular magnetism* (VCH Publishers, Inc., 1993) p. 393.
- [168] S. E. Sebastian, P. Tanedo, P. A. Goddard, S.-C. Lee, A. Wilson, S. Kim, S. Cox, R. D. McDonald, S. Hill, N. Harrison, C. D. Batista, and I. R. Fisher, *Phys. Rev. B* **74**, 180401 (2006).
- [169] B. S. Conner, H. D. Zhou, Y. J. Jo, L. Balicas, C. R. Wiebe, J. P. Carlo, Y. J. Uemura, A. A. Aczel, T. J. Williams, and G. M. Luke, *Phys. Rev. B* **81**, 132401 (2010).
- [170] B. Wolf, Y. Tsui, D. Jaiswal-Nagar, U. Tutsch, A. Honecker, K. Remov-Langer, G. Hofmann, A. Prokofiev, W. Assmus, G. Donath, and M. Lang, *PNAS* **108**, 6862 (2011).
- [171] S. E. Sebastian, P. A. Sharma, M. Jaime, N. Harrison, V. Correa, L. Balicas, N. Kawashima, C. D. Batista, and I. R. Fisher, *Phys. Rev. B* **72**, 100404 (2005).
- [172] V. S. Zapf, D. Zocco, B. R. Hansen, M. Jaime, N. Harrison, C. D. Batista, M. Kenzelmann, C. Niedermayer, A. Lacerda, and A. Paduan-Filho, *Phys. Rev. Lett.* **96**, 077204 (2006).
- [173] T. Giamarchi, C. Ruegg, and O. Tchernyshyov, *Nat Phys* **4**, 198 (2008).
- [174] G. Chaboussant, M.-H. Julien, Y. Fagot-Revurat, M. Hanson, L. Lvy, C. Berthier, M. Horvatic, and O. Piovesana, *Eur. Phys. J. B* **6**, 167 (1998).
- [175] T. Nikuni, M. Oshikawa, A. Oosawa, and H. Tanaka, *Phys. Rev. Lett.* **84**, 5868 (2000).
- [176] R. Dell'Amore, A. Schilling, and K. Krämer, *Phys. Rev. B* **79**, 014438 (2009).
- [177] M. Clémancey, H. Mayaffre, C. Berthier, M. Horvatić, J.-B. Fouet, S. Miyahara, F. Mila, B. Chiari, and O. Piovesana, *Phys. Rev. Lett.* **97**, 167204 (2006).
- [178] J. Sirker, A. Weie, and O. P. Sushkov, *Europhys. Lett.* **68**, 275 (2004).

- [179] S. A. Zvyagin, J. Wosnitzer, C. D. Batista, M. Tsukamoto, N. Kawashima, J. Krzystek, V. S. Zapf, M. Jaime, N. F. Oliveira, and A. Paduan-Filho, *Phys. Rev. Lett.* **98**, 047205 (2007).
- [180] T. Radu, H. Wilhelm, V. Yushankhai, D. Kovrizhin, R. Coldea, Z. Tyliczynski, T. Lühmann, and F. Steglich, *Phys. Rev. Lett.* **95**, 127202 (2005).
- [181] R. Coldea, D. A. Tennant, K. Habicht, P. Smeibidl, C. Wolters, and Z. Tyliczynski, *Phys. Rev. Lett.* **88**, 137203 (2002).
- [182] S. Ghannadzadeh, J. D. Wright, F. R. Foronda, S. J. Blundell, S. J. Clarke, and P. A. Goddard, *Phys. Rev. B* **89**, 054502 (2014).
- [183] Y. Kamihara, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya, and H. Hosono, *J. Am. Chem. Soc.* **128**, 10012 (2006).
- [184] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, *J. Am. Chem. Soc.* **130**, 3296 (2008).
- [185] C. Wang, L. Li, S. Chi, Z. Zhu, Z. Ren, Y. Li, Y. Wang, X. Lin, Y. Luo, S. Jiang, X. Xu, G. Cao, and Z. Xu, *Europhys. Lett.* **83**, 67006 (2008).
- [186] A. A. Kordyuk, *Low Temp. Phys.* **38**, 888 (2012).
- [187] P. M. R. Brydon, M. Daghofer, C. Timm, and J. van den Brink, *Phys. Rev. B* **83**, 060501 (2011).
- [188] A. Chubukov, *Annu. Rev. Condens. Matter Phys.* **3**, 57 (2012).
- [189] V. G. Kogan and R. Prozorov, *Rep. Prog. Phys.* **75**, 114502 (2012).
- [190] A. Gurevich, *Phys. Rev. B* **67**, 184515 (2003).
- [191] A. Gurevich, *Physica C* **456**, 160 (2007).
- [192] D. R. Parker, M. J. Pitcher, P. J. Baker, I. Franke, T. Lancaster, S. J. Blundell, and S. J. Clarke, *Chem. Commun.*, 2189 (2009).
- [193] C. Chu, F. Chen, M. Gooch, A. Guloy, B. Lorenz, B. Lv, K. Sasmal, Z. Tang, J. Tapp, and Y. Xue, *Physica C* **469**, 326 (2009).
- [194] G. F. Chen, W. Z. Hu, J. L. Luo, and N. L. Wang, *Phys. Rev. Lett.* **102**, 227004 (2009).
- [195] S. Li, C. de la Cruz, Q. Huang, G. F. Chen, T.-L. Xia, J. L. Luo, N. L. Wang, and P. Dai, *Phys. Rev. B* **80**, 020504 (2009).
- [196] 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, *Nat Mater* **8**, 310 (2009).
- [197] C. Fang, H. Yao, W.-F. Tsai, J. Hu, and S. A. Kivelson, *Phys. Rev. B* **77**, 224509 (2008).

- [198] K. Kusakabe and A. Nakanishi, *J. Phys. Soc. Jpn.* **78**, 124712 (2009).
- [199] S. T. Cui, S. Y. Zhu, A. F. Wang, S. Kong, S. L. Ju, X. G. Luo, X. H. Chen, G. B. Zhang, and Z. Sun, *Phys. Rev. B* **86**, 155143 (2012).
- [200] 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, *Phys. Rev. Lett.* **104**, 057007 (2010).
- [201] J. D. Wright, T. Lancaster, I. Franke, A. J. Steele, J. S. Möller, M. J. Pitcher, A. J. Corkett, D. R. Parker, D. G. Free, F. L. Pratt, P. J. Baker, S. J. Clarke, and S. J. Blundell, *Phys. Rev. B* **85**, 054503 (2012).
- [202] A. F. Wang, X. G. Luo, Y. J. Yan, J. J. Ying, Z. J. Xiang, G. J. Ye, P. Cheng, Z. Y. Li, W. J. Hu, and X. H. Chen, *Phys. Rev. B* **85**, 224521 (2012).
- [203] G. Tan, P. Zheng, X. Wang, Y. Chen, X. Zhang, J. Luo, T. Netherton, Y. Song, P. Dai, C. Zhang, and S. Li, *Phys. Rev. B* **87**, 144512 (2013).
- [204] C. He, Y. Zhang, B. P. Xie, X. F. Wang, L. X. Yang, B. Zhou, F. Chen, M. Arita, K. Shimada, H. Namatame, M. Taniguchi, X. H. Chen, J. P. Hu, and D. L. Feng, *Phys. Rev. Lett.* **105**, 117002 (2010).
- [205] Z.-H. Liu, P. Richard, Y. Li, L.-L. Jia, G.-F. Chen, T.-L. Xia, D.-M. Wang, J.-B. He, H.-B. Yang, Z.-H. Pan, T. Valla, P. D. Johnson, N. Xu, H. Ding, and S.-C. Wang, *Appl. Phys. Lett.* **101**, 202601 (2012).
- [206] Z.-H. Liu, P. Richard, K. Nakayama, G.-F. Chen, S. Dong, J.-B. He, D.-M. Wang, T.-L. Xia, K. Umezawa, T. Kawahara, S. Souma, T. Sato, T. Takahashi, T. Qian, Y. Huang, N. Xu, Y. Shi, H. Ding, and S.-C. Wang, *Phys. Rev. B* **84**, 064519 (2011).
- [207] S. Deng, J. Köhler, and A. Simon, *Phys. Rev. B* **80**, 214508 (2009).
- [208] H.-M. Jiang, Z.-J. Yao, and F.-C. Zhang, *Europhys. Lett.* **100**, 47004 (2012).
- [209] V. K. Anand, H. Kim, M. A. Tanatar, R. Prozorov, and D. C. Johnston, *Phys. Rev. B* **87**, 224510 (2013).
- [210] G. Levy, R. Sutarto, D. Chevrier, T. Regier, R. Blyth, J. Geck, S. Wurmehl, L. Harnagea, H. Wadati, T. Mizokawa, I. S. Elfimov, A. Damascelli, and G. A. Sawatzky, *Phys. Rev. Lett.* **109**, 077001 (2012).
- [211] M. P. Allan, T.-M. Chuang, F. Massee, Y. Xie, N. Ni, S. L. Bud'ko, G. S. Boebinger, Q. Wang, D. S. Dessau, P. C. Canfield, M. S. Golden, and J. C. Davis, *Nat. Phys.* **9**, 220 (2013).
- [212] G. Prando, O. Vakaliuk, S. Sanna, G. Lamura, T. Shiroka, P. Bonfà, P. Carretta, R. De Renzi, H.-H. Klauss, C. G. F. Blum, S. Wurmehl, C. Hess, and B. Büchner, *Phys. Rev. B* **87**, 174519 (2013).
- [213] H. Suzuki, T. Yoshida, S. Ideta, G. Shibata, K. Ishigami, T. Kadono, A. Fujimori, M. Hashimoto, D. H. Lu, Z.-X. Shen, K. Ono, E. Sakai, H. Kumigashira, M. Matsuo, and T. Sasagawa, *Phys. Rev. B* **88**, 100501 (2013).

- [214] N. Spyrisson, M. A. Tanatar, K. Cho, Y. Song, P. Dai, C. Zhang, and R. Prozorov, *Phys. Rev. B* **86**, 144528 (2012).
- [215] G. Blatter, M. V. Feigel'man, V. B. Geshkenbein, A. I. Larkin, and V. M. Vinokur, *Rev. Mod. Phys.* **66**, 1125 (1994).
- [216] F. Hunte, J. Jaroszynski, A. Gurevich, D. C. Larbalestier, R. Jin, A. S. Sefat, M. A. McGuire, B. C. Sales, D. K. Christen, and D. Mandrus, *Nature* **453**, 903 (2008).
- [217] J. Kim, N. Haberkorn, K. Gofryk, M. J. Graf, L. Civale, F. Ronning, A. S. Sefat, and R. Movshovich, *arXiv e-prints* (2013), arXiv:1302.0074 .
- [218] B. S. Chandrasekhar, *Appl. Phys. Lett.* **1**, 7 (1962).
- [219] A. M. Clogston, *Phys. Rev. Lett.* **9**, 266 (1962).
- [220] Y. Matsuda and H. Shimahara, *J. Phys. Soc. Jpn.* **76**, 051005 (2007).
- [221] F. Zuo, J. S. Brooks, R. H. McKenzie, J. A. Schlueter, and J. M. Williams, *Phys. Rev. B* **61**, 750 (2000).
- [222] L. N. Cooper, *Phys. Rev. Lett.* **8**, 367 (1962).
- [223] L. P. Gor'kov, *Soviet Journal of Experimental and Theoretical Physics* **21**, 1186 (1965).
- [224] P. W. Anderson, *Phys. Rev. Lett.* **3**, 325 (1959).
- [225] R. A. Ferrell, *Phys. Rev. Lett.* **3**, 262 (1959).
- [226] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, *Phys. Rev.* **147**, 295 (1966).
- [227] G. Cody, *Proceedings of the 1968 Summer Study on Superconducting Devices and Accelerators* **2**, 405 (1968).
- [228] K. Maki, *Phys. Rev.* **148**, 362 (1966).
- [229] G. Fuchs *et al.*, *New Journal of Physics* **11**, 075007 (2009).
- [230] M. Rasolt and Z. Tesanović, *Rev. Mod. Phys.* **64**, 709 (1992).
- [231] J. Singleton, P. A. Goddard, A. Ardavan, A. I. Coldea, S. J. Blundell, R. D. McDonald, S. Tozer, and J. A. Schlueter, *Phys. Rev. Lett.* **99**, 027004 (2007).
- [232] J. Singleton and C. Mielke, *Contemporary Physics* **43**, 63 (2002).
- [233] M.-S. Nam, J. A. Symington, J. Singleton, S. J. Blundell, A. Ardavan, J. A. A. J. Perenboom, M. Kurmoo, and P. Day, *J. Phys.: Condens. Matter* **11**, L477 (1999).
- [234] H.-S. Lee, M. Bartkowiak, J.-H. Park, J.-Y. Lee, J.-Y. Kim, N.-H. Sung, B. K. Cho, C.-U. Jung, J. S. Kim, and H.-J. Lee, *Phys. Rev. B* **80**, 144512 (2009).

- [235] F. Weickert, M. Nicklas, W. Schnelle, J. Wosnitza, A. Leithe-Jasper, and H. Rosner, *J. Appl. Phys.* **110**, 123906 (2011).
- [236] K. Haule, J. H. Shim, and G. Kotliar, *Phys. Rev. Lett.* **100**, 226402 (2008).
- [237] A. G. Lebed, *Pisma Zh. Eksp. Teor. Fiz.* **44**, 89 (1986), [*JETP Lett.* 44, 144 (1986)].
- [238] N. Dupuis, G. Montambaux, and C. A. R. Sá de Melo, *Phys. Rev. Lett.* **70**, 2613 (1993).
- [239] R. A. Klemm, A. Luther, and M. R. Beasley, *Phys. Rev. B* **12**, 877 (1975).
- [240] J. Jaroszynski, F. Hunte, L. Balicas, Y.-j. Jo, I. Raičević, A. Gurevich, D. C. Larbalestier, F. F. Balakirev, L. Fang, P. Cheng, Y. Jia, and H. H. Wen, *Phys. Rev. B* **78**, 174523 (2008).
- [241] T. Dahm and N. Schopohl, *Phys. Rev. Lett.* **91**, 017001 (2003).
- [242] C. Zhang, H.-F. Li, Y. Song, Y. Su, G. Tan, T. Netherton, C. Redding, S. V. Carr, O. Sobolev, A. Schneidewind, E. Faulhaber, L. W. Harriger, S. Li, X. Lu, D.-X. Yao, T. Das, A. V. Balatsky, T. Brückel, J. W. Lynn, and P. Dai, *Phys. Rev. B* **88**, 064504 (2013).
- [243] P. Fulde and R. A. Ferrell, *Phys. Rev.* **135**, A550 (1964).
- [244] A. Larkin and Y. Ovchinnikov, *Zh. Eksp. Teor. Fiz.* **47**, 1136 (1964).
- [245] R. Lortz, Y. Wang, A. Demuer, P. H. M. Böttger, B. Bergk, G. Zwicknagl, Y. Nakazawa, and J. Wosnitza, *Phys. Rev. Lett.* **99**, 187002 (2007).
- [246] T. Okada, H. Takahashi, Y. Imai, K. Kitagawa, K. Matsubayashi, Y. Uwatoko, and A. Maeda, *Phys. Rev. B* **86**, 064516 (2012).
- [247] A. Gurevich, *Phys. Rev. B* **82**, 184504 (2010).
- [248] S. Khim, B. Lee, J. W. Kim, E. S. Choi, G. R. Stewart, and K. H. Kim, *Phys. Rev. B* **84**, 104502 (2011).
- [249] H. Q. Yuan, J. Singleton, F. F. Balakirev, S. A. Baily, G. F. Chen, J. L. Luo, and N. L. Wang, *Nature* **457**, 565 (2009).
- [250] S. Khim, J. S. Kim, J. W. Kim, S. H. Lee, F. Balakirev, Y. Bang, and K. H. Kim, *Physica C* **470**, S317 (2010).
- [251] A. Pérez-González, *Phys. Rev. B* **54**, 16053 (1996).
- [252] M. Schossmann and J. P. Carbotte, *Phys. Rev. B* **39**, 4210 (1989).
- [253] J. P. Carbotte, *Rev. Mod. Phys.* **62**, 1027 (1990).
- [254] R. M. Fernandes, L. H. VanBebber, S. Bhattacharya, P. Chandra, V. Keppens, D. Mandrus, M. A. McGuire, B. C. Sales, A. S. Sefat, and J. Schmalian, *Phys. Rev. Lett.* **105**, 157003 (2010).

- [255] R. Hu, E. D. Mun, M. M. Altarawneh, C. H. Mielke, V. S. Zapf, S. L. Bud'ko, and P. C. Canfield, *Phys. Rev. B* **85**, 064511 (2012).
- [256] J. L. Zhang, L. Jiao, F. F. Balakirev, X. C. Wang, C. Q. Jin, and H. Q. Yuan, *Phys. Rev. B* **83**, 174506 (2011).
- [257] E. Mun, N. Ni, J. M. Allred, R. J. Cava, O. Ayala, R. D. McDonald, N. Harrison, and V. S. Zapf, *Phys. Rev. B* **85**, 100502 (2012).
- [258] T. Schneider and A. Schmidt, *Phys. Rev. B* **47**, 5915 (1993).
- [259] *Remanent Fields in MPMS Superconducting Magnets*, Quantum Design USA, 1st ed. (2001).
- [260] S. Oh, A. M. Mounce, J. A. Lee, W. P. Halperin, C. L. Zhang, S. Carr, and P. Dai, *Phys. Rev. B* **87**, 174517 (2013).
- [261] J. L. Tallon, J. W. Loram, J. R. Cooper, C. Panagopoulos, and C. Bernhard, *Phys. Rev. B* **68**, 180501 (2003).
- [262] R. T. Gordon, H. Kim, N. Salovich, R. W. Giannetta, R. M. Fernandes, V. G. Kogan, T. Prozorov, S. L. Bud'ko, P. C. Canfield, M. A. Tanatar, and R. Prozorov, *Phys. Rev. B* **82**, 054507 (2010).
- [263] R. Prozorov and V. G. Kogan, *Rep. Prog. Phys.* **74**, 124505 (2011).
- [264] L. Luan, T. M. Lippman, C. W. Hicks, J. A. Bert, O. M. Auslaender, J.-H. Chu, J. G. Analytis, I. R. Fisher, and K. A. Moler, *Phys. Rev. Lett.* **106**, 067001 (2011).
- [265] A. B. Vorontsov, M. G. Vavilov, and A. V. Chubukov, *Phys. Rev. B* **79**, 140507 (2009).
- [266] E. H. Brandt, *Phys. Rev. B* **60**, 11939 (1999).
- [267] T. Lancaster, S. J. Blundell, and F. L. Pratt, *Physica Scripta* **88**, 068506 (2013).
- [268] M. Imada, A. Fujimori, and Y. Tokura, *Rev. Mod. Phys.* **70**, 1039 (1998).
- [269] Charles Mielke, National High Magnetic Field Laboratory, USA, *private communication*.
- [270] D. E. Graf, R. L. Stillwell, K. M. Purcell, and S. W. Tozer, *High Pressure Research* **31**, 533 (2011).