#### MUON SPIN ROTATION STUDIES OF URU<sub>2</sub>SI<sub>2</sub> AND DICHALCOGENIDE SUPERCONDUCTORS

# MUON SPIN ROTATION STUDIES OF $URU_2SI_2$ AND DICHALCOGENIDE SUPERCONDUCTORS

MURRAY NEFF WILSON, B.Sc., M.Sc.

A Thesis Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy

> McMaster University ©Copyright by Murray Neff Wilson, 2017.

DOCTOR OF PHILOSOPHY (2017) (Physics)

McMaster University Hamilton, Ontario

TITLE: Muon spin rotation studies of URu<sub>2</sub>Si<sub>2</sub> and dichalcogenide superconductors AUTHOR: Murray Neff Wilson, B.Sc., M.Sc. SUPERVISOR: Dr. Graeme Luke NUMBER OF PAGES: xi, 115

### Abstract

This dissertation details studies of two different material classes: isoelectronically doped  $URu_2Si_2$ , and dichalcogenide superconductors, both of which are primarily studied with the muon spin rotation ( $\mu$ SR) experimental technique.

The objective of the work on URu<sub>2</sub>Si<sub>2</sub> was to probe how the low temperature "hidden order" state, which transitions into antiferromagnetism under hydrostatic pressure, evolves when perturbed by isoelectronic chemical doping.  $\mu$ SR measurements of iron doped URu<sub>2</sub>Si<sub>2</sub>, which produces positive chemical pressure, show long range magnetic order. Neutron diffraction measurements demonstrate that this magnetic order is antiferromagnetism, and both muon spin rotation and neutron scattering suggest that the magnetic moment increases with increasing doping in contrast to the pressure independent moment seen in the pressure induced antiferromagnetic state of URu<sub>2</sub>Si<sub>2</sub>. Inelastic neutron scattering measurements show a significantly larger commensurate gap at the (1 0 0) position compared to that seen in the pressure induced antiferromagnetic phase. Osmium doping, which gives negative effective chemical pressure, shows similar behaviour in  $\mu$ SR measurements to the iron doped samples. This suggests that these samples are also antiferromagnetic and that the evolution from hidden order to antiferromagnetism is not solely caused by changes in the lattice size. This is further supported by  $\mu$ SR measurements on germanium doped samples that do not show magnetic order despite giving similar negative chemical pressure to the osmium doped samples.

Work on the dichalcogenide superconductors involved using transverse field  $\mu$ SR to measure the temperature dependence of the magnetic penetration depth of two different materials, Pt<sub>0.05</sub>Ir<sub>0.95</sub>Te<sub>2</sub> and PbTaSe<sub>2</sub>. The  $\mu$ SR data on Pt<sub>0.05</sub>Ir<sub>0.95</sub>Te<sub>2</sub> were supplemented by magnetometry measurements of the penetration depth. Zero field  $\mu$ SR measurements were also performed on PbTaSe<sub>2</sub>, and rule out any time reversal symmetry breaking field greater than 0.05 G. These measurements all suggest that both materials are fully gapped superconductors.

## Acknowledgements

During my research they are numerous people who have provided invaluable assistance, without whom much of the work would not have been completed.

I would first like to thank my supervisor, Graeme Luke, for providing a wonderful environment at McMaster. His willingness to allow me to explore my own scientific paths while providing quick feedback on ideas played a large role in making my PhD an enjoyable experience. The immense array of collaborations with other groups also opened up many doors to valuable opportunities for me to learn new skills.

To Travis Williams: thank you for helping my hit the ground running when I arrived at McMaster and for the continued collaboration through my degree. Having a ready-made project dropped in my lap immediately on arriving made for a very productive first two years.

There were also many other graduate students I would like to thank. Tim Munsie: thank you for initiating me on the muon spin rotation technique, helping keep the group organized, and in particular, dealing with the nonsense of our SQUID so that I didn't have to. Your absence has certainly been noticed since you graduated. Alannah Hallas, it was wonderful to have a friend in the group coming through all stages of our studies together. You have certainly helped make this a memorable experience. To Yipeng Cai, our frequent heated discussions often exposed scientific points about which I was less sure than I had thought. Thank you for helping clear these up, and learning the lesson to never be overconfident in my own knowledge. Finally, to James Beare, Casey Marjerrison, Connor Buhariwalla, and all the many others whom I have not the time to name, thank you for all your help and for making the McMaster physics department such a welcoming environment.

My research would have been much more difficult without the assistance of numerous technicians and beamline scientists. I would first like to thank all of the staff at TRIUMF; particularly Bassam Hitti, Gerald Morris, and Donald Arsenault. I admire your dedication to helping any users of the  $\mu$ SR facilities at TRIUMF. Having such knowledgeable people available to ask for help, even at late hours and on the weekend, is a wonderful resource, not to mention all of the work that goes on behind the scenes keeping all of the instruments running in tip-top shape. To Adam Aczel, Matthew Stone, and the other staff at Oak Ridge National Lab, thank you for giving such great help to allow even less experienced people like myself perform successful neutron scattering experiments. I would also like to thank Paul Dube and Jim Garret at McMaster for their invaluable assistance in many aspects of my research.

## Contents

1	Intr	roduction	1	
	1.1	Superconductivity	1	
	1.2	Heavy Fermions	10	
	1.3	$\mathrm{URu}_2\mathrm{Si}_2$	12	
		1.3.1 Symmetry Breaking	14	
		1.3.2 Pressure	16	
		1.3.3 Doping effects	17	
	1.4	Dichalcogenides	21	
		1.4.1 $IrTe_2 \dots \dots$	22	
		1.4.2 $PbTaSe_2 \dots \dots$	25	
2	Exp	perimental Methods	29	
	2.1	Crystal Growth	29	
	2.2	SQUID Magnetometry	34	
	2.3	Muon Spin Rotation	37	
	2.4	Neutron Scattering	42	
3	UR	$\mathbf{u}_2 \mathbf{Si}_2$	48	
	3.1	Summary of Publication I: $\mu$ SR studies of Fe and Os doped URu <sub>2</sub> Si <sub>2</sub>	48	
	3.2	Summary of Publication II: Neutron scattering studies of Fe doped $URu_2Si_2$	60	
	3.3	Comparison of iron doping results with recent literature	71	
	3.4	$\mu$ SR studies of Ge-doped URu <sub>2</sub> Si <sub>2</sub>	72	
		3.4.1 Contributions to this work	79	
4	Dic	halcogenide Superconductors	80	
	4.1	Summary of Publication III: $Ir_{0.95}Pt_{0.05}Te_2$	80	
	4.2	Summary of Publication IV: $PbTaSe_2$	88	
5	Conclusions and Future Directions			
	5.1	$\mathrm{URu}_2\mathrm{Si}_2$	98	
		5.1.1 Conclusions on various dopings	98	
		5.1.2 Future Directions	99	

#### CONTENTS

5.2	Dichal	lcogenides	100
	5.2.1	Conclusions	100
	5.2.2	Future Directions	101

## List of Figures

1.1	(a) Resistance vs. temperature graph for mercury cooled into the superconducting	
	state [5]. (b) Typical magnetic susceptibility as a function of temperature for a	
	superconductor	2
1.2	Specific heat as a function of temperature in arbitrary units for the normal metallic	
	state (black solid line) and the superconducting state (red dashed line)	3
1.3	Characteristic triangular vortex lattice for a superconductor. The black circles show	
	the vortex cores, and the colours show the field strength outside the cores ranging	
	from high fields (red) through low fields (blue).	5
1.4	Magnetization as a function of temperature for a Type I (black solid line) and Type II	
	(red dashed line) superconductor. The thermodynamic $(H_c)$ , lower $(H_{c1})$ and upper	
	$(H_{c2})$ critical fields are shown by the location of the arrows.	6
1.5	Temperature dependence of the superconducting gap, $\Delta$ , normalized to the value	
	at zero temperature, $\Delta_0$ . The black curve is the true BCS temperature dependence	
	given by the equation	7
1.6	Temperature dependence of the superconducting fluid density for an s-wave super-	
	conductor (black), typical d-wave superconductor (blue), and nonmonotonic d-wave	
	(red). Figure taken from Ref. [21].	9
1.7	Temperature dependence of the superfluid density for three different multi-band	
	superconductors. (a) Data for $BaFe_2As_2$ taken from Ref. [24]. (b) MgB <sub>2</sub> data taken	
	from Ref. [32]. (c) Data for NbSe <sub>2</sub> from Ref. [33]. $\ldots$ $\ldots$ $\ldots$	10
1.8	Crystal structure of URu <sub>2</sub> Si <sub>2</sub> . Yellow atoms are uranium, blue are ruthenium, and	
	grey are silicon	13
1.9	Specific heat of URu <sub>2</sub> Si <sub>2</sub> divided by temperature $(T)$ plotted versus $T^2$ (top) to give	
	the linear slope and intercept representing $\gamma$ and $\Theta_D$ , and versus T (bottom) showing	
	the two transitions that occur at 1.1 K and 17.5 K. Reproduced from Ref. [45]	14
1.10	Magnetic susceptibility of $URu_2Si_2$ plotted as a function of temperature in a field of	
	2 T applied parallel to the c-axis or a-axis as indicated on the graph. Reproduced	
	from Ref. [45]	15
1.11	Pressure-temperature phase diagram of $URu_2Si_2$ . Reproduced from Ref. [75]	17

1.12	Periodic table summarizing the various dopings that have been performed on $URu_2Si_2$	
	and their dominant effects. The background color of each cell shows which site the	
	atom has been doped onto: yellow for the uranium site, blue for the ruthenium site,	
	grey for the silicon site, and white if it has not been studied. The symbol colour	
	shows what magnetic state arises with doping: green for antiferromagnetism, red	
	for ferromagnetism, blue for remaining hidden order, and black for cases that are	
	unknown, unclear, or enter some other state. The arrows show whether the transition	
	temperature increases with doping (upwards pointing arrow), decreases (downwards	
	arrow), or stays mostly unchanged (horizontal dashed line)	18
1.13	(i) Temperature-doping phase diagram for iron doping on the ruthenium site of	
	$URu_2Si_2$ . (a) shows the phase diagram measured by resistivity, magnetization, and	
	specific heat. (b) shows the residual resistivity ratio of the samples. Reproduced	
	from Ref. [102] (ii) Temperature-doping phase diagram for osmium doping on the	
	ruthenium site of $URu_2Si_2$ measured by magnetization, resistivity, and specific heat.	
	Reproduced from Ref. [103]	20
1.14	IrTe <sub>2</sub> $P\bar{3}m1$ crystal structure. Blue atoms are tellurium and red atoms are iridium.	
	(a) Looking along the c-axis showing the triangular arrangement of iridium atoms in	
	the plane. (b) Looking along the ab direction showing the separation of neighbouring	
	planes	23
1.15	Doping-temperature phase diagram for $Pt_x Ir_{1-x} Te_2$ . Trigonal denotes the $P\bar{3}m1$	
	phase, Monoclinic denotes the $C2/m$ phase, and SC denotes the superconducting	
	state. Closed squares show the CDW transition measured on warming, while open	
	squares show the CDW transition on cooling. Circles show the superconducting	
	transition measured by specific heat. Figure reproduced from Ref. [130]	24
1.16	Structure of $TaSe_2$ ((b) and (d)) and $PbTaSe_2$ ((a) and (c)). (a) and (b) show the	
	structures looking down the c-axis, while (c) and (d) show the structures looking	
	along the planes perpendicular to the c-axis. Green atoms are selenium, brown atoms	
	are tantalum, and dark grey atoms are lead	26
2.1	Picture of the tri-arc furnace during the growth of a crystal. This picture shows the	
	bright molten sample sitting on the copper hearth, the stingers producing electrical	

arcs to heat the sample, and the rotating seed rod pulling the crystal out of the melt. 30

2.2	Schematic of the Czochralski crystal growth process. (a) shows the crystal being	
	drawn out of the melt. The blue area represents the molybdenum seed rod that the	
	material initially solidifies on. The gray represents the crystal that is being grown,	
	with the black lines indicating boundaries between different crystal grains. The red	
	region shows where the melt is solidifying to form the crystal, and the orange shows	
	the molten material. (b) shows the crystal after separating from the melt.	33
2.3	$URu_{1.6}Os_{0.4}Si_2$ crystal grown using the tri-arc furnace.	34
2.4	Schematic of a DC squid showing the two Josephson junctions in blue, with a bias	
	current of $I$ , flux through the loop of $\Phi$ , and voltage across the device of $V$	35
2.5	Schematic of the second order gradiometer setup found in our magnetometer. The	
	pickup loops are shown in black and create a field through an rf SQUID with a single	
	Josephson junction. The sample, in red, is contained inside a plastic straw which is	
	non-magnetic, and is swept through the pickup coils by a motor that is connected to	
	the straw by a long non-magnetic rod.	36
2.6	Coherent neutron scattering length for many nuclei. All data is taken from Ref. [163].	43
2.7	Schematic of a triple axis neutron spectrometer. The neutron path is shown in red	45
3.1	Magnetization (a) and derivitive of magnetization with respect to temperature $dM/dT$	
3.1	Magnetization (a) and derivitive of magnetization with respect to temperature $dM/dT$ (b) for URu <sub>2</sub> Si <sub>2-x</sub> Ge <sub>x</sub> with doping levels of x = 0 (green), x = 0.1 (black), x = 0.2	
3.1	Magnetization (a) and derivitive of magnetization with respect to temperature $dM/dT$ (b) for URu <sub>2</sub> Si <sub>2-x</sub> Ge <sub>x</sub> with doping levels of $x = 0$ (green), $x = 0.1$ (black), $x = 0.2$ (blue) and $x = 0.35$ (red). All measurements were performed on warming, after cooling	
3.1	Magnetization (a) and derivitive of magnetization with respect to temperature $dM/dT$ (b) for URu <sub>2</sub> Si <sub>2-x</sub> Ge <sub>x</sub> with doping levels of $x = 0$ (green), $x = 0.1$ (black), $x = 0.2$ (blue) and $x = 0.35$ (red). All measurements were performed on warming, after cooling in zero applied magnetic field and applying a field of 1000 Oe at 2 K. Temperature	
3.1	Magnetization (a) and derivitive of magnetization with respect to temperature $dM/dT$ (b) for URu <sub>2</sub> Si <sub>2-x</sub> Ge <sub>x</sub> with doping levels of x = 0 (green), x = 0.1 (black), x = 0.2 (blue) and x = 0.35 (red). All measurements were performed on warming, after cooling in zero applied magnetic field and applying a field of 1000 Oe at 2 K. Temperature values with arrows on (b) show the transition temperatures inferred based on the	
3.1	Magnetization (a) and derivitive of magnetization with respect to temperature $dM/dT$ (b) for URu <sub>2</sub> Si <sub>2-x</sub> Ge <sub>x</sub> with doping levels of $x = 0$ (green), $x = 0.1$ (black), $x = 0.2$ (blue) and $x = 0.35$ (red). All measurements were performed on warming, after cooling in zero applied magnetic field and applying a field of 1000 Oe at 2 K. Temperature values with arrows on (b) show the transition temperatures inferred based on the dM/dT data.	74
3.1 3.2	Magnetization (a) and derivitive of magnetization with respect to temperature $dM/dT$ (b) for URu <sub>2</sub> Si <sub>2-x</sub> Ge <sub>x</sub> with doping levels of $x = 0$ (green), $x = 0.1$ (black), $x = 0.2$ (blue) and $x = 0.35$ (red). All measurements were performed on warming, after cooling in zero applied magnetic field and applying a field of 1000 Oe at 2 K. Temperature values with arrows on (b) show the transition temperatures inferred based on the dM/dT data	74
3.1 3.2	Magnetization (a) and derivitive of magnetization with respect to temperature $dM/dT$ (b) for URu <sub>2</sub> Si <sub>2-x</sub> Ge <sub>x</sub> with doping levels of $x = 0$ (green), $x = 0.1$ (black), $x = 0.2$ (blue) and $x = 0.35$ (red). All measurements were performed on warming, after cooling in zero applied magnetic field and applying a field of 1000 Oe at 2 K. Temperature values with arrows on (b) show the transition temperatures inferred based on the dM/dT data	74
3.1 3.2	Magnetization (a) and derivitive of magnetization with respect to temperature $dM/dT$ (b) for URu <sub>2</sub> Si <sub>2-x</sub> Ge <sub>x</sub> with doping levels of $x = 0$ (green), $x = 0.1$ (black), $x = 0.2$ (blue) and $x = 0.35$ (red). All measurements were performed on warming, after cooling in zero applied magnetic field and applying a field of 1000 Oe at 2 K. Temperature values with arrows on (b) show the transition temperatures inferred based on the dM/dT data	74
3.1 3.2	Magnetization (a) and derivitive of magnetization with respect to temperature $dM/dT$ (b) for URu <sub>2</sub> Si <sub>2-x</sub> Ge <sub>x</sub> with doping levels of $x = 0$ (green), $x = 0.1$ (black), $x = 0.2$ (blue) and $x = 0.35$ (red). All measurements were performed on warming, after cooling in zero applied magnetic field and applying a field of 1000 Oe at 2 K. Temperature values with arrows on (b) show the transition temperatures inferred based on the dM/dT data	74 75
3.1 3.2 3.3	Magnetization (a) and derivitive of magnetization with respect to temperature $dM/dT$ (b) for URu <sub>2</sub> Si <sub>2-x</sub> Ge <sub>x</sub> with doping levels of $x = 0$ (green), $x = 0.1$ (black), $x = 0.2$ (blue) and $x = 0.35$ (red). All measurements were performed on warming, after cooling in zero applied magnetic field and applying a field of 1000 Oe at 2 K. Temperature values with arrows on (b) show the transition temperatures inferred based on the dM/dT data	74 75
<ul><li>3.1</li><li>3.2</li><li>3.3</li></ul>	Magnetization (a) and derivitive of magnetization with respect to temperature $dM/dT$ (b) for URu <sub>2</sub> Si <sub>2-x</sub> Ge <sub>x</sub> with doping levels of x = 0 (green), x = 0.1 (black), x = 0.2 (blue) and x = 0.35 (red). All measurements were performed on warming, after cooling in zero applied magnetic field and applying a field of 1000 Oe at 2 K. Temperature values with arrows on (b) show the transition temperatures inferred based on the dM/dT data	74 75
<ul><li>3.1</li><li>3.2</li><li>3.3</li></ul>	Magnetization (a) and derivitive of magnetization with respect to temperature $dM/dT$ (b) for URu <sub>2</sub> Si <sub>2-x</sub> Ge <sub>x</sub> with doping levels of $x = 0$ (green), $x = 0.1$ (black), $x = 0.2$ (blue) and $x = 0.35$ (red). All measurements were performed on warming, after cooling in zero applied magnetic field and applying a field of 1000 Oe at 2 K. Temperature values with arrows on (b) show the transition temperatures inferred based on the dM/dT data	74 75
<ul><li>3.1</li><li>3.2</li><li>3.3</li></ul>	Magnetization (a) and derivitive of magnetization with respect to temperature $dM/dT$ (b) for URu <sub>2</sub> Si <sub>2-x</sub> Ge <sub>x</sub> with doping levels of $x = 0$ (green), $x = 0.1$ (black), $x = 0.2$ (blue) and $x = 0.35$ (red). All measurements were performed on warming, after cooling in zero applied magnetic field and applying a field of 1000 Oe at 2 K. Temperature values with arrows on (b) show the transition temperatures inferred based on the dM/dT data	74 75
<ul><li>3.1</li><li>3.2</li><li>3.3</li></ul>	Magnetization (a) and derivitive of magnetization with respect to temperature $dM/dT$ (b) for URu <sub>2</sub> Si <sub>2-x</sub> Ge <sub>x</sub> with doping levels of $x = 0$ (green), $x = 0.1$ (black), $x = 0.2$ (blue) and $x = 0.35$ (red). All measurements were performed on warming, after cooling in zero applied magnetic field and applying a field of 1000 Oe at 2 K. Temperature values with arrows on (b) show the transition temperatures inferred based on the dM/dT data	74

3.4	Relaxation rate, $\lambda,$ extracted from fits of the $\mu {\rm SR}$ data in Fig. 3.3 to equation 3.1	77
3.5	Transition temperature, $T_N$ for the transition into antiferromagnetism, or $T_{HO}$ for the	
	transition into hidden order, plotted against the peak in the magnetization, $T_p$ . This	
	data is plotted for pure $URu_2Si_2$ (orange star), iron doping (red squares), osmium	
	doping (blue circles), germanium doping (black diamonds), and rhodium doping	
	taken from Ref. [176] (green triangles). $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$ $\ldots$	79

### Preface

This is a sandwich thesis containing four published articles and unpublished work in Section 3.4. A general introduction to the subject area is provided along with a summary of each publication. Aside from Section 3.4 all original research is contained within the publications themselves.

Publication I: "Antiferromagnetism and Hidden Order in Isoelectronic Doping of URu<sub>2</sub>Si<sub>2</sub>", M.
N. Wilson, T. J. Williams, Y.-P. Cai, A. M. Hallas, T. Medina, T. J. Munsie, S. C. Cheung, B. A. Frandsen, L. Liu, Y. J. Uemura, and G. M. Luke. Physical Review B 93, 064402 (2016).
Reproduced from Ref. [1] with permission, copyrighted by the American Physical Society.

**Publication II**: "Hidden order signatures in the antiferromagnetic phase of  $U(Ru_{1-x}Fe_x)_2Si_2$ ", T. J. Williams, A. A. Aczel, M. N. Stone, M. N. Wilson, and G. M. Luke. Physical Review B **95**, 104440 (2017).

Reproduced from Ref. [2] with permission, copyrighted by the American Physical Society.

Publication III: "µSR and magnetometry study of superconducting 5% Pt-doped IrTe<sub>2</sub>", M. N.
Wilson, T. Medina, T. J. Munsie, S. C. Cheung, B. A. Frandsen, L. Liu, J. Yan, D. Mandrus, Y. J. Uemura, and G. M. Luke. Physical Review B 94, 184504 (2016).
Reproduced from Ref. [3] with permission, copyrighted by the American Physical Society.

Publication IV: "µSR study of the noncentrosymmetric superconductor PbTaSe<sub>2</sub>", M. N. Wilson, A. M. Hallas, Y. Cai, S. Guo, Z. Gong, R. Sankar, F. C. Chou, Y. J. Uemura, and G. M. Luke. Physical Review B 95, 224506 (2017).

Reproduced from Ref. [4] with permission, copyrighted by the American Physical Society.

The following publication represents collaborative work where I did not play a leading role, and therefore I do not include it as part of my thesis. However, as it is on a research area very similar to my thesis topic, I include it here for reference.

Publication V: "Electrodynamics of the antiferromagnetic phase in URu<sub>2</sub>Si<sub>2</sub>", Jesse S. Hall, M. Rahimi Movassagh, M. N. Wilson, G. M. Luke, N. Kanchanavatee, K. Huang, M. Janoschek, M. B. Maple, and T. Timusk. Physical Review B 92, 195111 (2015).

Chapter \_

## Introduction

#### 1.1 Superconductivity

Superconductivity is an emergent phenomena that has fascinated physicists since it was first discovered in 1911 [5]. The most striking feature of this state is that the direct current resistivity is zero at low temperature, and there is no further barrier to current flow. Currents set up in superconductors have been shown to persist for years without measurable change, putting a limit on the resistivity of less than  $10^{-21} \Omega$ -cm [6]. This extremely low resistivity gives the potential for useful applications in magnet technology and power transmission to substantially reduce wasted energy. Currently, superconductors are widely used for high field magnets in such applications as magnetic resonance imaging machines, particle accelerators, and physics laboratories, but the lack of superconductors that work at room temperature limits the possible application to power transmission for the time being. The continued search for better understanding of the mechanisms behind superconductivity in order to hopefully unlock the secret of higher temperature superconductors ensures that this will be an active research research area for the foreseeable future.

Superconductivity manifests as a sharp drop in the resistivity of a material below the critical temperature,  $T_C$ , as shown in Fig. 1.1 (a). For pure superconductors, this drop happens over a very small temperature range, and the state immediately above  $T_C$  is typically metallic. This zero resistivity state was originally thought of as a simple perfect conductor. However, a second key feature of superconductivity, the Meissner effect [7], distinguishes superconductivity from simple perfect conductivity: when cooled below  $T_C$ , superconductors expel any magnetic flux inside them and become perfect diamagnets, as shown in Fig. 1.1 (b). This is in contrast to what

would be expected of a hypothetical "normal" perfect conductor where any magnetic flux in the material as it was cooled into the perfectly conductive state would remain trapped, rather than be expelled. This feature of perfect diamagnetism brings possible applications for frictionless magnetic-superconductor bearings and levitating trains that could significantly reduce energy use in transportation.



Figure 1.1: (a) Resistance vs. temperature graph for mercury cooled into the superconducting state [5]. (b) Typical magnetic susceptibility as a function of temperature for a superconductor.

Superconductivity comes about from electrons in the metallic state pairing up into bosons called Cooper pairs that consist of one spin-up and one spin-down electron (for conventional BCS superconductors). This was first recognized by Leon Cooper who showed that electrons on the surface of the Fermi sea are unstable to pairing from arbitrarily small attractive interactions [8]. Bardeen, Cooper, and Schrieffer then came up with a successful theory, BCS theory, for how these pairs could form in typical superconducting materials, mediated by the electron-phonon interaction, and described how these pairs form a superconducting state [9]. As electrons are fermions, no two electrons can be in the same state described by all of the same quantum numbers; this is the Pauli exclusion principal and gives some explanation for why electron motion always comes with energy loss. As electrons occupy all different states, they will move independently, scatter off of one another and off defects in the lattice, and lose energy. Bosons, however, are not constrained by the Pauli exclusion principle and can all be in the same state. They can therefore form a collective phase called the Bose-Einstein condensate where all bosons exist in the ground state and move together. In a superconductor, the Cooper pairs condense into a collective state

similar to a Bose-Einstein condensate, allowing dissipationless flow of charge. Excitations out of this state occur by breaking breaking Cooper pairs to leave Bogoliubov quasiparticles.

The presence of Cooper pairs with finite binding energy leads to an energy gap in the excitation spectrum that can be measured by many different techniques. This notably appears in measurements of the specific heat,  $C_v$ , which has the form shown in Fig. 1.2 as a function of temperature. Fig. 1.2 shows a sharp jump as the superconducting state is entered, indicating the occurrence of a phase transition, and has the exponential dependence characteristic of a gapped state,  $C_V \propto exp(-\Delta/2k_BT)$  [10], where  $\Delta$  is the energy gap,  $k_B = 8.617 \times 10^{-5}$  eV/K is the Boltzmann constant, and T is temperature. The presence of this exponential behaviour in the specific heat is one of the key features that led to the development of BCS theory.



Figure 1.2: Specific heat as a function of temperature in arbitrary units for the normal metallic state (black solid line) and the superconducting state (red dashed line).

Superconductors can be divided into two main classes based on their response to a magnetic field, called type I and type II. Both of these exhibit perfect conductivity in zero applied magnetic field, but can be distinguished by the behaviour of the magnetic susceptibility and sometimes conductivity as a function of magnetic field. Type I superconductors simply exhibit perfect diamagnetism, with the magnetic susceptibility ideally sitting at a constant value of -1 (dimensionless) for applied field below the critical field  $H_C$ . Above this field the material ceases to be a superconductor and changes back into the normal metal state that would exist

above  $T_C$ . This thermodynamic critical field comes about when the free energy cost of expelling the magnetic field exceeds the energy gained by the binding energy of the Cooper pairs in the superconducting state.

Type II superconductors were first proposed by Alexei Abrikosov in 1957 [11]. They show perfect diamagnetism up to a lower critical field,  $H_{C1}$ , which is smaller than the expected thermodynamic critical field, and do not directly transition back into a normal state. Instead, these materials show a mixed state where vortices form whose cores are in the normal state and each allow one magnetic flux quantum,  $\phi_0 = 2.067 \times 10^{-15}$  Wb, to penetrate through. One consequence of the vortices is that type II superconductors can exhibit finite electrical resistivity at fields above  $H_{C1}$  due to dissipation from moving vortex cores.

Outside of the vortex cores, the magnetic field relaxes exponentially down to zero, with a length scale given by the penetration depth,  $\lambda$ . This penetration depth is also the characteristic length scale that magnetic fields will penetrate into any superconductor, and can be defined for both Type I and Type II superconductors. In type II superconductors, one measure of the vortex core size is given by the coherence length,  $\xi$ . This is the characteristic length scale for the superconducting order parameter to recover from zero at the centre of the vortex to the value in the superconducting bulk and is also the characteristic size of Cooper pairs. The details of the vortex core structure cannot entirely be captured by a single length scale, and typically depend on field and temperature [12]. Nevertheless, the coherence length can be a useful parameter to compare different type II superconductors.

The Type II superconducting state arises when the mixed state is more energetically favourable than either a pure superconducting state or a pure normal state. It allows part of the energy gain from the pairing energy of Cooper pairs, while also partially relaxing out the energy cost of expelling the magnetic field by allowing flux penetration through the vortex cores. Type II superconductors are found to occur when the ratio of the penetration depth to coherence length satisfies  $\lambda/\xi > \frac{1}{\sqrt{2}}$ . This gives a condition where the vortex cores are sufficiently small not to remove too much superconducting volume, while the penetration depth is sufficiently large so that not too much magnetic flux need penetrate through the vortex cores. These vortex cores usually form into a close packed two dimensional array, as shown in Fig. 1.3. As the field is increased, each vortex still allows one flux quantum to penetrate, but the separation between them continually decreases. The upper critical field,  $H_{c2}$ , where type II superconductors transition fully into the normal state, comes when the vortex cores cannot be packed any more tightly. Through geometric arguments assuming a triangular lattice of vortex cores and a fixed coherence length, this is given by  $H_{c2} = \frac{\phi_0}{2\pi\xi^2}$ . The characteristic field dependence of magnetization for Type I and Type II superconductors is shown in Fig. 1.4, which shows the sharp transition back to the normal state for Type I superconductors, and the more gradual evolution for type II.



Figure 1.3: Characteristic triangular vortex lattice for a superconductor. The black circles show the vortex cores, and the colours show the field strength outside the cores ranging from high fields (red) through low fields (blue).

One parameter that is commonly quoted to compare different superconductors is the superfluid density. This can be thought of as the density of electrons that contribute to the superconducting state. In any superconductor, paired electrons only exist on top of a large Fermi sea of normal electrons, so this density does not approach unity. Typically, the penetration depth is measured directly by experiments, and the superfluid density can then be determined as,

$$n_s = \frac{m^* c^2}{4\pi e^2 \lambda^2},\tag{1.1}$$

where  $m^*$  is the effective electron mass, c = 299,792,458 m/s is the speed of light, and  $e = 1.602 \times 10^{-19}$  C is the electron charge. This quantity is often reported as  $n_s/m^*$  because, while  $m^*$  should equal the bare electron mass for conventional superconductors, in many unconventional



Figure 1.4: Magnetization as a function of temperature for a Type I (black solid line) and Type II (red dashed line) superconductor. The thermodynamic  $(H_c)$ , lower  $(H_{c1})$  and upper  $(H_{c2})$  critical fields are shown by the location of the arrows.

cases it does not, and can be difficult to measure. Superfluid density has proven to be a particularly useful parameter for high temperature cuprates where the Uemura plot shows a linear scaling between the low temperature superfluid density and  $T_C$  [13].

BCS theory provides expectations for what the temperature dependence of various parameters should be. The most important temperature dependence is that of the superconducting gap which determines the temperature dependence of many other parameters. This is given by the self-consistent equation [10],

$$\frac{1}{V} = \frac{1}{2} \sum_{k} \frac{\tanh(\beta/2(E_k^2 + \Delta^2)^{1/2})}{(E_k^2 + \Delta^2)^{1/2}},$$
(1.2)

where  $\Delta$  is the gap, V is the pairing potential,  $E_k$  is the k-vector dependent energy above the Fermi energy, and  $\beta = (k_B T)^{-1}$ . This equation cannot be solved analytically, and it is therefore useful to consider analytical approximations for the temperature dependence of the gap. One such commonly used approximation is [14],

$$\Delta(T) = \Delta_0 tanh\left(1.742\sqrt{\frac{T_c}{T}} - 1\right)$$
(1.3)

where  $\Delta_0$  is the zero temperature value of the gap, which BCS theory predicts should be related to  $T_C$  by  $2\Delta = 3.52k_BT_C$ . This approximation enables fitting of data in a computationally reasonable manner and matches the true temperature dependence well, as shown by Fig. 1.5.



Figure 1.5: Temperature dependence of the superconducting gap,  $\Delta$ , normalized to the value at zero temperature,  $\Delta_0$ . The black curve is the true BCS temperature dependence given by the equation

The temperature dependence of other parameters such as the penetration depth, and hence superfluid density, depends on the spatial symmetry of the gap function and hence the pairing symmetry. In particular, the temperature dependence of the superfluid density is given by,

$$\frac{n_s(T)}{n_0} = \oint_{FS} dS_k \left[ 1 - 2 \int_{\Delta(T,k)}^{\infty} dE \left( -\frac{\partial F}{\partial E} \right) \frac{E}{\sqrt{E^2 - \Delta^2(T,k)}} \right].$$
(1.4)

Here, E is the energy difference above the Fermi energy,  $F = \frac{1}{e^{E/k_B T} + 1}$  is the Fermi function,  $\Delta(T, k)$  is the temperature and directional dependent gap function, and the outer integral is over the Fermi surface. In BCS theory, pairing is mediated by the electron - phonon interaction which has full spatial symmetry and gives an s-wave superconducting state. In this case, the gap function is isotropic and hence the outer integral vanishes, leaving the simpler expression,

$$\frac{n_s(T)}{n_0} = \left[1 - 2\int_{\Delta(T)}^{\infty} dE\left(-\frac{\partial F}{\partial E}\right)\frac{E}{\sqrt{E^2 - \Delta^2(T)}}\right].$$
(1.5)

As the BCS pairing mechanism is the phonon interaction, the transition temperature should scale like the phonon Debye temperature, and is expected to reach at most 40 K for light transition metal compounds [15]. The discovery of high temperature superconductivity in the cuprates, first at temperatures of 30 K [16], and soon after up to 90 K [17], highlighted the importance of exploring other possible pairing mechanisms. The  $T_C$  of these superconductors is well over what is expected from the Debye temperature that is limited due to the heavy atoms in the structure, and hence the superconductivity cannot be explained by the phonon interaction. Although the pairing mechanism in cuprate superconductors is still up for debate, it has been determined that the pairing symmetry is not s-wave [18]. From this example, and other prominent examples of non-isotropic superconductivity such as various heavy fermion superconductors [19] and the iron pnictides [20], it is clear that we must consider pairing symmetries beyond s-wave.

Pairing symmetries beyond s-wave are generally anisotropic, which complicates calculations and, for instance, requires reverting to the more complicated Eq. 1.4 for the superfluid density. Some such anisotropic gap functions can have nodes for certain wave-vectors, which have a substantial influence on the temperature dependence of the parameters describing the superconductor. These are typically more difficult to calculate as many possible asymmetric pairing symmetries can exist, but often result in a temperature dependence persisting down to low temperatures replacing the flat curve seen for s-wave superconductors. Measuring the superfluid density can be a good way to distinguish the pairing symmetry in these materials. These measurements must be performed down to very low temperatures, as qualitative differences appear most obviously as temperature is reduced to a small fraction ( $\approx 10-20\%$ ) of  $T_C$ . Figure 1.1 taken from Ref. [21] shows examples of the expected superfluid density temperature dependence for an s-wave superconductor, and two examples of d-wave superconductors.

In addition to anisotropic pairing symmetries, some superconductors show multi-band behaviour. In these cases, superconductivity exists on multiple bands which results in multiple different superconducting gaps opening up. In principal, these gaps could open up at different temperatures, but it is usually observed that coupling between bands will result in the Tc being the same on all bands. In this case, the superfluid density can be determined by adding two components of the form of Eq. 1.4. Well known examples of multi-band superconductors include NbSe<sub>2</sub> [22], MgB<sub>2</sub> [23], and BaFe<sub>2</sub>As<sub>2</sub> [24]. These result in varied temperature dependences for the superfluid density, depending on the size of the gaps on the different bands. Figure 1.7 highlights this with data from BaFe<sub>2</sub>As<sub>2</sub> (a), showing an upturn at low temperature, MgB<sub>2</sub> (b), showing linear behaviour down to a lower temperature than expected for a single band s-wave superconductor, and NbSe<sub>2</sub> (c), showing only small deviations from the expected single band behaviour.

Another method of distinguishing conventional fully-gapped, anisotropic, and multi-gap superconductivity is by determining the field dependence of the penetration depth. In fully gapped s-wave superconductors, the penetration depth is expected to increase with a quadratic



Figure 1.6: Temperature dependence of the superconducting fluid density for an s-wave superconductor (black), typical d-wave superconductor (blue), and nonmonotonic d-wave (red). Figure taken from Ref. [21].

dependence on the applied field,  $\lambda(H,T) - \lambda(0,T) \propto \beta_s(T)H^2$  [25]. This field dependence arises because the screening current produced by an applied field is weakened by pair breaking quasiparticle excitations that cause a backward current. This reduction in the screening current allows the field to penetrate further into the superconductor, which is an increase in  $\lambda$  [26]. However, in a fully gapped state quasiparticle excitations can only occur at finite temperature so it is expected that  $\beta_s(T) \to 0$  as  $T \to 0$ . By contrast, in anisotropic superconductors such as d-wave states, nodes in the energy gap allow quasiparticles to occur at any temperature and the field dependence of the penetration depth is expected to be  $\lambda(H,T) - \lambda(0,T) \propto \alpha_s(T)H$  [25], where  $\alpha_s(T)$  need not approach zero as temperature approaches zero.

These expected field dependencies have, for example, been observed in materials such as V<sub>3</sub>Si (s-wave) [27], Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>y</sub> (d-wave) [25], and other d-wave cuprates [28]. In superconductors that show multiple isotropic gaps, such as NbSe<sub>2</sub> [29] and MgB<sub>2</sub> [30], nearly linear field dependencies of  $\lambda$  have been observed, which arise from excess quasiparticles that can be excited across



Figure 1.7: Temperature dependence of the superfluid density for three different multi-band superconductors. (a) Data for BaFe<sub>2</sub>As<sub>2</sub> taken from Ref. [24]. (b) MgB<sub>2</sub> data taken from Ref. [32]. (c) Data for NbSe<sub>2</sub> from Ref. [33].

the smaller gap. In all of these cases, interpreting experimentally determined field dependencies can be complicated as additional factors, such as non-local effects and the exact model of the vortex lattice used to extract the penetration depth, can give significant contributions [31].

#### **1.2 Heavy Fermions**

The materials known as "heavy fermions" are those which, at low temperature, behave as though the dominant charge carriers have masses far in excess of the bare electron mass [34]. This apparent mass comes directly from electron bands that only weakly depend on energy (low dispersion), which leads to a high density of states at the Fermi energy. Approximating the band structure locally as the free electron dispersion,  $E(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2\mathbf{m}^*}$ , where the electron mass has been replaced by the effective mass, a high effective mass corresponds to low band dispersion. This effective mass is often determined by measuring the specific heat at low temperatures. The specific heat is a measurement of the energy input required to change the temperature of a material, and its dominant contributions in crystalline systems can be written as,

$$c = \gamma T + \alpha T^3, \tag{1.6}$$

where T is the temperature,  $\gamma$  is the Sommerfeld coefficient for the electronic contribution to specific heat, and  $\alpha$  is the coefficient for the lattice (phonon) contribution to specific heat. At high temperatures the lattice specific heat will dominate, but if the temperature is lowered far enough the linear term can be measured. The Sommerfeld coefficient depends linearly on the density of states at the Fermi energy, and hence the effective mass of the carriers. The carrier mass can also be inferred from other measurements sensitive to the density of states, such as de Haas-van Alphen or other quantum oscillation measurements [35].

Heavy fermion behavior arises from a sea of conduction electrons interacting with a lattice of highly localized moments that usually come from f-electrons [34], although some examples of heavy fermion states in materials without f-electrons do exist, such as LiV<sub>2</sub>O<sub>4</sub> [36]. The behaviour of such a system comes about from the competition between two different factors, the Kondo effect and the RKKY (Rudermann Kittel Kasuya Yosida) interaction.

The Kondo effect is produced by an antiferromagnetic contact interaction between the conduction electrons and local moments that causes the moments to be effectively screened out by the conduction electrons to form Kondo singlets. This screening causes an increase in the effective mass of the conduction electrons, and increases their overall scattering rate. The strength of the interaction grows with decreasing temperature and produces the characteristic upturn in the resistivity at low temperature that is commonly seen in metals with dilute magnetic impurities [37]. In materials with a lattice of local moments, scattering from the Kondo singlets becomes coherent, and a characteristic temperature scale,  $T_K$ , can be defined, below which the system transitions into a paramagnetic fermi liquid state that is known as Kondo lattice. In this state, the coherent scattering reduces the electrical resistivity, leading to a maximum resistivity at  $T_K$  and a  $T^2$  temperature dependence below  $T_K$ .

Along with the Kondo effect, a system of localized moments within a sea of conductions electrons also produces the RKKY interaction, which is indirect exchange between neighbouring localized moments. This exchange is mediated by Friedel oscillations in the spin polarization of the conduction electrons and therefore has a changing sign with distance from the moment [38]. Dilute systems, where the distances between neighbouring moments vary considerably, will not show ordered magnetism from this interaction. However, in a lattice of local moments, the RKKY interaction can produce ordered magnetism, which is most often antiferromagnetic [37], but can be ferromagnetic in systems with the correct spacing between the magnetic ions [39].

As the Kondo effect promotes a ground state which is not magnetically ordered, and the RKKY interaction tends to promote antiferromagnetism, heavy fermion materials where these two interactions are of comparable magnitude exist in a delicate balance. However, both of these interactions depend on the strength of the coupling of the local moments with the conduction electrons,  $\rho J$ , with the Kondo temperature varying as  $T_K \propto e^{-1/(2J\rho)}$ , and the antiferromagnetic transition temperature produced by the RKKY interaction varying as  $T_N \propto J^2 \rho$  [40]. These

different temperature dependencies leads to the characteristic Doniach phase diagram for heavy fermion compounds [41].

Significant interest in heavy fermion compounds came from the discovery of unconventional superconducting and magnetic states at low temperature [34, 42]. Steglich et al. discovered the first superconductivity in a heavy fermion while studying CeCu<sub>2</sub>Si<sub>2</sub> [43]. These measurements prompted significant interest as, despite the relatively low superconducting transition temperature  $(T_C)$ , the ratio of  $T_C$  to the Fermi temperature,  $T_C/T_F = 0.05$ , was found to be quite high. This immediately suggested an unconventional origin to superconductivity in the material that could not be explained by typical phonon-coupling models. Furthermore, specific heat measurements across  $T_C$  show a very large peak that is consistent with what would be expected if the heavy fermions were condensing into Cooper pairs to form the superconducting state, rather than standard electrons [43]. This suggests that the heavy fermion state and the superconductivity are connected, which is initially surprising as heavy fermion behaviour fundamentally comes from a magnetic interaction, and magnetism is conventionally thought to be antagonistic to superconductivity.

Since these first heavy fermion superconductors were measured, many others have been discovered, mainly in compounds containing praseodymium, cerium, and uranium, although some other examples do exist [19]. In many of these materials, magnetically ordered states exist in close proximity to, or coexistence with, the superconductivity. In particular, the  $CeM_2X_2$  materials, where M is a transition metal and X is silicon or germanium [19], show a variety of magnetic states where superconductivity often appears as a function of pressure or doping when the magnetic order is suppressed. This clear interplay between superconductivity and magnetism makes it important to understand the magnetic states that exist in these materials so that we can better determine how they might promote superconductivity.

#### 1.3 URu<sub>2</sub>Si<sub>2</sub>

URu<sub>2</sub>Si<sub>2</sub> is a particular example of a heavy fermion material that has been subject to considerable study over the past three decades [44]. This material has the tetragonal I4/mmm crystal structure shown in Fig. 1.8. At low temperatures, two transitions appear in the specific heat as shown in Fig. 1.9 [45]. The lower temperature transition is known to be a transition into a superconducting state, however the nature of the state between the two transitions is still under debate and has been labelled "hidden order". Early neutron scattering measurements of the hidden order state suggested an antiferromagnetic state with ordered moments of  $\mu_{ord} = 0.04 \ \mu_B$  per uranium atom [46]. However, this explanation immediately encountered difficulties as this moment is too small to account for the entropy change at the transition of  $\Delta S = 0.2Rln2$  inferred from specific heat measurements [47]. Muon spin rotation measurements later suggested that the moment was even smaller [48], and it is now widely accepted that the magnetic moment measured in these early studies is not intrinsic to the hidden order state.



Figure 1.8: Crystal structure of  $URu_2Si_2$ . Yellow atoms are uranium, blue are ruthenium, and grey are silicon.

Despite this lack of an ordered moment, the hidden order transition shows up prominently in measurements of the magnetic susceptibility, with a kink at 17.5 K or a peak in the derivative with respect to temperature. The susceptibility is also highly anisotropic, showing Ising behaviour with a much larger value along the c-axis than perpendicular to it, as shown in Fig. 1.10. This figure also shows the maximum in the susceptibility that occurs around 80 K, thought to be a result of the electrons hybridizing to form the heavy fermion state out of which hidden order arises [45].

Inelastic neutron scattering measurements of this material have found magnetic excitations with two main minima, at the commensurate position  $Q_0 = (0, 0, 1)$ , and at the incommensurate position  $Q_1 = (0.6, 0, 0)$  [49]. These excitations exist as an ungapped continuum above the hidden order transition, and become gapped below  $T_{HO}$  with  $\Delta_0 \approx 2$  meV and  $\Delta_1 \approx 4$  meV. The origin of these excitations is still not fully understood, but Wiebe et al. were able to show that the entropy change at the transition can be fully accounted for by the gapping of these



Figure 1.9: Specific heat of URu<sub>2</sub>Si<sub>2</sub> divided by temperature (*T*) plotted versus  $T^2$  (top) to give the linear slope and intercept representing  $\gamma$  and  $\Theta_D$ , and versus *T* (bottom) showing the two transitions that occur at 1.1 K and 17.5 K. Reproduced from Ref. [45].

excitations, which suggests that they are a key feature of the hidden order state [50]. Infrared reflectance measurements find a gap, presumably related to these excitations, whose structure is similar to that found in more conventional spin-density-wave systems [51]. By contrast, STM measurements show a gap opening up that does not look like a conventional density wave, and so the situation is far from clear [52].

#### 1.3.1 Symmetry Breaking

One common feature in studies of URu<sub>2</sub>Si<sub>2</sub> is the search for broken symmetries in the hidden order state [53]. The presumed lack of an intrinsic ordered moment along the c-axis suggests that there is no time-reversal symmetry breaking. However, other ordered moments could exist, and some prominent theories including rank 5 spin density wave order [54], dotriacontapolar (32-polar) order [55], and Hastatic order [56] suggest an in-plane moment on the order of 0.01  $\mu_B/$  U or



Figure 1.10: Magnetic susceptibility of  $URu_2Si_2$  plotted as a function of temperature in a field of 2 T applied parallel to the c-axis or a-axis as indicated on the graph. Reproduced from Ref. [45].

smaller. A recent neutron scattering study by Ross et al. puts a limit of  $< 0.0011 \mu_B/U$ , which substantially constrains such theories [57] that require any time-reversal symmetry breaking.

Another possible broken symmetry that is under recent investigation is rotation symmetry of the lattice. Torque magnetometry measurements have suggested a breaking of rotational symmetry in the hidden order state which would change the crystal symmetry to orthorhombic [58]. One puzzling feature of this result is that the signal size does not scale linearly with sample volume as expected, and instead can only be observed in the smallest samples. This has been suggested to be the result of randomly oriented orthorhombic domains whose signals will average out in large samples [58]. Recent Raman measurements find a sharp feature appearing primarily in the  $A_{2g}$  channel at the hidden order transition [59] as expected for a tetragonal system in the  $D_{4h}$  point group. However, they also see weaker excitations in the  $A_{1g}$  and  $B_g$  channels, which are forbidden for tetragonal symmetries, again suggesting that tetragonal symmetry is broken. Cyclotron resonance [60, 61], NMR [62], elastoresistivity [63], and some X-ray diffraction measurements [64] also support the presence of tetragonal symmetry breaking, albiet with some unusual dependence on sample quality. However, other X-ray diffraction measurements in a different geometry [65], polarized light microscopy measurements [66], and inelastic neutron / x-ray scattering measurements [67] all find no evidence for this symmetry breaking. It is fair to say that the presence or absence of a small orthorhombic distortion in the hidden order state is still not a settled question.

A broken symmetry that is fairly well accepted is translational symmetry. Evidence for this comes primarily from reconstruction of the fermi surface consistent with a doubling of the unit cell length along the c-axis, measured using various probes such as angle-resolved photoemission spectroscopy (ARPES) [68, 69], de Hass-van Alphen measurements [70], and Shubnikov-de Haas measurements [71]. Significantly, measurements under pressure have found no significant differences between the Fermi surface in the hidden order state and that in the antiferromagnetic state [72]. This similarity between the two states makes further study of the antiferromagnetism important to look for further clues about hidden order.

#### 1.3.2 Pressure

When URu<sub>2</sub>Si<sub>2</sub> is placed under hydrostatic pressure, the hidden order state transforms into a more conventional antiferromagnetic state above a critical pressure of 0.7 GPa. This has been well established by neutron scattering [73], as well as muon spin rotation [74] and other techniques. Neutron scattering and  $\mu$ SR measurements both suggest that the magnetic moment quickly reaches a steady value above the critical pressure, and then does not increase further with application of pressure [74,75]. The phase diagram in Fig. 1.11 shows that antiferromagnetism appears at the pressure where superconductivity is suppressed, suggesting that hidden order is connected to superconductivity in this material. Throughout the entire pressure range studied, the hidden order / antiferromagnetic transition temperature slightly increases with applied pressure. This diagram also demonstrates some of the difficulties of doing measurements under applied pressure, as different studies measure substantially different critical pressures, depending on the method of applying pressure.

The evolution of the excitation spectrum and energy gap with pressure has also been studied with neutron scattering and resistivity measurements that paint a somewhat contradictory picture. Various works agree that the incommensurate gap increases upon entering the antiferromagnetic state [76–78], which also results in an increase in the total gap determined from resistivity measurements [77]. However, there is disagreement on what happens to the commensurate excitation. Some works suggest that it disappears upon entering the hidden order state [77–79], while others suggest that it still exists with a similar energy gap and slightly reduced scattering intensity [76].

Uniaxial pressure has also been shown to cause a transition into the antiferromagnetic state for pressure along the [100] and [110] axes [80]. These results have suggested the role of the c/aaxis ratio in determining which state is most stable. The c/a axis ratio is also the presently accepted explanation for the early measurements of a finite antiferromagnetic moment in URu<sub>2</sub>Si<sub>2</sub> at ambient pressure. Localized stress from inevitably imperfect crystals is thought to cause



Figure 1.11: Pressure-temperature phase diagram of URu<sub>2</sub>Si<sub>2</sub>. Reproduced from Ref. [75].

pockets of higher c/a ratio that will give a small volume fraction of the antiferromagnetic state within the dominant hidden order state. As neutron scattering measurements give an average of the moment over the entire measured sample volume, this would appear as a smaller moment than what is expected in the antiferromagnetic state [80]. By contrast, the  $\mu$ SR measurements are expected to be better able to distinguish this sort of impurity effect because they can measure both the internal field strength of a phase and the volume fraction of the phase. This highlights the importance of a volume sensitive probe for the study of URu<sub>2</sub>Si<sub>2</sub>.

#### 1.3.3 Doping effects

One potentially useful avenue for studying the antiferromagnetic state of  $URu_2Si_2$  is to induce it by chemical substitution / doping rather than by applying external pressure. This has the significant advantage that many experimental techniques are substantially simpler to perform at ambient pressure than they are at high pressure. It would also avoid discrepancies between measurements under different pressure media as was shown in Fig. 1.11.

Numerous doping studies have been performed on  $URu_2Si_2$  ranging over all three atomic sites. These include doping the uranium site with thorium, neptunium, yttrium, scandium, and most of the rare earth elements, doping the ruthenium site with manganese, iron, technetium, rhenium, osmium, iridium, and rhodium, and doping the silicon site with germanium, phosphorus, and aluminum. Figure 1.12 summarizes the effects of the various dopings that have been studied. They are discussed in more detail below.



Figure 1.12: Periodic table summarizing the various dopings that have been performed on  $URu_2Si_2$  and their dominant effects. The background color of each cell shows which site the atom has been doped onto: yellow for the uranium site, blue for the ruthenium site, grey for the silicon site, and white if it has not been studied. The symbol colour shows what magnetic state arises with doping: green for antiferromagnetism, red for ferromagnetism, blue for remaining hidden order, and black for cases that are unknown, unclear, or enter some other state. The arrows show whether the transition temperature increases with doping (upwards pointing arrow), decreases (downwards arrow), or stays mostly unchanged (horizontal dashed line).

Doping of the uranium site by rare earths tends to produce complicated magnetic behaviour, with additional transitions showing up at lower temperature [81]. The higher temperature transition also appears to be suppressed by doping in all cases except for samarium doping where it is unchanged for small doping levels, although most of the rare earth doping series have not been well studied. Lanthanum doping has been studied by multiple groups. This nonmagnetic doping first causes the transition temperature to be suppressed up to a doping level of about 0.05 [82],

followed by an increase for higher doping levels [83]. Along with this increase in transition temperature the magnetic susceptibility begins to look far more like that of a conventional antiferromagnet [81, 83]. This has been suggested to be caused by dilution of the uranium making RKKY interactions less important and increasing the localization of the moments [83,84]. Thorium, another nonmagnetic dopant, also suppresses the transition temperature and possibly produces an antiferromagnetic state at higher doping, similar to lanthanum doping [85,86]. This behaviour has been explained as a combination of negative chemical pressure and introduction of Kondo holes through replacement of some of the magnetic uranium atoms with nonmagnetic dopants [85]. Measurements on yttrium doped samples show little change in the transition temperature with doping, but suggest a change to glassy magnetism at higher doping levels, while scandium doping suppresses the magnetic transition by a doping level of 0.1 [87]. Finally, neptunium doping of the uranium site shows a slight increase in the transition temperature with doping [88], and Mössbauer [89] as well as resonant X-ray scattering [90] show antiferromagnetism. However, this antiferromagnetic behaviour is complicated by additional transitions appearing even for low doping levels [88], and magnetism existing on both the uranium and neptunium atoms [90].

Doping of the silicon site by aluminum or germanium shows only a slight suppression of the transition temperature [87], with no change in the character of the transition from bulk measurements. Little work has been performed on these dopings with local magnetic probes, but some NMR measurements suggest that no long range magnetic order appears [91]. By contrast, phosphorus doping, which adds an electron, rapidly suppresses the transition temperature [92], shows a broad doping range with no order, and recovers antiferromagnetic order at higher doping [93] as evidenced by NMR measurements [94].

Manganese, technetium, and rhenium doping (URu<sub>2-x</sub>M<sub>x</sub>Si<sub>2</sub>) all supress the hidden order transition temperature and eventually promote a ferromagnetic ground state [95, 96]. While manganese and technetium doping have only been studied using bulk characterization such as magnetization, resistivity, and specific heat, rhenium doping has been studied with a variety of techniques. Neutron scattering [97] and NMR measurements [98] are both consistent with a long range ferromagnetic state with a moment around 0.5  $\mu_B$  per uranium at higher doping levels. Detailed measurements of the phase diagram using specific heat and resistivity show that the hidden order is suppressed by a doping level of x = 0.1 before ferromagnetism appears at around x = 0.15 [99] and superconductivity quickly vanishes by a doping level of x = 0.01 [100]. In this case, there is no evidence for hidden order transitioning to antiferromagnetism before the hidden order transition is suppressed to zero temperature.

Iridium and rhodium doping also cause a decrease in the transition temperature for low doping levels [100]. Iridium doping appears to result in complete suppression of superconductivity by x = 0.03, and hidden order by x = 0.06; however, little work has been done to understand whether the hidden order transforms into some other magnetic state before it is suppressed. Rhodium doping also causes the hidden order to be suppressed by about x = 0.1; however, there is significant evidence that the hidden order changes into antiferromagnetism before the transition is completely suppressed [101], and a separate antiferromagnetic order re-appears at high doping. This case is very similar to that of phosphorus doping of the silicon site, suggesting that the dominant cause for this behaviour is the addition of extra electrons into the system.



Figure 1.13: (i) Temperature-doping phase diagram for iron doping on the ruthenium site of URu<sub>2</sub>Si<sub>2</sub>. (a) shows the phase diagram measured by resistivity, magnetization, and specific heat. (b) shows the residual resistivity ratio of the samples. Reproduced from Ref. [102] (ii) Temperature-doping phase diagram for osmium doping on the ruthenium site of URu<sub>2</sub>Si<sub>2</sub> measured by magnetization, resistivity, and specific heat. Reproduced from Ref. [103].

Iron and osmium doping of the ruthenium site, in contrast to almost all other dopings, cause the transition temperature to continuously increase over a wide range of doping levels [102,103]. Figure 1.13 shows the temperature-doping phase diagram for both of these dopings. Osmium shows a continuous increase in the transition temperature for the full range of samples studied, while iron doping increases the transition up to about 40% doping followed by a slow suppression. The particular significance of these dopings is that they do not involve changes to the number of electrons in the material, or direct changes to the f-shell. Therefore, the dominant effect of the doping is expected to be chemical pressure. Iron is smaller than ruthenium and therefore results in a positive chemical pressure, similar to the application of applied hydrostatic pressure [102]. In contrast, osmium is a larger atom, and results in a small negative chemical pressure effect [103]. As both of these studies of osmium and iron used only bulk probes, the exact magnetic ground state (antiferromagnetic or hidden order) could not be determined. However, if iron doping behaved like hydrostatic pressure as expected, there should be a transition to antiferromagnetism around 5% doping, which would allow this pressure-induced antiferromagnetic state to be studied by techniques that are difficult to use under applied pressure.

#### 1.4 Dichalcogenides

Transition metal dichalcogenides are a group of materials with the  $TX_2$  chemical formula, where T is a transition metal and X is a chalcogenide (oxygen, sulfur, selenium, or tellurium). These materials have been studied for decades as a result of their widely varying properties and potential applications in many different areas [104]. Most of these materials form a layered structure where the inter-layer distance between neighbouring transition metal atoms is frequently a factor of 1.5 or more larger than the interlayer distance, and the chalcogenide atoms are spaced relatively closely to the transition metals. This structure leaves a great deal of space between the layers, which can be taken up by intercalated atoms that substantially modify the properties of the material [105].

It is very common for these materials to undergo a charge-density wave (CDW) structural transition below room temperature, as was first recognized in the group V (V, Nb, Ta) dichalcogenides [106–108]. These CDW transitions show up as a peak in the resistivity that is hysteretic in temperature. Such transitions have now been seen in a wide variety of dichalcogenide materials, including TiSe<sub>2</sub> [109], and IrTe<sub>2</sub> [110]. These CDW states exhibit a variety of properties, and have been well studied in their own right. One further interesting feature that arises is how they interact with other ground states that might exist such as superconductivity and magnetism. Dichalcogenide materials are generally weakly diamagnetic or paramagnetic down to low temperature and do not intrinsically show interesting magnetic behaviour. However, doping or intercalating typical magnetic atoms such as chromium, manganese, iron, cobalt, and nickel can cause magnetism to appear [111]. Such doping also usually suppresses the charge density wave transition, and the magnetic order appears only after the CDW has disappeared.

Superconductivity has been seen in a number of dichalcogenide compounds, most notably in

NbSe<sub>2</sub>, which has been known to be superconducting since the 1960s [112]. After the original discovery, it was found that the transition temperature strongly depends on small variations in stoichiometry [113], and is very sensitive to the application of applied pressure [114]. This sensitivity is thought to be caused by a correlated suppression of the CDW transition temperature with applied pressure, suggesting that CDW order is antagonistic to superconductivity in these systems [114]. Unconventional features of the superconductivity in NbSe<sub>2</sub>, such as multi-band superconductivity [22], has renewed interest in the superconducting dichalcogenides. In recent years, superconductivity associated with the suppression of the CDW transition has been studied in a number of other dichalcogenides including TaS<sub>2</sub> [115], IrTe<sub>2</sub> [110, 116], TiSe<sub>2</sub> [117], and TaSe<sub>2</sub> [118].

TiSe<sub>2</sub> shows significantly different behaviour from NbSe<sub>2</sub>. While in NbSe<sub>2</sub> superconductivity exists at ambient pressure, where a CDW is present, in TiSe<sub>2</sub> superconductivity only appears once the CDW is suppressed by doping [117]. This points to slightly different mechanisms for the competition (or lack thereof) between these phases in TiSe<sub>2</sub> and NbSe<sub>2</sub>, despite both showing competition between superconductivity and the CDW.

#### 1.4.1 $IrTe_2$

IrTe<sub>2</sub> is a dichalcogenide that is composed of relatively heavy elements, and therefore will have the potentially interesting feature of high spin orbit coupling, alongside the physics shared by other dichalcogenides. It forms in the layered trigonal  $P\bar{3}m1$  space group with the structure shown in Fig. 1.15. This structure has triangular planes of iridium and tellurium well separated from each other, allowing ample space for intercalated atoms. IrTe<sub>2</sub> undergoes a structural CDW transition at 250 K into a triclinic P $\bar{1}$  space group, below which it is weakly diamagnetic with no additional ordering appearing as temperature is decreased [119]. The low temperature CDW state in this material is commensurate stripe order with a periodicity 6 times larger than the underlying lattice [120, 121].

Intercalation or substitution on the Ir site by a variety of transition metals is shown to suppress the CDW transition temperature [110, 116, 122–125]. In contrast, substitution of selenium on the tellurium site, or applied hydrostatic pressure, increases the temperature of the transition into the CDW state [126]. This increase is possibly associated with a change in the periodicity of the CDW state [126]. In the case of Se substitution or hydrostatic pressure where the CDW transition temperature is increased, no additional ordered phases are seen at low temperature. In contrast, when the CDW transition is suppressed, superconductivity has been observed for



Figure 1.14: IrTe<sub>2</sub>  $P\bar{3}m1$  crystal structure. Blue atoms are tellurium and red atoms are iridium. (a) Looking along the c-axis showing the triangular arrangement of iridium atoms in the plane. (b) Looking along the ab direction showing the separation of neighbouring planes.

palladium, platinum, or rhodium substitution and for copper intercalation [110, 116, 122–124]. For intercalation with iron, a spin glass state emerges after the CDW is suppressed; however, intercalation with other magnetic transition metals such as cobalt or nickel leads to a low temperature paramagnet [125].

Copper intercalation, along with platinum and palladium doping, all cause an increase in the unit cell volume by a large increase in the a-axis along with a small decrease in the c-axis [110,116]. Palladium intercalation, which shows similar superconductor properties to Pd and Pt doping, also results in a slight increase in the unit cell volume, but by an increase in both the c-axis and a-axis [110]. In these cases, the structural transition is suppressed by less than 4% doping or intercalation, at which point superconductivity emerges. By contrast, rhodium doping shows essentially no change in the unit cell volume, and requires a doping level of 10% to suppress the structural transition and promote superconductivity [122]. This contrast, along with the increase of the CDW transition temperature with Se substitution of hydrostatic pressure, both of which decrease the unit cell volume, suggest the importance of the lattice parameters for modulating the CDW transition. Further evidence for this is that application of hydrostatic pressure to Pt doped samples increases the temperature of the CDW transition for Rh doping where the volume does not change suggests that other factors are involved, which are not fully understood.

In each of these cases the superconducting transition temperature appears to be about the same, with a maximum of 3 K for Pd doping [110], 3.1 K for Pt doping [116], 2.8 K for Cu

intercalation [124], and 2.6 K for Rh doping [122]. This suggests that the superconducting state in each of these cases is the same, and that all that is required to promote it is suppression of the CDW transition by non-magnetic dopants. However, measurements of  $H_{c2}$  for  $H \parallel$  c-axis of 0.16 T for Pd<sub>0.05</sub>Ir<sub>0.95</sub>Te<sub>2</sub> [128] compared with 0.09 T for Pt<sub>0.05</sub>Ir<sub>0.95</sub>Te<sub>2</sub> [129], does suggest some differences.



Figure 1.15: Doping-temperature phase diagram for  $Pt_xIr_{1-x}Te_2$ . Trigonal denotes the  $P\bar{3}m1$  phase, Monoclinic denotes the C2/m phase, and SC denotes the superconducting state. Closed squares show the CDW transition measured on warming, while open squares show the CDW transition on cooling. Circles show the superconducting transition measured by specific heat. Figure reproduced from Ref. [130].

The doping-temperature phase diagram for  $Pt_x Ir_{1-x} Te_2$  is shown in Fig. 1.15. This shows that the superconducting transition is highest as the CDW transition is suppressed, and decreases for higher dopings [130]. Other work also shows a small region where the SC state and CDW coexist, or at least, the SC emerges out of the CDW state rather than out of the high temperature trigonal state [116]. This feature is also seen in Pd doped and intercalated  $IrTe_2$  [110], but has not been demonstrated for Cu intercalation or Rh doping, possibly as a result of too-sparse doping measurements [122, 124]. This behaviour would be similar to that of Cu-intercalated  $TiSe_2$  where the superconductivity also appears before superconductivity is fully suppressed [117]. There have also been recent reports of superconductivity appearing in un-doped  $IrTe_2$  crystals [131, 132],
which may be evidence for variable stoichiometry between different "pure"  $IrTe_2$  crystals changing the stability of the superconducting state.

Superconductivity in IrTe<sub>2</sub> is particularly interesting to study as the high spin orbit coupling could promote exotic superconducting states such as topological superconductivity, or non-trivial pairing symmetries [133,134]. The superconducting pairing symmetry of  $Pt_{0.05}Ir_{0.95}Te_2$  has been investigated by thermal conductivity [129]. These measurements show no evidence for a residual linear temperature dependence at low temperatures, which suggests that the superconducting gap has no nodes. Scanning tunnelling microscopy (STM) measurements on  $Pd_{0.05}Ir_{0.95}Te_2$ similarly show evidence for fully gapped superconductivity [128]. However, as STM is a surface sensitive technique, care must be taken in generalizing these results to the bulk material. No bulk measurements of the superfluid density or penetration depth have been reported. These would give a more definitive answer about the pairing symmetry of this material.

### 1.4.2 PbTaSe<sub>2</sub>

TaSe<sub>2</sub> is a dichalcogenide that shows a CDW state below 100K, and a superconducting state with a very small  $T_C$  of 0.13 K [135]. Raman scattering measurements of lead intercalated TaSe<sub>2</sub> show that intercalation continuously suppresses the CDW transition [136], which is similar behaviour to that of other intercalated dichalcogenides such as Cu<sub>x</sub>TiSe<sub>2</sub> [117] and Pd<sub>x</sub>IrTe<sub>2</sub> [110]. As the lead intercalation is increased to the stoichiometric level of PbTaSe<sub>2</sub>, the structure changes from the  $P6_3/mmc$  space group of TaSe<sub>2</sub> to the noncentrosymmetric  $P\bar{6}m2$  space group, shown in Fig. 1.16. This figure demonstrates that the overall structure of the TaSe<sub>2</sub> planes remains about the same, and the main effect of the Pb intercalation is to increase the layer spacing to give room for the Pb atoms to sit in between. As a result of this structure, one can think of PbTaSe<sub>2</sub> as a stoichiometric version of a heavily intercalated transition metal dichalcogenide, and consider the properties in comparison to other dichalcogenides.

Similarly to  $Cu_x TiSe_2$  and  $Pd_x IrTe_2$ , a superconducting state exists in PbTaSe<sub>2</sub> in the absence of the CDW state, with a  $T_C$  of 3.72 K [137]. This superconducting state is particularly interesting, as the lack of inversion symmetry in the crystal structure means that asymmetric spin-orbit coupling is possible, which could give rise to mixed parity superconductivity [138]. The strong spin orbit coupling brought on by heavy tantalum and lead atoms may also lead to topologically nontrivial properties.

Early DFT calculations of this material do suggest interesting topological behaviour, with a slightly gapped three dimensional Dirac cone just below the Fermi energy at the K point of the



Figure 1.16: Structure of  $TaSe_2$  ((b) and (d)) and PbTaSe\_2 ((a) and (c)). (a) and (b) show the structures looking down the c-axis, while (c) and (d) show the structures looking along the planes perpendicular to the c-axis. Green atoms are selenium, brown atoms are tantalum, and dark grey atoms are lead.

Brillouin zone [137]. ARPES measurements support this picture and show the presence of Dirac surface states [139,140]. This comes about from the bulk Dirac point being gapped out by the high spin-orbit coupling, resulting in an insulating bulk with metallic surface states, that is, a topological insulator [139]. Such a state occurring in a material that is also superconducting is extremely interesting as, if there is conventional fully-gapped superconductivity in the bulk and Dirac surface states, helical superconductivity may be induced on the surface which could host Majorana modes in the vortex cores [139]. As the Dirac surface states do exist, the important question is whether the superconducting state is fully gapped.

The first measurements of superconductivity in this material found a specific heat jump that could be fit assuming a fully gapped superconductor, but suggested that it had a quite high upper critical field of  $H_{c2}(0) = 1.47$  T, with an upwards curvature of  $H_{c2}$  with respect to temperature that may indicate unconventional pairing and a non-fully gapped superconducting state [137]. However, the relatively high base temperature (2.2 K) of these measurement limits the interpretation of the results, as most information about the pairing structure is contained at low temperatures. This work was extended by other groups down to under 0.5 K, where the anomalous upward curvature is still seen [141,142]. This is taken to be evidence for either multi-band superconductivity, or unconventional pairing symmetries. Unconventional pairing symmetry is suggested to be less likely as the upper critical field does not exceed the Pauli limit as might be expected for triplet superconductivity [141]. One of these studies also reports a non-monotonic pressure dependence of  $T_C$ , which could indicate a change in the pairing symmetry with applied pressure [141]. Further pressure dependent measurements have clarified that this change in  $T_C$  is associated with the appearance of a structural transition above a pressure of 0.25 GPa, and the upwards curvature of  $H_{c2}$  persists at higher pressures, but the pairing symmetry has not been investigated [143,144].

Thermal conductivity measurements in ambient pressure show no residual linear temperature dependence at low temperature [145] and therefore suggest a conventional fully gapped superconducting state. However, the field dependence of the thermal conductivity has an unexpected S-shape, which does not match typical fully gapped superconductors. Instead, it more closely resembles the field dependence of thermal conductivity in NbSe<sub>2</sub>, which is a well-known multiband superconductor [146]. This therefore suggests that PbTaSe<sub>2</sub> could also be a multi-band superconductor, consistent with STM [147] and ARPES [148] band structure measurements that show multiple bands near the Fermi surface that could contribute to superconductivity.

Tunnel diode oscillator measurements of the penetration depth show exponential behaviour, asymptoting to a temperature independent value by 0.4 K [148]. This suggests a conventional single band superconductor, which is inconsistent with the picture from thermal conductivity and  $H_{c2}$  measurements that point towards multi-band superconductivity. Tunnel diode oscillator measurements typically have excellent accuracy for determining the temperature dependence of the penetration depth, but suffer from a couple of drawbacks that may be significant in this case. First, the absolute signal strength is sensitive to the sample size and geometry, which means that these measurements are unable to determine an absolute value of the penetration depth, and can only determine values relative to other measured temperatures. Second, tunnel diode oscillator measurements inherently look at penetration of magnetic fields from the vacuum into the superconductor, and this is therefore a somewhat surface sensitive technique. As the penetration depth is relatively long, with  $\lambda(0) \approx 250$  nm according to measurements of  $H_{c1}$  [137], this should not be extremely important, but may affect the results somewhat, especially as topological surface states have been shown to exist in this material. It would therefore be of interest to have measurements of the penetration depth by another technique that is more bulk sensitive, but these have not yet been performed. As the superconducting state in this material is, owing to the layered structure, quite anisotropic [149], it would also be useful to have directionally sensitive penetration depth measurements to confirm whether sample orientation plays a role in some of these discrepancies.

# Chapter

# Experimental Methods

This chapter introduces the main experimental methods that were used for the work in this thesis: tri-arc Czochralski crystal growth, SQUID magnetometry, muon spin rotation, and neutron scattering. All of these are well established techniques that have been described in detail in multiple other works. As no substantial modifications or improvements were made to these methods, this section will mainly serve to highlight the aspects most important to this thesis, and not attempt to give an exhaustive overview of the techniques.

## 2.1 Crystal Growth

The crystals of doped URu<sub>2</sub>Si<sub>2</sub> discussed in this thesis were grown at McMaster university with a tri-arc furnace following a Czochralski crystal growth method. This growth method was first reported on by Jan Czochralski in 1918 when he used it to grow crystals of various pure metals and investigate how fast they crystallized [150]. Since that time, it has expanded to become an extremely technologically important technique, particularly for growing large, high quality, crystals of semiconductor materials for electronics applications. As such, there are many excellent sources discussing the technique in detail, such as the Springer Handbook of Crystal Growth [151].

The Czochralski method essentially consists of melting a boule of material, lowering a seed rod into the resulting melt, and drawing the seed slowly upwards to allow material to solidfy on it and form a crystal. There are many different techniques that can be used to heat the boule, all of which come with some advantages and disadvantages. In our growths, we melted the boules using an electrical arc in a tri-arc furnace similar to that described in Ref. [152]. A



Figure 2.1: Picture of the tri-arc furnace during the growth of a crystal. This picture shows the bright molten sample sitting on the copper hearth, the stingers producing electrical arcs to heat the sample, and the rotating seed rod pulling the crystal out of the melt.

picture of the furnace during a growth is shown in Fig. 2.1. Briefly, this consists of a rotating water-cooled copper hearth that the boule sits on, a counter-rotating molybdenum seed rod to draw the crystal out with, and three tungsten stingers to produce the electrical arcs. Typically, only two stingers were used during the growth as we only had two power supplies available and running two stingers off of a single power supply caused instabilities in the arcs that complicated the growth. This setup is enclosed in a glass and copper walled vacuum chamber that is filled with argon.

Using a tri-arc furnace has multiple advantages. First, electrical arcs are able to supply a large amount of heat to produce high temperatures. This allows melting of compounds that may not be possible with other furnaces, for example ruthenium, with a melting point of 2617 K. Using multiple arcs also lets the heat be supplied more uniformly around the sample, reducing hot spots that may lead to evaporation and a change in sample stoichiometry. This would be improved by using three or more arcs; however, rotating the hearth also helps with the heating uniformity, making this less necessary. Furthermore, cooling the hearth with water means that there will be a solid layer of sample surrounding the melt, which minimizes incorporations of impurities from the hearth material into the melt and hence the crystal. This water cooling is especially important when heating with electrical arcs, as the hearth must be conductive, ruling out standard high melting point crucible materials such as alumina. To pull the crystal from

the melt, a molybdenum seed rod is used as it has a very high melting point and is relatively non-reactive, which reduces the possibility of contamination from the seed rod into the crystal. If higher purity is necessary, a seed crystal of the desired material can be attached to the end of the molybdenum, preventing direct contact between the molten sample and the molybdenum. Finally, filling the chamber with argon prevents oxidation of the material at the high temperatures used for the growths.

A typical crystal growth proceeds as follows:

First, stoichiometric amounts of the pure elements are weighed out, aiming for a total sample mass of around 5 - 10 grams. Where possible, small previously melted pieces of the metals are used in preference to powders, as the temperature gradients caused by the electrical arc can cause the argon gas to flow rapidly, blowing some of the powders off the hearth and introducing errors in the stoichiometry. These weighed pieces are then placed on a water cooled copper hearth in a mono-arc furnace and melted together under an argon atmosphere. In this step, the sample is usually only left molten for several seconds before the arc is turned off and the sample allowed to cool, which minimizes the chances of the sample oxidizing from impurities in the argon or material evaporating from hot spots. The mono-arc furnace is used for this initial melt rather than the tri-arc as it is a simpler vacuum chamber that requires less effort to assemble, and the additional temperature uniformity of the tri-arc is unnecessary for this step. After melting, the sample is flipped and re-melted several times. This ensures that the sample is well mixed. If the sample is not flipped, the solid crust on the bottom touching the hearth would remain unmixed, again introducing uncertainty in the stoichiometry.

After the sample is thoroughly mixed and allowed to cool, it is transferred into the tri-arc furnace. At this stage, the vacuum chamber is pumped down to a pressure of 200 mBar or lower, backfilled with just over 1 bar of argon, and then evacuated and re-filled twice more to minimize oxygen contamination. It is then left with slightly over one atmosphere of argon flowing into the chamber and out through a check valve. This slight overpressure means that any vacuum leaks will result mainly in argon being forced out of the system rather than oxygen and nitrogen being pulled in. Through the entire growth, the argon flowing into the system first passes through a gettering furnace where it flows over titanium heated to 1100 K that will strip away any oxygen impurities. This whole process ensures that the oxygen impurity level in the furnace is very low, allowing intermetallic materials to be heated for hours without oxidizing.

Once the argon is flowing through the system, and the water supply to the copper hearth and seed rod is turned on, the sample is re-melted in the tri-arc furnace by applying current with arcs through the two stingers set up symmetrically on opposite sides of the sample, and the hearth rotation is turned on to ensure uniform heating. The seed rod is then lowered into the molten material about half a centimetre below the surface. The temperature of the melt is then increased until it wets up onto the surface of the seed rod, and the seed rod rotation is started, in the opposite direction of the hearth. This counter rotation minimizes the chance of concentrating impurities on a certain cooler side of the seed rod as the material solidifies. Once the rotation is set up, the seed rod is slowly pulled up out of the melt while adjusting the temperature to allow material to slowly solidify. The motor on our tri-arc setup can pull the seed rod at speeds between about 0.1 and 5 cm / hour, but we most commonly used a speed of about 2.5 cm / hour. Faster speeds allow a quicker growth, but can promote nucleation of additional polycrystalline grains, rather than growing a single crystal. In contrast, growing a material too slowly increases the potential for an unwelcome interruption to the growth caused, for example, by a power supply fluctuation, and also increases the amount of material lost to evaporation through the growth process, which can be particularly important if certain elements in the desired sample have a particularly high vapour pressure compared to the others.

While the seed rod is being pulled from the melt, the goal is to grow a large single crystal grain, rather than many smaller grains. Typically when the material first solidifies on the seed rod, multiple grains will be nucleated, as shown on the schematic in Fig. 2.2 (a). These grains will then grow outwards as the crystal is pulled from the melt, until they are forced out by another larger grain. Eventually, if the growth is controlled so that additional grains are not nucleated during the pulling process, a single grain will come to dominate the crystal. This process can be hastened by temporarily narrowing the crystal by increasing the temperature of the melt. Determining when the material has become a single crystal is often challenging. If the crystal structure is anisotropic, as in the case of tetragonal  $URu_2Si_2$ , the cross section can sometimes change from a circle to a noticeable ellipse when it becomes dominantly single grain, depending on the orientation of the crystal. Alternatively, facets sometimes appear on the sides that suggest it is a single grain. However, frequently neither of these features appear, despite the material being composed of a single grain. This can happen in highly symmetric crystal structures (cubic), and also if something like a tetragonal structure grows such that the structure is symmetric in the cross section (c-axis along the long side of the crystal, a-a plane in the cross-section). Therefore, often one must simply wait until a centimetre or two of material is



Figure 2.2: Schematic of the Czochralski crystal growth process. (a) shows the crystal being drawn out of the melt. The blue area represents the molybdenum seed rod that the material initially solidifies on. The gray represents the crystal that is being grown, with the black lines indicating boundaries between different crystal grains. The red region shows where the melt is solidifying to form the crystal, and the orange shows the molten material. (b) shows the crystal after separating from the melt.

solidified and hope that it has become a single crystal.

Once the sample is thought to be a single crystal, the melt can be cooled slightly to widen the crystal to the desired size. At this point, the crystal is left to grow out of the melt, while adjusting the current through the stingers as necessary to maintain the width of the crystal. Typically the current will need to be decreased as the growth proceeds. This is necessary because the size of the melt shrinks as material is solidified into the crystal, necessitating less power to achieve a given temperature in the smaller volume, and the distance from the solidification zone to the water cooled seed rod increases, necessitating a reduced melt temperature to allow solidification on the warmer crystal.

Once the melt is close to being used up, or the crystal is sufficiently long, the growth is ideally ended in a controlled fashion by slowly increasing the temperature of the melt. This will narrow the crystal, eventually separating it from the melt and ending the growth in a rounded point as shown in Fig. 2.2 (b). The current through the electrical arcs can then be shut off to allow the sample to cool in the argon. After cooling, the crystal is removed from the seed rod to be used for the desired experiments. Crystals grown with this method are typically 0.5 - 1 cm in diameter and 2 - 5 cm long, although growing somewhat larger or smaller are crystals is possible.



Figure 2.3: URu<sub>1.6</sub>Os<sub>0.4</sub>Si<sub>2</sub> crystal grown using the tri-arc furnace.

An example of a crystal of  $URu_{1.6}Os_{0.4}Si_2$  grown in the tri-arc furnace is shown in Fig. 2.3.

## 2.2 SQUID Magnetometry

Superconducting QUantum Interference Device (SQUID) magnetometry is an extremely sensitive method to measure the bulk magnetization of samples. This technique relies on Faraday's law of induction to produce a current in a loop of wire in response to a changing magnetic field. In this case, the changing magnetic field is caused by moving a magnetic sample with respect to a fixed loop of wire. The current through the wire is then monitored by a SQUID device in order to get a sensitive measure of the sample magnetization.

A SQUID consists of a superconducting loop of wire broken by one or more thin nonsuperconducting "weak links", to form what is called a Josephson junction. As first predicted by B. D. Josephson [153], supercurrent can tunnel through such a junction with zero applied voltage. The magnitude of the supercurrent will oscillate with the phase difference between the two superconductors as,  $I_s = I_c \sin \Delta \phi$ , where  $\Delta \phi$  is the phase difference and  $I_c$  is the critical current of the superconductor. This, combined with the requirement that the phase be single valued within any unbroken superconductor, gives rise to the behaviour of a DC SQUID where two Josephson junctions are set up in parallel. If a loop with flux penetrating through it is set up with such junctions, as shown in Fig. 2.4, then the current around the loop will oscillate as the magnetic flux through the loop is changed, with a period given by the flux quantum,  $\Phi_0$ , according to the equation,  $I = 2I_c |\cos(\pi \Phi/\Phi_0)|$ . This can be thought of as the current around the loop changing to keep the total flux equal to an integer multiple of  $\Phi_0$ .

Typically DC SQUID devices are operated with a bias current applied to the loop, and therefore the voltage, V, across the device will be given by [10],

$$V = \frac{R}{2} \sqrt{I_b^2 - [2I_c \cos(\frac{\pi\Phi}{\Phi_0})]^2},$$
(2.1)



Figure 2.4: Schematic of a DC squid showing the two Josephson junctions in blue, with a bias current of I, flux through the loop of  $\Phi$ , and voltage across the device of V.

where R is the net resistance of the two junctions in parallel and  $I_b$  is the bias current. Such a device therefore gives a sensitive way of converting magnetic flux to voltage for measurements.

A radio frequency (rf) SQUID works on a similar principle, but contains only a single Josephson junction. If such a single-junction loop is driven by an AC current, as by irradiation with microwaves, then the current-voltage curve will show discrete steps whose separation is given by integer multiple of  $f\Phi_0$ , where f is the frequency of the AC current [154]. If an LC resonant circuit is inductively coupled to the rf SQUID loop, the resonant behavior of the LC circuit, and hence the output voltage, will vary with the flux through the SQUID, again allowing magnetic flux to be converted to an output voltage [10].

For the measurements in this thesis, a Quantum Design MPMS XL-3 magnetometer was used for all magnetization measurements. This instrument uses an rf SQUID coupled to a second order gradiometer setup of pickup loops, as shown in Fig. 2.5. To measure the magnetic moment of a sample, it is placed in a non-magnetic plastic straw and moved through the pickup loops in a controlled fashion, thereby changing the magnetic field passing through the loops and generating a current that can be converted into a voltage by the SQUID. If there are background fields that are relatively spatially constant, the current induced by them in the top and bottom loop will have the opposite sign compared to that induced in the central two loops, and hence the background current will sum to zero. By contrast, as a result of the proximity of the sample to the loops, the current induced by the sample will not cancel out, and will instead vary reproducibly



Figure 2.5: Schematic of the second order gradiometer setup found in our magnetometer. The pickup loops are shown in black and create a field through an rf SQUID with a single Josephson junction. The sample, in red, is contained inside a plastic straw which is non-magnetic, and is swept through the pickup coils by a motor that is connected to the straw by a long non-magnetic rod.

with sample position. Fitting this expected position dependence therefore gives the second-order gradiometer setup substantial signal to noise improvement over a single pickup loop.

The result of such a measurement is the magnetic moment, m, of a sample in emu. Often, we want to know the intrinsic magnetization, M, of a sample per volume, v, or the susceptibility,  $\chi = M/H$ , where H is the magnetic field. This is expressed as M = m/v (in emu / cm<sup>3</sup>) or  $4\pi M = m/v$  (in Gauss). One complication that arises in measurements where the susceptibility is large is that the field produced by the sample, called the demagnetizing field, can be an appreciable fraction of the applied field,  $H_{ext}$ , and hence the total field inside the sample will be significantly different from the applied field. For irregularly shaped objects, the demagnetizing field will not be constant across the entire interior, and inferring sample properties from bulk magnetization measurements becomes complicated. However, for certain shapes such as ellipsoids, symmetry creates a constant demagnetizing field and the effective internal field can be expressed as,

$$H_{eff} = H_{ext} - 4\pi N. \tag{2.2}$$

This equation uses CGS units where H is expressed in Oe, and N is the demagnetization factor.

In three special cases the demagnetization factor is easy to determine; it is 0 for an infinite cylinder with fields parallel to the long axis, 1 for fields applied perpendicular to an infinite plate, and 1/3 for a sphere. In the case of a general ellipsoid, the calculation is lengthy but has been worked out carefully in the literature [155]. While the demagnetizing field is not generally constant across the sample for shapes other than an ellipsoid, it is common to determine an average field and hence define an effective demagnetization factor that can be used in Eq. 2.2. Such average values have been worked out for arbitrary rectangular prisms and can be found in Ref. [156].

## 2.3 Muon Spin Rotation

Muon spin rotation ( $\mu$ SR) is a technique that can sensitively measure the internal field of a sample. It can probe the magnitude of the internal field, the shape of the field distribution, the volume fraction taken up by different magnetic (or non-magnetic) phases, and dynamics on the time scale of nanoseconds to several microseconds. As such,  $\mu$ SR can be very useful in the study of interesting magnetic systems.

This technique relies on the Larmor precession of muons in a magnetic field. Muons are fundamental particles that in many ways behave like a heavier version of an electron. They have a spin of  $\frac{1}{2}$ , a charge of  $\pm e$  (the positive muon is usually used for  $\mu$ SR), and a mass approximately 207 times the electron mass. This mass and charge combine to give muons a gyromagnetic ratio of  $\gamma_{\mu} = 135.54$  MHz / T, which is substantially smaller than that of an electron. This quantity sets the frequency at which a muon will precess in an applied field as  $\nu = \gamma_{\mu} |\mathbf{B}_{loc}|$ , where  $\nu$  is the frequency and  $\mathbf{B}_{loc}$  is the local field at the position of the muon [157].

Despite the similarities with electrons, muons are unlike electrons in one crucial manner: they are unstable particles and decay with a characteristic lifetime of  $\tau_{\mu} = 2.197 \ \mu s$  into an electron (from a negative muon) or positron (from a positive muon) and a pair of neutrinos. As a result of parity violation in the weak-force decay of muons, the positron or electron will be preferentially emitted in the direction the muon spin is pointing when it decays. The physics of the weak interaction sets this preference as  $W(\theta) \propto [1 + a \cos \theta]$ , where W is the probability for the positron to be emitted at an angle  $\theta$  relative to the muon spin direction, and a is an energy dependent asymmetry parameter [157]. Over all positron energies, we expect an average direction asymmetry of 1/3. This asymmetry allows the average direction of muon spins in a sample at any given time to be determined in a relatively simple way by tracking which direction the positrons or electrons are emitted, even with a small number of muons [157].

The first step of a  $\mu$ SR experiment is the production of a muon beam. As positive muons are most frequently used in  $\mu$ SR experiments, the following discussion will focus on them rather than both positive and negative muons. At TRIUMF laboratory in Vancouver, where the experiments discussed in this thesis were conducted, these are produced using a hydrogen ion accelerator. H<sup>-</sup> ions are accelerated up to an energy of 500 MeV by a cyclotron, stripped of their two electrons to leave a bare proton, and then collided into a target made of light nuclei, often beryllium or carbon. These collisions produce pions ( $\pi^+$ ) which quickly decay into a muon and a muon neutrino,  $\pi^+ \rightarrow \mu^+ + \nu_{\mu}$  [158]. In most cases, surface muons are used, which come from pions that decay at rest on the surface of the target. These decays emit only positive muons, as negative muons would interact with nuclei and not leave the target. As a result of maximal parity violation in the weak-process decay, these muons will be almost entirely polarized with their spin oriented anti-parallel to their momentum [159]. Furthermore, surface muons arising from pions decaying at rest are mono-energetic with a relatively small momentum of 29.8 MeV / c. This is useful as it means that muons will stop within a short distance in a sample, around 0.3 mm for copper [159], avoiding the need for large samples.

Once produced, the muons will pass down the beamline and be steered by various magnets to hit the sample of interest. Beamlines at TRIUMF include a momentum selector consisting of crossed electric and magnetic fields shortly before the sample. This has the effect of filtering out any positrons coming from the target or from a small number of muons that decayed in flight, and can be used to tune the beam momentum to a certain value as, for example, if one wished to prevent muon penetration through a thin sample. Furthermore, this momentum selector can, by setting the magnetic field to a high value, be used to rotate the direction of the muon spin prior to hitting the sample. This gives rise to two typical modes for the  $\mu$ SR experiments: Spin Rotated (SR) mode where the muon spins are rotated to an angle between 70 and 90 degrees from their momentum vector (x - direction), and Non Spin Rotated (NSR) mode where the muon spins are left pointing essentially antiparallel to their momentum vector (z - direction). These two modes are useful if one wishes to probe the magnetic fields in different directions in a sample, or for measurements in large magnetic fields. As muons are charged particles, they will feel a Lorentz force,  $\mathbf{F} = e\mathbf{v} \times \mathbf{B}$ , when they are in a magnetic field. If a large field is applied that is not parallel to the muon momentum, the Lorentz force will change the muon beam direction, possibly causing it to miss the sample entirely. Therefore, large fields are in practice only applied in parallel to the incident muon beam and the SR mode must be used if one wishes to perform measurements with a field applied perpendicular to the incident muon spin.

Once the muon beam hits the sample, muons will rapidly thermalize and come to rest at a "muon stopping site". To allow unique determination of the time interval that a muon is in a sample, the muon beam intensity is usually set such that only one muon will be stopped in the sample at a time; this is backed up by electronic gating used to throw away any events that arise when two or more muons are simultaneously stopped in the sample. As a result of the positive charge of surface muons, the muon stopping sites typically occur at positions of high electron concentration in the sample. For oxide or fluoride materials, this is near oxygen or fluorine atoms owing to their large electronegativity, but in other materials it is often not obvious where muons are likely to stop. To accurately determine where these muon stopping sites are, it is necessary to perform density functional theory calculations to determine the position of electrostatic potential minima where the muons will come to rest [160]. Such minima are often not unique in a crystal and there are instead two or more metastable positions where muons may stop. In these cases, the multiple stopping sites will give rise to multiple signals in the  $\mu$ SR data that must be accounted for. This sort of analysis can be challenging, especially as the presence of the muon itself will perturb the electronic structure, changing the position of the minima. In many cases, knowledge of the exact muon stopping site is not necessary to extract useful information from the results, and such detailed analysis is avoided.

Wherever muons eventually stop, they will feel a field  $B_{loc}$  given by the sum of any applied external field and the internal field produced by magnetism in the sample. This field will cause the spin of the muon to precess with a frequency of  $\nu = \gamma_{\mu} |\mathbf{B}_{loc}|$ , as stated above. Once the muon decays, the emitted positron is observed by detectors generally sitting on either side of the sample. For a NSR  $\mu$ SR experiment these detectors are arranged in line with the incident muon momentum, on the front (F) and back (B) of the sample. The time difference between when the muon entered the sample, determined by a transparent (to muons) counter placed in the muon beam before the sample, and when the positron was detected, determines how long the muon had to precess in the sample. By observing the sequential decay of many muons that stop and decay in the sample one after another, histograms of the number of counts as a function of time, in the F and B counters, can be constructed. These histograms will contain information about both the muon lifetime and the z component (parallel to the incident momentum) of the muon spin polarization, and have the form,

$$N_{B,F}(t) = N_0 e^{t/\tau_{\mu}} (1 \pm A_{B,F} P_z(t)) + B_{B,F}.$$
(2.3)

Here,  $N_0$  is a normalization factor taking into account the total number of decays, A is the total measured muon asymmetry, taking into account experimental factors as well as the physics of the positron emission, P(t) is the time-dependent muon polarization, B is a time-independent background rate, and the  $\pm$  as well as the F and B indices refer to the front or back detectors.

Since in  $\mu$ SR experiments we are interested in the time evolution of the muon spin polarization, we compute the asymmetry between the front and back counters as,

$$A(t) = AP_z(t) = \frac{(N_B(T) - B_B) - \alpha(N_F(t) - B_F)}{(N_B(t) - B_B) + \alpha(N_F(t) - B_F)}.$$
(2.4)

Here, A is the total asymmetry of the signal, and  $\alpha$  is a parameter introduced to account for experimental differences between the F and B counters caused mainly by differing efficiencies and solid angle coverage. Equation 2.4 assumes  $A_B$  and  $A_F$  are the same, which is usually a good assumption and has been used throughout this thesis. Small differences from one come from the details of the decay asymmetry distribution of positrons and how it depends on the energy. If, for instance, there is substantially more absorbing material in front of one of the detectors, it will preferentially detect high energy positrons, changing the asymmetry in that counter.

The asymmetry in Eq. 2.4 is directly proportional to the muon polarization function and therefore contains information about the local magnetic field distribution. It is the quantity usually plotted as the result of  $\mu$ SR experiments. The procedure for SR measurements is very similar, except that detectors to the right and left of the sample, or above and below (or all four), are used instead of forward and back counters, and therefore the x or y components of the polarization function ( $P_x$  or  $P_y$ ) are probed.

Given a distribution,  $D_v(\mathbf{B}_{loc})$ , of local fields, the x and z components of the muon polarization can be computed as shown in equations 2.5 and 2.6 [157].

$$P_x(t) = \int \left\{ \left(\frac{B_{loc}^x}{B_{loc}}\right)^2 + \left[1 - \left(\frac{B_{loc}^x}{B_{loc}}\right)^2\right] \cos(2\pi\nu_\mu t) \right\} D_v(\mathbf{B}_{loc}) d^3 \mathbf{B}_{loc}$$
(2.5)

$$P_z(t) = \int \left\{ \left(\frac{B_{loc}^z}{B_{loc}}\right)^2 + \left[1 - \left(\frac{B_{loc}^z}{B_{loc}}\right)^2\right] \cos(2\pi\nu_\mu t) \right\} D_v(\mathbf{B}_{loc}) d^3 \mathbf{B}_{loc}$$
(2.6)

If a single crystal sample has a fixed internal field direction at an angle  $\theta$  to the incident muon momentum, then Eq. 2.6 can be integrated to,

$$P_z(t) = \cos^2 \theta + \sin^2 \theta \cos(2\pi\nu_\mu t).$$
(2.7)

This will have the fixed value of 1 for  $\theta = 0$ , representing a net field parallel to the incident muon beam, and  $P_z(t) = \cos(2\pi\nu_\mu t)$  for  $\theta = \pi/2$ , representing a perpendicular field. This demonstrates that  $\mu$ SR measurements of a sample in a constant applied field, or samples in which there is perfect static magnetic order, will show an oscillating signal that is undamped, or only slightly damped due to nuclear dipole moments. In real systems, slight variations in the magnitude of the field across the sample, or fluctuations in the magnetic order, will cause a finite width to the field distribution. This will result in a damping term being added to Eq. 2.7, often approximated by multiplying this by an exponential,  $e^{-\lambda t}$ , or a Gaussian,  $e^{-0.5(\sigma t)^2}$ , where  $\lambda$  and  $\sigma$  are relaxation rates. Furthermore, if there are multiple muon sites, each with a different fixed  $\mathbf{B}_{loc}$ , then the net polarization function will be a sum of terms like Eq. 2.7, resulting in a signal with multiple frequencies.

By contrast, if the local field has a random Gaussian distribution, as expected for a dense array of randomly oriented static moments, the polarization function, called the Kubo-Toyabe function, works out to be [161],

$$P_z(t) = \frac{1}{3} + \frac{2}{3}(1 - \Delta^2 t^2)e^{-0.5\Delta^2 t^2/2},$$
(2.8)

where  $\gamma_{\mu}\Delta$  is the width of the field distribution.

Equations 2.7 and 2.8 demonstrate two possibilities for the polarization function measured by a  $\mu$ SR experiment. There are of course countless other possibilities which could be determined by evaluating Eq. 2.6 for any assumed  $D_v(\mathbf{B}_{loc})$ . While  $\mu$ SR experiments essentially measure the field distribution at the various muon sites, it is very difficult to directly compute what the magnetic behaviour of a sample is from a given field distribution. Therefore, analysis of  $\mu$ SR data typically involves generating expected polarization functions from physical models of the magnetic behaviour that could exist in the sample, comparing them to the measured data, and then iterating until satisfactory agreement is found. If different regions of the sample show different magnetism, this can necessitate multiple different components being added together to determine the overall polarization function. For example, if a fraction, F, of a sample is magnetically ordered with a field given by Eq. 2.7, and the rest shows no internal field  $(P_z(t) = 1)$ , then the overall signal will be a sum of these components,  $P_z^{tot} = F \cos(2\pi\nu_{\mu}t) + (1-F)$ , assuming  $\theta = \pi/2$ . In the general case, looking at the ratio of the amplitude of different signals can give a measure of the volume fraction taken up by different phases in an inhomogeneous sample. This feature of muons being a volume sensitive real-space probe of magnetism makes it a good complement to recipricol space techniques such as neutron scattering that average signals over the entire sample volume.

## 2.4 Neutron Scattering

For decades neutron scattering has been a leading technique used to investigate crystalline systems. This technique is often the best method to determine the magnetic and crystal structure of materials, and can yield important information about structural excitations such as phonons, as well as magnetic excitations such as magnons and crystal field excitations. The importance of this technique is highlighted by the 1994 Nobel Prize in Physics that was awarded to Clifford Shull and Bertram Brockhouse for their early development of neutron diffraction and spectroscopy respectively [162].

Neutron scattering makes use of neutron beams that are produced either by fission in the core of a nuclear reactor, or by spallation from a source such as the SNS at Oak Ridge National Laboratory, which collides high energy protons with a mercury target to produce a spray of neutrons and other byproducts. Such neutrons can be moderated by passing them through water at room temperature to yield thermal neutrons with an energy in the range of tens of meV and corresponding wavelengths of a few Angstrom. This energy and wavelength is particularly well suited to the study of condensed matter systems, as the wavelength is similar to typical interatomic spacings, allowing neutrons to be used for conventional diffraction, and the energy is similar to that of many excitations, allowing these to be accurately probed [162].

Neutrons, being uncharged particles, interact only weakly with matter, primarily via the strong nuclear force, although as the neutron has a spin of 1/2, it does couple to magnetism as well. Therefore, by contrast to X-rays or other electromagnetic waves, neutrons interact primarily with the nuclei of atoms rather than the electron cloud surrounding them, interacting with the electrons magnetically only if unpaired spins are present. As neither the magnetic nor nuclear interaction depends directly on the charge of the atom, the interaction strength does not continuously increase with the size of the atom, as is the case for X-rays, but rather depends on details of the nuclei through the nuclear scattering length, b, and on the magnetic scattering length, p. The nuclear scattering length does not vary systematically as the size of the nucleus is



Figure 2.6: Coherent neutron scattering length for many nuclei. All data is taken from Ref. [163].

increased, and, as demonstrated by Fig. 2.6 which shows the thermal neutron scattering lengths for most nuclei, can even vary substantially for different nuclei of the same element [163]. Of particular importance to the study of condensed matter systems is that the scattering length and cross sections of oxygen and other light elements is quite similar to that of heavier elements. This means that neutron scattering can be sensitive to the positions of both light elements and heavy elements, which allows refinement of crystal structures that may not be possible with X-ray techniques such as proteins and other biological molecules where the hydrogen positions are important. Furthermore, the magnetic scattering length, p, of a neutron scattering from an atom with a magnetic moment  $\mu$  expressed in units of  $\mu_B$ , is  $p = 2.7\mu$  fm. For typical magnetic moments of  $\approx 1$  to 10  $\mu_B$ , this is comparable to the nuclear scattering length, which means that for neutrons, magnetic scattering is of similar intensity to nuclear scattering [162].

To determine how a neutron beam will interact with a sample, the quantity of interest is the differential scattering cross section. As neutrons are only weakly interacting, this can be determined by Fermi's Golden Rule as [162],

$$\frac{d^2\sigma}{d\Omega_f dE_f} = \frac{k_f}{k_i} \left(\frac{m_n}{2\pi\hbar^2}\right)^2 |\langle \mathbf{k_f} \lambda_f | V | \mathbf{k_i} \lambda_i \rangle|^2 \delta(\hbar\omega + E_i - E_f)$$
(2.9)

In this equation,  $\Omega_f$  is the solid angle the neutron is scattered to,  $E_{f,i}$  are the final and initial energies of the neutron,  $k_{f,i}$  are the final and initial momenta of the neutron,  $m_n$  is the neutron mass,  $\hbar$  is the reduced Planck constant,  $\lambda_{f,i}$  are the final and initial states of the sample, V is the interaction potential, and  $\hbar\omega$  is the energy change of the sample. The product in the center of this equation can, for nuclear scattering, be expanded as,

$$\langle \mathbf{k}_{\mathbf{f}} \lambda_f | V | \mathbf{k}_{\mathbf{i}} \lambda_i \rangle = V(\mathbf{Q}) \langle \lambda_f | \sum_l e^{i\mathbf{Q} \cdot \mathbf{r}_1} | \lambda_i \rangle, \qquad (2.10)$$

where  $\mathbf{Q} = \mathbf{k_f} - \mathbf{k_i}$  is the momentum change,  $r_l$  are the positions of the nuclei, and  $V(\mathbf{Q}) = b(2\pi\hbar^2/m_n)$ . This shows how the nuclear scattering length, b, comes into the expression for the differential cross section [162].

For magnetic scattering, the equations are in general more complicated, as the scatters can no longer be treated as point objects. In this case, the general differential cross section is written as,

$$\frac{d^2\sigma}{d\Omega_f dE_f} = \frac{k_f}{k_i} \sum_{i,f} P(\lambda_i) |\langle| \sum_l e^{i\mathbf{Q} \cdot \mathbf{r}_1} U_l^{s_i s_f} |\lambda_i\rangle|^2 \delta(\hbar\omega + E_i - E_f).$$
(2.11)

Here, the  $U_l^{s_i s_f}$  is the scattering amplitude between spin states  $s_i$  and  $s_f$ . Additional details on the calculation of differential cross sections can be found in Ref. [162], chapter 2.

In the case of elastic neutron scattering, no energy is transferred to or from the lattice, and neutrons will diffract from periodic structures as expected for any wave. Taking a crystal to be a series of atomic planes separated by a distance d, incident neutron plane waves will scatter from the planes and interfere constructively and destructively with each other. Constructive interference occurs when the incidence angle is such that the difference in path length for neutrons scattering off adjacent planes is equal to an integer multiple of the neutron wavelength. This gives the scattering condition commonly called Bragg's Law [164],  $n\lambda = 2d \sin \theta$ , from which the expected position of sharp scattering peaks for a given crystal structure can be derived. This condition can also be expressed in terms of the momentum transfer as  $|\mathbf{Q}| = \frac{4\pi \sin(\theta)}{\lambda}$ .

For inelastic neutron scattering, the energy transfer is non-zero, and both the energy and momentum differences between the incoming and outgoing neutrons must be considered. In this case, the energy transfer is given by  $\hbar\omega = E_i - E_f = \frac{\hbar^2}{2m_n}(k_i^2 - k_f^2)$ , and conservation of energy and momentum somewhat restricts the range of momentum and energy transfers that can be measured.

The two most common instrument types used for inelastic neutron scattering measurements are triple-axis and time of flight spectrometers. Both of these have various advantages and disadvantages which will be discussed below.

A triple-axis instrument briefly consists of a neutron source, a monochromator, a sample



Figure 2.7: Schematic of a triple axis neutron spectrometer. The neutron path is shown in red.

goniometer, an analyzer, and a neutron detector. A schematic of this setup is shown in Fig. 2.7. The neutron beam produced by the source, which will have a range of energies given by the Maxwell-Boltzmann distribution appropriate for the temperature of the moderator, first hits a variable monochromator, which selects an incident energy. This is commonly done by scattering the incident beam off of a crystal with known lattice parameters, such as a pyrolitic graphite monochromator. At any given scattering angle, there will one defined wavelength that satisfies Bragg's law for the known lattice parameters of the monochromator crystal, as well as weaker diffraction from integer multiples of this wavelength that can often be ignored, or filtered out by a second monochromator. Therefore, the neutron beam coming from such a monochromator will nominally have a single defined energy,  $E_i$ , that can be varied by changing the angle of the monochromator. This monochromatic beam of neutrons then shines on the sample, which will diffract the beam for appropriate incident angles onto an analyzer crystal, which is similar to the monochromator. The analyzer crystal can then be rotated to select a given final neutron energy,  $E_f$ .

The combination of a monochromator and analyzer allows selection of a given energy transfer,  $\Delta E = E_f - E_i$ . Rotation of the sample goniometer  $\theta - 2\theta$  angle allows one to vary the momentum transfer, **Q**. Therefore, this three-axis setup in principle allows measurement of all kinematically allowed energy and momentum transfers, although rotation limits on the goniometers will set practical limits to what can be measured on any given instrument. This freedom allows one to map any desired excitation throughout reciprocal space. A triple axis spectrometer has the advantage of potentially very high resolution in  $\Delta E$  and  $\mathbf{Q}$ . However, as each individual point of  $\Delta E - \mathbf{Q}$  space must be individually measured, getting a map of excitations across a broad section of space will be a time consuming process and is generally not practical given the limited beam time that can be devoted to a given experiment.

This is where the other technique, whose widespread adoption has benefited from recent advances in detector technology and computing power, comes in: time of flight neutron scattering. In this technique, instead of using an analyzer after the sample to discriminate the energy at one given angle, the flight time of scattered neutrons between the time they exit the sample and the time they hit a large area detector a known distance away is used to determine their momentum and hence energy. This method is best suited for use with spallation neutron sources as opposed to reactor sources. This is because spallation sources produce pulses of neutrons, compared to a continuous beam coming from reactor sources. This lets one define an arrival time for neutrons based on when the pulse arrives, allowing accurate determination of the flight time without having to individually count the arrival time of each neutron. However, a continuous beam from a reactor source can be converted into a pulsed beam, with some loss in intensity, by using a chopper. This device consists of a rotating neutron-absorbing disc with a curved groove that will periodically allow neutrons through that have a given incident energy. Using a series of choppers will both result in a well defined incident energy, and turn a continuous source into a pulsed source that can be used for a time of flight instrument.

Using a large area detector with the time of flight method allows many momentum and energy transfer points to be measured simultaneously. To obtain a four dimensional map (three dimensions of  $\mathbf{Q}$  and one of  $\Delta E$ ) of the excitations, only one parameter needs to be changed, the angle of the sample relative to the incoming beam. This allows much quicker measurements and therefore allows practical measurement of excitations over broad regions of reciprocal space. This large advantage over triple axis instruments is paid for by two main disadvantages. First, the energy and Q resolution of time of flight instruments is inherently worse than that of triple axis instruments. This is because the area detectors have a finite pixel size which limits their angular resolution, compared to the movable single detector used for triple axis measurements, where slits can be used to achieve very angular resolution. Furthermore, the detectors used for time of flight measurements have a finite response time, which limits the resolution for the flight time measurement and hence the energy resolution. Secondly, these experiment result in a very large four dimensional data set that can be computationally difficult to handle, in contrast to a series of simple two dimensional data sets produced by triple-axis measurement. This second limitation is becoming less and less important as computing power improves but it still should be considered. If the broad energy and Q-space coverage of the time of flight technique is not needed, these drawbacks often make it more appropriate to fall back onto triple axis measurements.

# Chapter 3

# $URu_2Si_2$

# 3.1 Summary of Publication I: $\mu$ SR studies of Fe and Os doped URu<sub>2</sub>Si<sub>2</sub>

As discussed in Section 3, iron and osmium are the only two dopings known to increase the transition temperature of  $URu_2Si_2$  [102, 103], aside from the complicated case of neptunium. Prior to starting this work, it was not known whether this increase came along with a change in the ground state from hidden order to some other magnetic state. It was therefore of substantial interest to study these materials with a local magnetic probe to determine the ground state magnetism.

In this paper, we present  $\mu$ SR and magnetometry measurements of both Fe and Os doped URu<sub>2</sub>Si<sub>2</sub>. The  $\mu$ SR measurements allow us to determine whether there is long range magnetic order in the ground state, and what volume fraction this order takes up, while magnetometry measurements allow us to initially characterize the transition temperature and compare it to previous work.

Our  $\mu$ SR results on the iron doped samples show oscillations indicating long range magnetic order that, for doping levels between 5 and 30%, exists in over 90% of the sample volume at 2 K. This demonstrates that the magnetic order is coming from the bulk of the sample and is not an impurity effect as was seen in early measurements of "pure" URu<sub>2</sub>Si<sub>2</sub>. The higher doped samples show a smaller volume fraction that we attribute to non-magnetic impurities from chemical phase separation during the crystal growth of such highly doped samples. The lowest doping, 1% iron, shows a substantially reduced volume fraction of about 60% at 2 K, and shows a measured transition temperature from  $\mu$ SR that is 1.5 K lower than that measured by magnetometry. We attribute this to the sample being in a mixed hidden order - antiferromagnetic state that gives way to a pure hidden order state in a small temperature region near 17 K, similar to what is seen for pure URu<sub>2</sub>Si<sub>2</sub> close to the critical hydrostatic pressure [75].

For all samples, the signal seen is very similar to that of URu<sub>2</sub>Si<sub>2</sub> under hydrostatic pressure [74], with the significant differences that our measured internal field evolves with doping, compared to a pressure-independent internal field measured above the critical hydrostatic pressure, and we see evidence for two separate internal fields, compared to only one under hydrostatic pressure. Both of these might be explained by iron doping changing the likely muon stopping sites, moving them closer or further away from the uranium atoms and therefore modifying the internal field they see, but more work is needed to understand this effect. Despite this, the iron doped samples behave very much as would be expected from a chemical pressure argument looking at the reduction in the lattice volume with iron doping.

 $\mu$ SR measurements on the osmium doped samples show very similar behaviour; oscillations indicate long range magnetic order over > 95% volume fraction of all samples (5 - 20% doping), and the internal field is very similar to that of the iron doped samples. We do not see evidence for a second internal field, although the oscillation line-width is larger for the osmium doped samples which may obscure the presence of a second field. The similarity of the osmium doped measurements to the iron doped measurements presents somewhat of a puzzle, as osmium increases the lattice volume leading to a negative chemical pressure, and therefore chemical pressure arguments cannot explain the appearance of the antiferromagnetism. Our magnetometry measurements suggest that this may be a result of hybridization increasing for both osmium and iron doping; however, another explanation is that hidden order is a finely tuned state and pushing the lattice in either direction will destroy it. More work is needed to untangle these two possible effects.

Publication I: "Antiferromagnetism and Hidden Order in Isoelectronic Doping of URu<sub>2</sub>Si<sub>2</sub>",
M. N. Wilson, T. J. Williams, Y.-P. Cai, A. M. Hallas, T. Medina, T. J. Munsie, S. C. Cheung, B. A. Frandsen, L. Liu, Y. J. Uemura, and G. M. Luke. Physical Review B 93, 064402 (2016).

Reproduced from Ref. [1] with permission, copyrighted by the American Physical Society.

### Author Contributions:

- Experimental Concept: M. N. Wilson, T.J. Williams, and G.M. Luke.
- Sample Preparation: M. N. Wilson, T.J. Williams, and G.M. Luke.
- Magnetometry Experiments: M.N. Wilson, and G.M. Luke.
- μSR Experiments: M.N. Wilson, Y.-P. Cai, A.M. Hallas, T. Medina, T.J. Munsie, S.C. Cheung, B.A. Frandsen, L. Liu, Y.J. Uemura, and G.M. Luke.
- Data Analysis: M.N. Wilson, and G.M. Luke.
- Manuscript: M.N. Wilson, T.J. Williams, A.M. Hallas, B.A. Frandsen, and G.M. Luke.

#### PHYSICAL REVIEW B 93, 064402 (2016)

#### Antiferromagnetism and hidden order in isoelectronic doping of URu<sub>2</sub>Si<sub>2</sub>

M. N. Wilson,<sup>1</sup> T. J. Williams,<sup>2</sup> Y.-P. Cai,<sup>1</sup> A. M. Hallas,<sup>1</sup> T. Medina,<sup>1</sup> T. J. Munsie,<sup>1</sup> S. C. Cheung,<sup>3</sup> B. A. Frandsen,<sup>3</sup> L. Liu,<sup>3</sup> Y. J. Uemura,<sup>3</sup> and G. M. Luke<sup>1,4</sup>

<sup>1</sup>Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, Canada L8S 4M1

<sup>2</sup>Quantum Condensed Matter Division, Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

<sup>3</sup>Department of Physics, Columbia University, New York, New York 10027, USA

<sup>4</sup>Canadian Institute for Advanced Research, Toronto, Ontario, Canada M5G 1Z7

(Received 28 November 2015; published 1 February 2016)

We present muon spin rotation ( $\mu$ SR) and susceptibility measurements on single crystals of isoelectronically doped URu<sub>2-x</sub>T<sub>x</sub>Si<sub>2</sub> (T = Fe, Os) for doping levels up to 50%. Zero field (ZF)  $\mu$ SR measurements show long-lived oscillations demonstrating that an antiferromagnetic state exists down to low doping levels for both Os and Fe dopants. The measurements further show an increase in the internal field with doping for both Fe and Os. Comparison of the local moment-hybridization crossover temperature from susceptibility measurements and our magnetic transition temperature shows that changes in hybridization, rather than solely chemical pressure, are important in driving the evolution of magnetic order with doping.

DOI: 10.1103/PhysRevB.93.064402

#### I. INTRODUCTION

Heavy fermion systems frequently exhibit interesting electronic ground states arising from complex hybridization between conduction electrons and localized f electrons [1]. Compounds containing uranium are particularly interesting as the Coulomb interaction, spin-orbit coupling, and 5 f electron bandwidth are all of comparable energies, making exotic ground states possible [2]. A notable example of such a ground state is the hidden order (HO) arising in URu<sub>2</sub>Si<sub>2</sub> below  $T_0 = 17.5$  K that was first studied in 1985 [3,4]. The order in this state is termed "hidden" as, despite more than two decades of study, the order parameter for the 17.5 K transition has not yet been conclusively identified [2].

Early neutron scattering studies indicated that this state was antiferromagnetic with a moment of 0.02–0.04  $\mu_B$  per uranium [5,6]. However, other studies found unusual properties that could not be explained by simple antiferromagnetism, such as a gap opening up over a large portion of the Fermi surface indicated by specific heat [7] and infrared spectroscopy [8] measurements. Furthermore, the measured antiferromagnetic moment is too small to explain the 0.2*R*ln2 per f.u. entropy change across the transition determined from specific heat measurements [7].

Subsequent neutron scattering measurements conducted under applied hydrostatic pressure demonstrated a first-order transition into a large moment antiferromagnetic state (LMAF) with a moment of 0.4  $\mu_B$  [9] that occurs at a critical pressure of 0.5-0.8 GPa [10]. µSR measurements under applied pressure have also confirmed this first-order transition to the LMAF state, and demonstrate no pressure dependence of the internal fields from 0.5 to 1.5 GPa [11]. In addition,  $\mu$ SR [12,13] and NMR measurements [14] show that the weak antiferromagnetic moment seen at ambient pressure can be explained by a small phase separated volume fraction of the pressure-induced antiferromagnetic state coexisting with the hidden order state. It is now widely accepted that this low moment antiferromagnetism is extrinsic to the hidden order state and is caused by inhomogeneous strain in measured crystals [15].

The origin of the entropy change in URu<sub>2</sub>Si<sub>2</sub> seen from heat capacity measurements has recently been explained by a gap opening in the spin excitation spectrum at the transition, and does not require the presence of weak antiferromagnetism [16]. This gap is equivalent to the Fermi surface becoming gapped, and angle-resolved photoemission spectroscopy (ARPES) measurements [17,18] indicate that this gap arises from hybridization of the conduction band with the uranium 5f electrons. Scanning tunneling microscopy (STM) measurements [19] have lent support to this idea by observing a band splitting below the hidden order transition. However, these results have been disputed, with other STM researchers [17] claiming that the hybridization gap opens well above  $T_{\rm HO}$  and hence cannot explain the hidden order state. This leaves the importance of the hybridization gap as one of the many unanswered questions of URu2Si2.

Despite these significant advances in the understanding of HO a viable theory has not yet been accepted to explain this state, although numerous theories have been advanced over the years (see Ref. [20] for a recent overview). In order to constrain such theories it is advantageous to further study the hidden order state through various experimental perturbations. One such perturbation that has been extensively applied to URu<sub>2</sub>Si<sub>2</sub> is chemical doping. Previous studies have found that doping of the silicon site has only a weak effect on the electronic state which may be explained by a chemical pressure effect [21,22], while doping of the uranium [23,24] and ruthenium [25-28] sites cause much more dramatic changes in the behavior. This indicates that the electronic ground state depends much more strongly on d-f electron hybridization than it does on sp-fhybridization [22]. However, U-site doping is complicated as there is competition between dilution of the magnetic U atom, changes in lattice parameters, and hybridization all occurring with doping. This makes Ru-site doping interesting to study as it is a potentially simpler avenue to explore the effect of changing hybridization on the magnetic states.

Rhodium and rhenium doping are two cases that have been well studied, both of which suppress the HO state before 5% doping. However, the ground states that emerge after the suppression are distinctly different. For Re doping the

2469-9950/2016/93(6)/064402(9)

#### M. N. WILSON et al.

HO transition is suppressed by a 5% doping level, and above 7.5% doping a non-Fermi liquid ferromagnetic state emerges that persists up to high doping levels [29]. By contrast, Rh suppresses HO by 2% doping at which point a LMAF state emerges, which is in turn suppressed by 4% doping [30]. Above this doping level no magnetically ordered state is observed [30].

The Rh doped system has been a particularly valuable avenue to study the competition between the LMAF and HO states in the URu<sub>2</sub>Si<sub>2</sub> system, as the doping allows the transition to be studied without the experimentally challenging aspects of applied external pressure. This has allowed productive studies of the high field behavior of the HO state (see Ref. [2] and references therein), as well as proposed identification of universal parameters that cause the transition between the HO and LMAF states [30].

Despite the potential insights gained by studying Re and Rh doping, the interpretation of results from both of these systems is made more difficult because these dopings change multiple potentially important parameters simultaneously. In particular, doping of Re or Rh will change the number of electrons in the system, the d-f hybridization, and the lattice constants of the system. In order to more easily understand the mechanisms behind the transitions between HO and other phases it is beneficial to have systems that change as few parameters as possible in order to isolate their effects. This makes the isoelectronic dopings, osmium and iron, interesting to study as one does not have to consider the effect of changing electron numbers in this system.

Fe doping of URu<sub>2</sub>Si<sub>2</sub> has been studied for polycrystalline samples by Kanchanavatee et al. [31]. This work demonstrated that the full range of compositions  $URu_{2-x}Fe_xSi_2$  from x = 0to 2 can be produced, and that doping results in a monotonic decrease of the lattice parameters with no evidence for a change of structure. Furthermore, the temperature-doping phase diagram measured by bulk probes (specific heat, magnetization, and resistivity) shows an increase in transition temperature as a function of doping up to a maximum of 40 K. This increase parallels that of the pure compound under pressure, which led the authors to hypothesize a transition from HO to LMAF at a doping level of x = 0.1 and conclude that the effect of Fe doping on the system is fully explained by a chemical pressure effect [31]. However, the LMAF and HO states are largely indistinguishable to the bulk probes used in this study and the authors did not perform measurements with any microscopic probes that would allow the magnetic state to be identified, hence no firm conclusions could be drawn.

Recently, a second study has been published on Fe doping using neutron diffraction on single crystals [32]. In this work, elastic neutron scattering allowed the authors to identify a crossover from HO to AF at a doping level of x = 0.1 as would be expected from a chemical pressure argument. However, the moment of 0.8  $\mu_B$  per U that they observe is twice that seen in the pure material under pressure which indicates that chemical pressure is not the only factor governing the evolution of magnetism in this material. This discrepancy makes further study of Fe doping valuable to properly understand the HO to LMAF transition if it is to be used as an analog of the pressure induced transition.

#### PHYSICAL REVIEW B 93, 064402 (2016)

A cursory study of polycrystalline  $URu_{2-x}Os_xSi_2$  was first performed by Dalichaouch *et al.* in 1990 [27], and has been recently followed by a more detailed examination by Kanchanavatee *et al.* in 2014 [33]. These studies show that doping is possible up to x = 1.2 with no change in the structure and only a small increase in the lattice constant compared to the large decrease seen for Fe doping. Accompanying this small expansion of the lattice, the transition temperature dramatically increases up to a maximum of 50 K by x = 1.2. From resistivity and specific heat measurements Kanchanavatee *et al.* hypothesize a transition out of the HO state at x = 0.2. However, this study again did not involve any microscopic probes of magnetism and hence the true evolution of the magnetic ground state of  $URu_{2-x}Os_xSi_2$  is still an open question.

In this paper we present the results of  $\mu$ SR and susceptibility measurements on URu<sub>2-x</sub>T<sub>x</sub>Si<sub>2</sub> (T = Fe, Os) single crystals for doping levels up to x = 1. Our measurements demonstrate that an antiferromagnetic state arises for both of these compounds at low doping levels and highlight the importance of hybridization to fully understand the evolution of magnetic order in this system.

#### **II. EXPERIMENTAL METHODS**

Samples measured in this study were single crystals grown by the Czochralski method at McMaster University from starting materials of depleted U, Ru(99.95%), Fe(99.99%), Os(99.8%), and Si(99.9999%). These growths were performed in a tri-arc furnace from a water-cooled copper hearth under argon gettered at 900 °C. After the growths, crystallinity was confirmed and sample alignment performed by Laue x-ray scattering measurements. Doping levels stated in this paper are the nominal doping levels taken from the masses of the materials originally reacted.

Magnetic susceptibility measurements were performed on cleaved plates of the crystals in a Quantum Design MPMS XL-3. These measurements provide a measure of the transition temperature from the paramagnetic state to hidden order or antiferromagnetism, however they cannot readily distinguish hidden order from antiferromagnetism.

 $\mu$ SR is a sensitive microscopic magnetic probe that can distinguish antiferromagnetism from hidden order, but cannot readily distinguish hidden order from paramagnetism. In this technique, spin polarized positive muons are injected one at a time into a sample where they penetrate a few hundred microns, rapidly thermalize, and stop at a Coulomb potential minimum in the material. Once stopped, each muon spin precesses in the local magnetic field until it decays with average lifetime of 2.2  $\mu$ s and emits a positron preferentially in the direction of the muon spin at the time of decay. Detectors on either side of the sample register the decay of the positron and record the time interval between muon injection and decay. From many such events, a histogram of positron counts in both detectors,  $N_R$  and  $N_L$ , as a function of muon decay time is generated. Using these two histograms the asymmetry A is defined as  $A = \frac{N_R - N_L}{N_R + N_I}$ . This quantity gives a measure of how the muon polarization changes over time, and is limited by the physics of muon decay and instrumental factors to a maximum of about 0.3. The true maximum in any given experiment is

#### ANTIFERROMAGNETISM AND HIDDEN ORDER IN ...

determined from the total oscillating asymmetry seen after applying a small field transverse to the muon polarization in the paramagnetic regime.

In zero applied magnetic field, paramagnetic samples, where there is no static magnetism and the spin dynamics are very fast, will show a nearly time-independent asymmetry, with deviations from this caused by nuclear moments. The HO state will also have this signature, as there is no ordering of magnetic moments to produce a local magnetic field. By contrast, long-range ordered magnetic states such as antiferromagnetism will show an oscillating asymmetry where the frequency gives the strength of the internal field at the muon stopping site, provided this field is not parallel to the initial muon polarization. The ratio of the maximum amplitude of the oscillating asymmetry to the instrumental maximum gives the fraction of the sample that is in the magnetic state (the magnetic volume fraction). The amplitude of this oscillating signal damps down over time as a result of inhomogeneities and dynamics of the internal field.

Our  $\mu$ SR measurements were performed on the M15 and M20 beam lines at TRIUMF laboratory in Vancouver. The LAMPF time-differential spectrometer was used, which provides a He-4 cryostat for temperatures between 2 and 300 K and a time resolution of 0.2 ns in an ultralow background apparatus. This apparatus vetoes muons that miss the sample, ensuring that almost all of the measured positrons come from muons that stop in the sample. For these measurements the single crystals were cleaved into slices roughly 0.5-mm thick along the *c* axis which were then mounted in a mosaic covering 1–2 cm<sup>2</sup> on thin mylar tape. The *c* axes were co-aligned facing the muon beam but no attempt was made to co-align the samples in the *a*-*b* plane. We fit our  $\mu$ SR data using the  $\mu$ SRfit software package [34].

#### **III. RESULTS**

Figures 1 and 2 show the results of the magnetization measurements in a field of 0.1 T ( $H \parallel c$ ) on the Fe and Os doped samples, respectively. No significant differences were observed in any of these samples between field cooled and zero field cooled and hence only one set of measurements are shown. In these measurements a kink in the susceptibility indicates the transition into either the HO or LMAF states. The lower panels of these figures show plots of dM/dT to allow a more accurate determination of the temperature of this kink.

The measurements on the Fe doped samples show little change in the character of the transition with doping; the transition remains a relatively sharp peak in dM/dT up to higher dopings. The sharp peak is consistent with measurements on polycrystalline samples presented by Kanchanavatee *et al.* [31]. However, our measurements on single-crystal samples do not show evidence of the significant second peak seen in some of the polycrystalline samples in Ref. [31]. This likely indicates that those features were spurious results arising from disorder in the polycrystalline samples, as was also proposed by Das *et al.* [32]. Additionally, our x = 0.3 sample shows a significant low temperature upturn in the magnetization as well as the highest overall magnetization. During the crystal growth of this sample, a small number of needlelike protrusions were noticed on the outside of the crystal, likely indicating some

PHYSICAL REVIEW B 93, 064402 (2016)



FIG. 1. (a)  $URu_{2-x}Fe_xSi_2$  magnetization data measured in a field of  $H = 0.1T \parallel c$  for x = 0.02 (black circles), 0.1 (blue squares), 0.2 (red triangles), and 0.3 (green diamonds). (b) Temperature derivative of the data shown in (a) arrows on plot (b) show the measured transition temperatures.

phase separation that would cause a paramagnetic background in the magnetization measurements, as observed. We attribute this to a lower than nominal silicon level in the melt arising from evaporation as silicon has the highest vapor pressure of the elements present [35] and the growth for this doping was held at high temperature for a significantly longer period than the others.

The measurements on our Os doped samples show a somewhat different evolution in the character of the transition with doping. Rather then staying as a sharp peak, the transition broadens significantly and shifts to higher temperature as the doping level increases. This is consistent with the broadened transition seen in polycrystalline samples at x = 0.3 and 0.4 [33].

 $\mu$ SR data for the Fe samples at 2 K measured with the muon spins initially perpendicular to the *c* axis of the crystals in zero applied field (ZF) is shown in Fig. 3. Measurements in Fig. 3(b) were taken with higher statistics to better resolve the faster relaxing signal. This data exhibits clear oscillations for all samples, indicating that there is static magnetism with the field along the *c* axis at the muon stopping site. The amplitude





FIG. 2. (a)  $URu_{2-x}Os_xSi_2$  magnetization data measured in a field of  $H = 0.1T \parallel c$  for x = 0.1 (red circles), 0.2 (black squares), and 0.4 (blue triangles). (b) Temperature derivative of the data shown in (a). Arrows on plot (b) show the measured transition temperatures.

of the oscillations for the x = 0.02 sample is significantly lower than for the others and the asymmetry is shifted upwards by a nonrelaxing component. This indicates that the magnetic volume fraction is lower in this sample.

We found that applying a small field parallel to the c axis to any of these samples splits the observed internal field into two components separated by twice the applied field. This indicates that the magnetic order in these samples is antiferromagnetic. We also performed some measurements with the muon spins parallel to the c axis that show no oscillations for the low doping samples, indicating that the internal field is only along the c axis within the accuracy of our alignment. This is consistent with the antiferromagnetic phase seen in URu2Si2 under hydrostatic pressure [9] and by Das et al. in neutron scattering measurements on URu2-xFexSi2 [32] which has magnetic moments along the c axis. However, it should be noted that while the direction of the internal field often matches the moment direction, this is not always the case and full comparison depends on knowledge of the muon stopping site which we do not have.

Despite the apparent similarity of this antiferromagnetic state to that of URu<sub>2</sub>Si<sub>2</sub> under hydrostatic pressure, we found





FIG. 3. URu<sub>2-x</sub>Fe<sub>x</sub>Si<sub>2</sub>  $\mu$ SR Data measured at T = 2 K in zero applied external field with the muon spins initially perpendicular to the *c*-axis for (a) x = 0.02 (black circles), 0.1 (blue squares), 0.2 (red triangles), and 0.3 (green diamonds) and (b) x = 0.6 (cyan circles), x = 0.8 (purple squares), and x = 1 (orange triangles). Solid lines in (a) show fits to Eq. (1) and those in (b) show fits to Eq. (2).

that the fitting of the ZF data at low doping was significantly improved with a two component fit compared to the single component fit used by Amato *et al.* for the pure compound [11]. We therefore fit the data for x = 0.02-0.3 shown in Fig. 3(a) using the equation

$$A = A_T \{ 0.5F \left[ \cos(\gamma_\mu Bt) e^{-0.5(\sigma_1 t)^2} + \cos(\gamma_\mu BRt) \right. \\ \left. \times e^{-0.5(\sigma_2 t)^2} \right] + (1 - F) \}.$$
(1)

In this model the ratio of the asymmetries of the two components was fixed to 0.5 for consistency between different samples as fits with free asymmetry were found to refine to values near 0.5. Addition of a second frequency for the higher dopings x = 0.6 to 1.0 did not improve the fits compared to the single component model given by the equation

$$A = A_T [F \cos(\gamma_\mu Bt) e^{-0.5(\sigma t)^2} + (1 - F)].$$
(2)

#### ANTIFERROMAGNETISM AND HIDDEN ORDER IN ...

TABLE I. Relaxation rates used to fit the 2 K  $\mu$ SR data in Fig. 3 for URu<sub>2-x</sub>Fe<sub>x</sub>Si<sub>2</sub> and the temperature independent ratio of the two internal fields used in fits to Eq. (1).

Doping <i>x</i>	R	$\sigma_1~(\mu s^{-1})$ at 2 K	$\sigma_2 \ (\mu { m s}^{-1})$ at 2 K
0.02	$0.86 \pm 0.01$	$2.39\pm0.08$	$5.37 \pm 0.29$
0.1	$0.942\pm0.008$	$1.95 \pm 0.04$	$4.98\pm0.13$
0.2	$0.93\pm0.02$	$1.763 \pm 0.04$	$4.39\pm0.15$
0.3	$0.891 \pm 0.004$	$2.822\pm0.07$	$4.51 \pm 0.12$
0.6	-	$7.57 \pm 0.1$	-
0.8	-	$9.33 \pm 0.18$	-
1	-	$7.04 \pm 0.1$	-

Therefore, Eq. (2) was used to fit the data in Fig. 3(b). In these equations  $A_T$  is the total asymmetry, B is the larger internal field,  $\gamma_{\mu} = 135.53 \times 2\pi$  MHz/T is the muon gyromagnetic ratio, R is the ratio between the internal fields at the two muon sites, F is the magnetic volume fraction, and the  $\sigma_i$  are the relaxation rates. For each of the fits  $A_T$  and R were temperature independent parameters for each sample and the other parameters were allowed to vary with temperature.

The field ratio *R* varies between samples with no obvious doping dependence as shown in Table I. However, the relaxation rate also varies erratically from sample to sample, likely from differing amounts of disorder, and this will affect the fitting of a second frequency. Table I also shows the substantially larger single relaxation for the higher doped samples which obscures any possibility of fitting a second field to these data. We expect that a second frequency may still be present but increased disorder from growing crystals at high doping levels makes it impossible to distinguish.

Figure 4 shows plots of the fit average internal field [0.5(B + RB) for the lower dopings] and magnetic fraction *F*. In all samples the internal field smoothly decreases from a maximum at low temperature to zero at the transition, showing second order behavior. The magnetic fraction for all samples except for the x = 0.02 is mostly temperature independent up until the transition where a sharp fall off occurs. This fraction is close to 1 for the x = 0.1-0.3 samples and slightly lower for the higher dopings. In contrast to the others, the x = 0.02 sample shows a substantially reduced *F* of 0.63 at 2 K. Furthermore, this sample shows different temperature dependence with a smooth continuous drop off in the magnetic fraction over the entire temperature range. This may indicate a continuous volume-wise transition out of the AF state as a function of temperature.

 $\mu$ SR data collected at T = 5 K in zero field with the muon spins initially perpendicular to the *c* axis for the Os doped samples are shown in Fig. 5(a). For these samples the data again show clear oscillations indicating similar static order. However, there is no evidence for a second internal field component in these samples. Therefore, we fit the data using Eq. (2) and show the internal field and magnetic volume fraction in Figs. 5(c) and 5(d). These plots show similar temperature dependence to the Fe doped samples again indicating a second order transition in all samples.

The comparison of two internal fields for Fe at low doping compared to one frequency in Os is illustrated by the Fourier transform in Fig. 5(b). This plot shows that while two frequen-



FIG. 4. Fitting parameters for the  $\mu$ SR data of URu<sub>2-x</sub>Fe<sub>x</sub>Si<sub>2</sub> measured in zero applied field with the muon spins perpendicular to the *c*-axis. (a) Average internal field  $B_{av} = 0.5(B + RB)$  for dopings x = 0.02 (black circles), 0.1 (blue squares) 0.2 (red triangles) and 0.3 (green diamonds). (b) Internal field *B* for dopings x = 0.6 (cyan circles), 0.8 (purple squares) and 1 (orange triangles). (c) Magnetic volume fraction for dopings x = 0.02 (black circles), 0.1 (blue squares) 0.2 (red triangles) and 0.3 (green diamonds). (d) Magnetic volume fraction for dopings x = 0.6 (cyan circles), 0.8 (purple squares) and 1.3 (purple squares) 0.9 (purple squares)

cies appear in the Fe sample, the overall linewidth is similar for the Os sample. This means that the appearance of a second field for Os samples could be masked by the larger linewidth. Similarly, Table I shows that the relaxation rate (linewidth)



FIG. 5. URu<sub>2x</sub>–Os<sub>x</sub>Si<sub>2</sub>  $\mu$ SR data and fitting in zero external field measured with muon spins initially perpendicular to the *c* axis for *x* = 0.1 (red circles), 0.2 (black squares), and 0.3 (blue triangles). (a)  $\mu$ SR data measured at 5 K, (b) Fourier transform of URu<sub>1.9</sub>Os<sub>0.1</sub>Si<sub>2</sub> (red line) data measured at 5 K and URu<sub>1.8</sub>Fe<sub>0.1</sub>Si<sub>2</sub> (green line) data measured at 2 K, and (c) magnetic volume fraction *F* (d) internal field *B*. Solid lines in (d) correspond to fits to Eq. (2).

064402-5

#### PHYSICAL REVIEW B 93, 064402 (2016)

#### M. N. WILSON et al.

is much higher in the heavily doped Fe samples where two frequencies are not resolved. This is likely a result of chemical disorder in the samples and would explain why we cannot see two frequencies in these cases. A similar mechanism may explain the lack of a second field for the measurements under pressure done by Amato et al. [11]. In this case, the pressure was applied with an anvil cell using a transmitting medium that would be frozen at the relevant temperatures. This can cause nonuniformities in the applied pressure [36], which would introduce inhomogeneity in the samples, increasing the linewidth and masking the appearance of a second frequency. Furthermore, in any experiment with a pressure cell many muons are stopped outside the sample. This drops the signal to noise ratio of the data, further reducing the ability to resolve a possible second frequency. These explanations would allow for the magnetic state to be nearly identical in our Fe and Os samples as well as the pure URu2Si2 measured under pressure, despite the apparent differences in fitting.

The presence of a second internal field in any of these measurements indicates that the muons stop at two magnetically distinct sites at equivalent or near-equivalent Coulomb potential minima. The second magnetic site could either be explained by a more complex magnetic structure that breaks one of the symmetries of the underlying crystal lattice, or structural effects creating two muon sites. If this does appear only for doping, one possibility is that the Fe/Os atoms are being magnetically polarized and contributing to the moment seen by the muons. However, our measurements indicate that the relative volume fraction of the two magnetic sites is close to 50/50, which would not be expected if one of these was coming from the 1%–15% doping. Furthermore,  $UFe_2Si_2$  and UOs2Si2 are both nonmagnetic so we would not expect Fe and Os polarization [37,38]. Future detailed measurements of the temperature and doping dependence of the lattice parameters and structure symmetry would help clarify this issue.

#### IV. DISCUSSION

The fit parameters in Figs. 4 and 5 show two important features. First, for most samples the low temperature magnetic volume fraction is close to one. This tells us that the magnetism we see must be attributed in each case to the bulk of the sample rather than to a small impurity effect. The small nonmagnetic volume that does appear could be attributed to muons stopping in parts of the sample holder rather than the sample itself or slight misalignment of the samples with respect to the incoming muon beam. In the heavily doped samples where the volume fraction appears somewhat reduced, a small signal also appears in measurements with the muon spin rotated parallel to the aligned c axis. Misalignment would explain both the signal in the  $\mu || c$  measurements and the reduced signal/volume fraction for  $\mu \perp c$  as the measured asymmetry varies as  $\sin \theta$ , where  $\theta$  is the angle between the muon spins and the internal field.

Second, with the exception of the x = 0.02 Fe doped sample, the internal field falls off smoothly as a function of temperature to zero at a transition temperature consistent with that shown by the magnetization measurements. This indicates that the system transitions directly from the magnetically ordered to paramagnetic (PM) states without the transition





FIG. 6. Comparison of the transition temperatures measured by susceptibility to those measured by  $\mu$ SR for Fe doped samples (red squares) and Os doped samples (blue circles). The solid black line shows the expected 1:1 correspondence.

through HO that has been seen for intermediate pressures applied to URu<sub>2</sub>Si<sub>2</sub> [11,29,39,40]. In the Fe x = 0.02 sample the transition temperature from  $\mu$ SR is 1.5 K lower than that measured by SQUID. This small discrepancy is unlikely to be caused by thermometry differences, as the same thermometry was used for  $\mu$ SR measurements of all other samples where the transition temperatures appear more consistent as shown by Fig. 6. Furthermore, the distinctly different temperature dependence in the magnetic volume fraction of this sample compared to the others leads us to believe that the magnetic state may not be the same. One explanation for these discrepancies is if this sample is in a mixed HO/AF state below 17.5 K, with the volume fraction of the AF state decreasing up until 16 K leaving a pure HO state in a 1.5 K range between 16 and 17.5 K. In the pressure-temperature phase diagram of pure URu2Si2 there exists a small temperature range where decreasing temperature first causes a transition into hidden order and then to antiferromagnetism, so it would not be unexpected to find a similar region at low Fe dopings in our system. However, as the transitions measured by both techniques are reasonably broad, and the temperature discrepancy is small, it is not possible to draw firm conclusions about the existence of both HO and AF at different temperatures in this sample. Further measurements on this doping with other techniques, particularly those that show a direct signature of the HO state such as inelastic neutron scattering, which has been used to distinguish the two under pressure [29], will be required to clarify this issue.

The overall behavior of the  $\mu$ SR data presented in this work is similar to that seen in measurements on URu<sub>2</sub>Si<sub>2</sub> under hydrostatic pressure [11]. However, there are some notable differences. First, while the internal field measured at low temperature is comparable to that of Amato *et al.*, our measured internal fields for both Os and Fe increase with doping, while the internal field above some critical pressure is constant for URu<sub>2</sub>Si<sub>2</sub> under pressure [11]. This difference in behavior



ANTIFERROMAGNETISM AND HIDDEN ORDER IN ...

FIG. 7. Measured internal fields as a function of effective chemical pressure for Fe doped (red squares) and Os doped (blue circles), and as a function of applied hydrostatic pressure for pure URu<sub>2</sub>Si<sub>2</sub> (black triangles) from Ref. [11]. Error bars are not shown as in all cases they would lie within the symbols.

is clearly demonstrated in Fig. 7 showing the low temperature internal fields measured for all samples in this study plotted as a function of chemical pressure along with the data from Amato *et al.* For this plot the effective chemical pressure  $P_{ch}$ was calculated using  $P_{\rm ch} = (\Delta V)/(V_0)/\kappa$ , where  $\kappa = 5.2 \times$  $10^{-3}$  GPa<sup>-1</sup> is the bulk modulus for pure URu<sub>2</sub>Si<sub>2</sub> [41],  $\Delta V$ is the unit cell volume change from pure URu2Si2 taken from the crystallographic data in Refs. [31,33] using our nominal doping levels, and  $V_0$  is the unit cell volume of pure URu<sub>2</sub>Si<sub>2</sub>. This figure also indicates that the appearance of magnetic order cannot be attributed to chemical pressure across this system as the Os doped samples show similar internal fields at effective chemical pressures that are negative and whose magnitude is significantly lower than that for Fe doping. The Fe x = 0.02sample also shows magnetic order despite being at an effective chemical pressure less than a quarter of the pressure required to generate the LMAF in pure URu2Si2. We would like to point out that as we have not done elemental analysis of the samples it is possible that the doping level of our x = 0.02 sample is slightly higher than the nominal value bringing it closer to the expected HO-AF border, but it is unlikely that the doping level is far enough off to fully resolve this discrepancy.

It has been proposed in the past that the transition between HO and LMAF is governed by the  $\eta = c/a$  ratio as has been demonstrated for superconducting transitions in other f electron compounds [42], rather than uniform shrinking of the unit cell [33,43]. While both Fe and Os doping do increase  $\eta$ , the change is an order of magnitude smaller for Os doping than is seen for Fe doping or applied pressure. This indicates that the change in  $\eta$  alone cannot explain the development of magnetic order.

Susceptibility data on the lower doped samples show a clear broad maximum at high temperatures, shown in Figs. 8(a) and 8(b). Such a maximum is expected for heavy fermion compounds and arises from the crossover from local-moment



Temperature (K) Temperature (K) μ<sub>B</sub>/f.u.) μ<sub>8</sub>/f.u.) 0 20 100 0 80 100 40 60 80 20 40 60 20 64k 75K (a) (b) 70K Magnetization M (10<sup>-4</sup> Magnetization M (10<sup>-4</sup> 54K 65K 66K x = 0.02 86k = 0.1x = 0.1x = 0.2 x = 0.2x = 0.3 x = 0.4 5 35 (C) sition Temperature  $T_N(K)$ Fe Substitution 30 **Os Substitution** Pure 25 20 Fran 15 ∟ 50 55 60 65 75 80 85 90 70 Susceptibility Maxima T<sub>a</sub>(K)

FIG. 8. High temperature susceptibility data showing the broad maxima that appears for (a) Fe doped samples, x = 0.04 (black circles), 0.1 (blue squares), 0.2 (red triangles), and 0.3 (green diamond) and (b) Os doped samples, x = 0.1 (red circles), 0.2 (black squares), and 0.4 (blue triangles). (c) A plot of  $T_N$  from susceptibility vs the temperature of this susceptibility maxima for Fe doped (red squares), Os doped (blue circles), and pure URu<sub>2</sub>Si<sub>2</sub> (black triangle).

magnetism at high temperature to the heavy fermion state at low temperatures caused by the hybridization of the conduction electrons with the core f electrons [1]. Hence, the temperature of this crossover  $T_{\text{max}}$  can be taken as a rough proxy for the strength of hybridization in these systems. Our data shows an increase in  $T_{\text{max}}$  with doping for both Os and Fe, which suggests that hybridization between the U f electrons and the valence electrons increases with doping for both cases. Furthermore, Fig. 8 shows a similar linear correlation between  $T_N$  and  $T_{max}$  in both cases. In contrast, measurements by two different groups of  $T_{\text{max}}$  as a function of pressure for pure URu2Si2 show conflicting results, with Nishioka et al. finding a pressure-independent value of approximately 60 K over a range where the magnetic transition temperature increases from 16 to 18.5 K [44], while Pfleiderer et al. find that  $T_{\text{max}}$ increases over this same pressure range [45]. It is therefore unclear whether or not our samples are behaving the same as URu2Si2 under pressure. However, the similarity in behavior between Os and Fe doping indicates that hybridization is the driving force in these transitions rather than chemical pressure.

Our results for Fe doping show some discrepancies with those reported recently by Das *et al.* using neutron scattering on crystals that should be similar to ours [32]. First, our internal fields increase with doping, while the results of Das *et al.* show either doping independence or a slight decrease with doping. Second, our measured internal field is roughly consistent with URu<sub>2</sub>Si<sub>2</sub> under pressure, while Das *et al.* magnetic moment up to twice that measured for the LMAF in URu<sub>2</sub>Si<sub>2</sub>. Finally, we see similar magnetism down

#### M. N. WILSON et al.

to low doping levels while Das *et al.* see weakening of the magnetism below x = 0.1.

The first discrepancy could be explained by slight changes to the muon stopping site with doping. If the muons systematically stop closer to the magnetic U atoms as the Fe doping increases, this would cause a small increase in our observed internal field even if the magnetic moments are constant or slightly decreasing. However, in a simplistic viewpoint the dopant Fe atoms should have electron orbitals with smaller spatial extent than the Ru, and hence one would expect the muon stopping sites to move closer to the Fe atoms and further from the magnetic U ions. This would cause a decrease in the measured internal field rather than an increase. Detailed numerical calculations of the likely muon stopping sites would be required to quantitatively determine the effect of the Fe doping. Another explanation for the doping dependence is Fe site magnetism contributing to the internal field, which could potentially be clarified with Mössbauer measurements that could directly measure the Fe magnetism.

The second discrepancy is difficult to reconcile. While  $\mu$ SR cannot provide a numerical value of the magnetic moment without knowledge of the muon stopping site which we do not have, the comparison between the measured internal fields of samples with very similar structures should give a good idea of how the magnetic moment changes between these samples. Therefore, the Fe x = 0.1 sample should be reasonably comparable to the pure compound under pressure and hence seeing a similar internal field here should indicate that the magnetic moments are the same. While the doping could change the muon stopping site somewhat between pure  $URu_2Si_2$  and the Fe x = 0.1 sample, the structure and lattice constants remain mostly the same and it seems unlikely that this would be a large enough effect to cut the measured internal field in half to make our results consistent with the magnetic moment measured by Das *et al.* One possibility is that there is signal intensity at the magnetic Bragg peak positions from multiple scattering that Das et al. may not have taken into account and would artificially inflate the calculated magnetic moments.

The final discrepancy of our data showing magnetism down to lower doping levels may come down to slight variations in doping levels or internal strain between different crystals. In particular, the doping levels we state are the nominal dopings and were not independently measured so there may be some small discrepancies. However, our results are not

#### PHYSICAL REVIEW B 93, 064402 (2016)

entirely inconsistent with those of Das *et al.* They report that there is some magnetic scattering still appearing in the lower doped samples, it is just substantially reduced. This could come from magnetic moments that are the same as those measured in higher doping samples, but with a reduced magnetic volume fraction, as the Bragg peak intensity cannot distinguish volume fraction from magnetic moment. A reduced volume fraction with similar magnetic moment would be qualitatively consistent with the results we show for our nominal Fe x = 0.02 sample.

#### V. CONCLUSION

In conclusion, we have presented  $\mu$ SR measurements which demonstrate that URu<sub>2-x</sub>T<sub>x</sub>Si<sub>2</sub> (T = Os, Fe) display antiferromagnetic order. This order persists down to low doping levels, with our Fe x = 0.02 sample showing a lowered magnetic volume fraction that may indicate coexistence of HO and AF in this sample. Furthermore, the magnetic order persists down to Fe doping levels below that expected by a chemical pressure argument, and for Os dopings representing negative chemical pressure, which shows that the hidden order is very fragile and can easily be destroyed by even isoelectronic doping. These measurements, combined with the local moment-hybridization crossover temperature from susceptibility, demonstrate that magnetic order in isoelectronic doping is driven by changes in hybridization rather than purely structural changes.

#### ACKNOWLEDGMENTS

We thank Dr. G. D. Morris, Dr. B. S. Hitti and Dr. D. J. Arseneau (TRIUMF) for their assistance with the  $\mu$ SR measurements. Work at McMaster university was supported by the Natural Sciences and Engineering Research Council of Canada and the Canadian Foundation for Innovation. M.N.W. acknowledges support from the Alexander Graham Bell Canada Graduate Scholarship program. T.J.W. acknowledges support from the Wigner Fellowship program at Oak Ridge National Laboratory. A.M.H. acknowledges support from the Vanier Canada Graduate Scholarship program. G.M.L. acknowledges support from the Canadian Institute for Advanced Research. The Columbia University group acknowledges support from SSF DMR-1436095 (DMREF) and OISE-0968226 (PIRE), JAEA Reimei project, and Friends of U Tokyo, Inc.

- [2] J. A. Mydosh and P. M. Oppeneer, Rev. Mod. Phys. 83, 1301 (2011).
- [3] W. Schlabitz, J. Baumann, B. Pollit, U. Rauchschwalbe, H. M. Mayer, U. Ahlheim, and C. D. Bredl, Z. Phys. B: Condens. Matter 62, 171 (1986).
- [4] T. T. M. Palstra, A. A. Menovsky, J. van den Berg, A. J. Dirkmaat, P. H. Kes, G. J. Nieuwenhuys, and J. A. Mydosh, Phys. Rev. Lett. 55, 2727 (1985).
- [5] C. Broholm, J. K. Kjems, W. J. L. Buyers, P. Matthews, T. T. M. Palstra, A. A. Menovsky, and J. A. Mydosh, Phys. Rev. Lett. 58, 1467 (1987).
- [6] E. D. Isaacs, D. B. McWhan, R. N. Kleiman, D. J. Bishop, G. E. Ice, P. Zschack, B. D. Gaulin, T. E. Mason, J. D. Garrett, and W. J. L. Buyers, Phys. Rev. Lett. 65, 3185 (1990).
- [7] M. B. Maple, J. W. Chen, Y. Dalichaouch, T. Kohara, C. Rossel, M. S. Torikachvili, M. W. McElfresh, and J. D. Thompson, Phys. Rev. Lett. 56, 185 (1986).
- [8] D. A. Bonn, J. D. Garrett, and T. Timusk, Phys. Rev. Lett. 61, 1305 (1988).
- [9] H. Amitsuka, M. Sato, N. Metoki, M. Yokoyama, K. Kuwahara, T. Sakakibara, H. Morimoto, S. Kawarazaki, Y. Miyako, and J. A. Mydosh, Phys. Rev. Lett. 83, 5114 (1999).

<sup>[1]</sup> G. R. Stewart, Rev. Mod. Phys. 56, 755 (1984).

ANTIFERROMAGNETISM AND HIDDEN ORDER IN ...

- [10] N. P. Butch, J. R. Jeffries, S. Chi, J. B. Leão, J. W. Lynn, and M. B. Maple, Phys. Rev. B 82, 060408 (2010).
- [11] A. Amato, M. J. Graf, A. de Visser, H. Amitsuka, D. Andreica, and A. Schenck, J. Phys.: Condens. Matter 16, S4403 (2004).
- [12] D. E. MacLaughlin, D. W. Cooke, R. H. Heffner, R. L. Hutson, M. W. McElfresh, M. E. Schillaci, H. D. Rempp, J. L. Smith, J. O. Willis, E. Zirngiebl, C. Boekema, R. L. Lichti, and J. Oostens, Phys. Rev. B 37, 3153 (1988).
- [13] G. M. Luke, A. Keren, L. P. Le, Y. J. Uemura, W. D. Wu, D. Bonn, T. Taillefer, J. D. Garret, and Y. Onuki, Hyperfine Interact. 85, 397 (1994).
- [14] K. Matsuda, Y. Kohori, T. Kohara, K. Kuwahara, and H. Amitsuka, Phys. Rev. Lett. 87, 087203 (2001).
- [15] H. Amitsuka, K. Matsuda, I. Kawasaki, K. Tenya, M. Yokoyama, C. Sekine, N. Tateiwa, T. C. Kobayashi, S. Kawarazaki, and H. Yoshizawa, J. Magn. Magn. Mater. **310**, 214 (2007).
- [16] C. R. Wiebe, J. A. Janik, G. J. MacDougall, G. M. Luke, J. D. Garrett, H. D. Zhou, Y.-J. Jo, L. Balicas, Y. Qiu, J. R. D. Copley, Z. Yamani, and W. J. L. Buyers, Nat. Phys. 3, 96 (2007).
- [17] A. F. Santander-Syro, M. Klein, F. L. Boariu, A. Nuber, P. LeJay, and F. Reinert, Nat. Phys. 5, 637 (2009).
- [18] S. Chatterjee, J. Trinckauf, T. Hänke, D. E. Shai, J. W. Harter, T. J. Williams, G. M. Luke, K. M. Shen, and J. Geck, Phys. Rev. Lett. 110, 186401 (2013).
- [19] A. R. Schmidt, M. H. Hamidian, P. Wahlm F. Meier, A. Balatsky, J. D. Garret, T. J. Williams, G. M. Luke, and J. C. Davis, Nature (London) 465, 570 (2010).
- [20] J. A. Mydosh and P. M. Oppeneer, Philos. Mag. 94, 3640 (2014).
- [21] S. K. Dhar, R. J. Begum, P. Raj, P. Suryanarayana, L. C. Gupta, and R. Vijayaraghavan, Solid State Commun. 83, 965 (1992).
- [22] J.-G. Park and B. R. Coles, J. Phys.: Condens. Matter 6, 1425 (1994).
- [23] M. Ocko and J.-G. Park, Physica B 230-232, 71 (1997).
- [24] H. Amitsuka, K. Kuwahara, M. Yokoyama, K. Tenya, T. Sakakibara, M. Mihalik, and A. A. Menovský, Phys. B: Condens. Matter 281–282, 326 (2000).
- [25] H. Amitsuka, K. Hyomi, T. Nishioka, Y. Miyako, and T. Suzuki, J. Magn. Magn. Mater. 76–77, 168 (1988).
- [26] Y. Dalichaouch, M. B. Maple, R. P. Guertin, M. V. Kuric, M. S. Torikachvili, and A. L. Giorgi, Physica B 163, 113 (1990).

#### PHYSICAL REVIEW B 93, 064402 (2016)

- [27] Y. Dalichaouch, M. B. Maple, J. W. Chen, T. Kohara, C. Rossel, M. S. Torikachvili, and A. L. Giorgi, Phys. Rev. B 41, 1829 (1990).
- [28] J.-G. Park, J. Phys.: Condens. Matter 6, 3403 (1994).
- [29] N. P. Butch and M. B. Maple, J. Phys.: Condens. Matter 22, 164204 (2010).
- [30] M. Yokoyama, H. Amitsuka, S. Itoh, I. Kawasaki, K. Tenya, and H. Yoshizawa, J. Phys. Soc. Jpn. 73, 545 (2004).
- [31] N. Kanchanavatee, M. Janoschek, R. E. Baumbach, J. J. Hamlin, D. A. Zocco, K. Huang, and M. B. Maple, Phys. Rev. B 84, 245122 (2011).
- [32] P. Das, N. Kanchanavatee, J. S. Helton, K. Huang, R. E. Baumbach, E. D. Bauer, B. D. White, V. W. Burnett, M. B. Maple, J. W. Lynn, and M. Janoschek, Phys. Rev. B 91, 085122 (2015).
- [33] N. Kanchanavatee, B. D. White, V. W. Burnett, and M. B. Maple, Philos. Mag. 94, 3681 (2014).
- [34] A. Suter and B. M. Wojek, Phys. Proc. 30, 69 (2012).
- [35] R. E. Honig, RCA Rev. 23, 567 (1962).
- [36] W. Yu, A. A. Aczel, T. J. Williams, S. L. Bud'ko, N. Ni, P. C. Canfield, and G. M. Luke, Phys. Rev. B 79, 020511(R) (2009).
- [37] A. Szytula, M. Slaski, B. Dunlap, Z. Sungaila, and A. Umezawa, J. Magn. Magn. Mater. 75, 71 (1988).
- [38] T. T. M. Palstra, A. A. Menovsky, G. J. Nieuwenhuys, and J. A. Mydosh, J. Magn. Magn. Mater. 54–57, 435 (1986).
- [39] F. Bourdarot, S. Raymond, and L.-P. Regnault, Philos. Mag. 94, 3702 (2014).
- [40] E. Hassinger, G. Knebel, K. Izawa, P. Lejay, B. Salce, and J. Flouquet, Phys. Rev. B 77, 115117 (2008).
- [41] K. Kuwahara, H. Sagayama, K. Iwasa, M. Kohgi, S. Miyazaki, J. Nozaki, J. Nogami, M. Yokoyama, H. Amitsuka, H. Nakao, and Y. Murakami, Acta Phys. Pol. B 34, 4307 (2003).
- [42] C. Pfleiderer, Rev. Mod. Phys. 81, 1551 (2009).
- [43] M. Yokoyama, H. Amitsuka, K. Tenya, K. Watanabe, S. Kawarazaki, H. Yoshizawa, and J. A. Mydosh, Phys. Rev. B 72, 214419 (2005).
- [44] T. Nishioka, H. Mukai, S. Nakamura, G. Motoyama, Y. Ushida, and N. K. Sato, J. Phys. Soc. Jpn. 69, 2415 (2000).
- [45] C. Pfleiderer, J. A. Mydosh, and M. Vojta, Phys. Rev. B 74, 104412 (2006).

# 3.2 Summary of Publication II: Neutron scattering studies of Fe doped URu<sub>2</sub>Si<sub>2</sub>

In this paper, we further the work of Section 3.1 by applying neutron scattering to study the Fe doped samples of URu<sub>2</sub>Si<sub>2</sub>. These measurements allow us to directly determine what the magnetic order seen by  $\mu$ SR is, confirm the transition temperatures, independently determine the magnetic moment size, and study the evolution of the magnetic excitations with doping.

Our elastic neutron scattering measurements at low temperature show Bragg peaks at the (1 0 0) and equivalent positions, with no magnetic intensity in the (0 0 1) peaks. This is consistent with the antiferromagnetic state seen in URu<sub>2</sub>Si<sub>2</sub> under pressure where the magnetic moments are aligned parallel to the c-axis [165]. The magnetic diffraction peaks are resolution limited, which shows that they come from long range order rather than short range correlations. The magnetic moment calculated from this data increases with doping from 0.51  $\mu_B$  / U at 2.5% Fe to 0.66  $\mu_B$  / U at 15% Fe, and is larger than the moment seen in URu<sub>2</sub>Si<sub>2</sub> under hydrostatic pressure of 0.4 $\mu_B$  / U. This suggests that the change in the internal field with doping seen in Section 3.1 is a real change in the magnetism, and not just due to changing muon stopping sites. Furthermore, the 1% doped sample shows a substantially reduced moment of 0.048  $\mu_B$  / U, which would be consistent with a larger moment existing over a smaller volume fraction, as suggested by the  $\mu$ SR measurements in Section 3.1.

Inelastic neutron scattering measurements show that the excitation spectra remain qualitatively similar from zero doping up to 15% Fe doping (the highest measured). In all of these measurements, two main magnetic excitations are seen: a commensurate excitation at the  $(1 \ 0 \ 0)$ position, and an incommensurate excitation at the  $(0.6 \ 0 \ 0)$  and equivalent  $(1.4 \ 0 \ 0)$  positions. There is also an excitation at the  $(2 \ 0 \ 0)$  position that does not change across the magnetic ordering transition and comes from a phonon. The data show that both commensurate and incommensurate excitations are initially ungapped above the transition temperature, and become gapped below, for both the pure sample and the doped samples. The gap for the incommensurate excitation is similar to that seen in the hidden order state of pure URu<sub>2</sub>Si<sub>2</sub>; however, the incommensurate excitation has substantially lower intensity and a much larger gap. In both the 5% and 15% Fe doped samples spin waves that would be expected for a conventional antiferromagnetic state are not observed.

Comparison of the temperature dependences of the magnetic Bragg peak intensity and the incommensurate excitation gap for the 1% doped sample shows that they do not onset at the
same temperature. As the incommensurate excitation becomes gapped for both the hidden order and antiferromagnetic state, while magnetic Bragg scattering is only observed in the antiferromagnetic state, this suggests that the hidden order state exists at temperatures just below 17.5 K in this sample, with a transition to antiferromagnetism at a lower temperature of about 15 K. This is similar to what was suggested by comparison of the magnetometry and  $\mu$ SR transition temperatures for a 1% doped sample in Section 3.1.

As a function of doping, both the commensurate and incommensurate gaps increase. The incommensurate gap appears to increase continuously with doping, in contrast with the discontinuous change across a critical pressure of 0.5 GPa for pure URu<sub>2</sub>Si<sub>2</sub> under hydrostatic pressure, but the value of this gap for our Fe doped samples remains similar to that measured under hydrostatic pressure [77]. The commensurate gap shows a sharp jump between doping levels of 1% and 2.5%, increasing by more than a factor of 3. While the evolution of the commensurate excitation with applied hydrostatic pressure is not fully resolved, with different studies either claiming it either disappears entirely [77, 78] or maintains the same energy gap but reduces in intensity [76], it is clear that our Fe doped samples behave differently than either of these scenarios. This suggests that the evolution of antiferromagnetism in Fe doped URu<sub>2</sub>Si<sub>2</sub> is not purely from chemical pressure.

**Publication II**: "*Hidden order signatures in the antiferromagnetic phase of*  $U(Ru_{1-x}Fe_x)_2Si_2$ ", T. J. Williams, A. A. Aczel, M. B. Stone, M. N. Wilson, and G. M. Luke. Physical Review B **95**, 104440 (2017).

Reproduced from Ref. [2] with permission, copyrighted by the American Physical Society.

# Author Contributions:

- Experimental Concept: T.J. Williams, A.A. Aczel, M.B. Stone, and G.M. Luke.
- Sample Preparation: M.N. Wilson, T.J. Williams, and G.M. Luke.
- Neutron Experiments: T.J. Williams, A.A. Aczel, M.N. Wilson, and M.B. Stone.
- Data Analysis: T.J. Williams, A.A. Aczel, M.N. Wilson, and M.B. Stone.
- Manuscript: T.J. Williams, A.A. Aczel, M.N. Wilson, M.B. Stone, and G.M. Luke.

 $(\Delta_{inc} = 4.5-4.8 \text{ meV} [11,13])$  and more intense [3,14]. It was determined that the gapping of these excitations results in an

entropy change of sufficient size to account for the specific

heat jump at  $T_0$  [14]. Below  $T_0$  additional, commensurate

excitations appear at the Z point of the BZ,  $\vec{Q}_{com} = (1 \ 0 \ 0)$ ,

with a gap of  $\Delta_{com} = 1.7-1.8$  meV [11,13]. This wave vector

is the ordering wave vector for the antiferromagnetic moment

in both the hidden order and more conventional magnetically

ordered phases. Since the transition at  $T_0$  is related to the

gapping of the incommensurate excitations and the emergence

of the commensurate ones, these have both been cited as

possible "signatures" of the hidden order state in neutron

enhance the hidden order state was through the use of

applied pressure. Application of pressure increased  $T_0$  slightly,

reaching 18.5 K at a pressure of 0.5 GPa [7]. However, at higher

pressures, this system still transitions to an antiferromagnetic

state; at T = 0 this occurs at approximately 0.8 GPa. Pressures

between 0.8 and 1.4 GPa have both a hidden order and a

Néel transition, while above 1.4 GPa the transition is directly

from paramagnetic to antiferromagnetic at  $T_N = 19.5$  K [7].

Due to this interplay of hidden order and antiferromagnetism,

studying the behavior under applied pressure has become of

particular interest in trying to determine the nature of the

unknown order parameter. Likewise, the chemical substituents

that enhance  $T_0$  have also become an interesting avenue of

research for determining the order parameter of the hidden

order state. Of the dozens of chemical dopings that have been

applied to  $URu_2Si_2$  only two dopings, both on the Ru site, have been shown to increase the value of  $T_0$ : Fe [15] and Os [16]. In both of these cases, the transition temperature

continues to increase as a function of doping, over a large

The first instance in which perturbations were found to

scattering experiments [5,11].

#### PHYSICAL REVIEW B 95, 104440 (2017)

# Hidden order signatures in the antiferromagnetic phase of $U(Ru_{1-x}Fe_x)_2Si_2$

T. J. Williams,\* A. A. Aczel, and M. B. Stone

Quantum Condensed Matter Division, Neutron Sciences Directorate, Oak Ridge National Lab, Oak Ridge, Tennessee, 37831, USA

M. N. Wilson

Department of Physics and Astronomy, McMaster University, Hamilton, ON, Canada L8S 4M1

G. M. Luke

Department of Physics and Astronomy, McMaster University, Hamilton, ON, Canada L8S 4M1 and Canadian Institute for Advanced Research, 180 Dundas St. W., Toronto, ON, Canada M5G 1Z7 (Received 19 July 2016; revised manuscript received 17 February 2017; published 31 March 2017)

We present a comprehensive set of elastic and inelastic neutron scattering measurements on a range of Fe-doped samples of U(Ru<sub>1-x</sub>Fe<sub>x</sub>)<sub>2</sub>Si<sub>2</sub> with 0.01  $\leq x \leq 0.15$ . All of the samples measured exhibit long-range antiferromagnetic order, with the size of the magnetic moment quickly increasing to 0.51  $\mu_B$  at 2.5% doping and continuing to increase monotonically with doping, reaching 0.69  $\mu_B$  at 15% doping. Time-of-flight and inelastic triple-axis measurements show the existence of excitations at (1 0 0) and (1.4 0 0) in all samples, which are also observed in the parent compound. While the excitations in the 1% doping are quantitatively identical to the parent material, the gap and width of the excitations change rapidly at 2.5% Fe doping and above. The 1% doped sample shows evidence for a separation in temperature between the hidden order and antiferromagnetic transitions, suggesting that the antiferromagnetic state emerges at very low Fe dopings. The combined neutron scattering data suggest not only discontinuous changes in the magnetic moment and excitations between the hidden order and antiferromagnetic phases, but that these changes continue to evolve up to at least x = 0.15.

DOI: 10.1103/PhysRevB.95.104440

#### I. INTRODUCTION

The heavy fermion material URu2Si2 has been a subject of long-standing interest since the discovery of a phase transition at  $T_0 = 17.5$  K, 30 years ago [1]. Initially thought to be an antiferromagnetic transition, the small antiferromagnetic moment of 0.03  $\mu_B$  that arises in this material is far too small to account for the large specific heat jump at  $T_0$  [2,3]. Three decades of research have produced a number of conclusions regarding the nature of this phase [4,5], but have failed to determine the order parameter, leading to this phase being dubbed the "hidden order" phase. To study the behavior of the hidden order phase, a large number of perturbations have been applied to the system in the form of applied field, hydrostatic pressure, and chemical substitution. In all cases, the hidden order phase is destroyed with relatively small perturbations: applied fields of >35 T [6], hydrostatic pressure >0.8 GPa [7], and chemical substitution of typically greater than 5% on any of the atomic sites [8-10]. In nearly every case, the hidden order state is suppressed continuously, and a ferro- or antiferromagnetic state emerges.

Neutron scattering has played an important role in determining the properties of the hidden order phase. For example, while careful study has shown that the small antiferromagnetic moment is present even in ultraclean samples [11], it is likely caused by inhomogeneous strain [12]. Within the paramagnetic phase above  $T_0$ , inelastic neutron scattering measurements observed gapless, weakly dispersing features at the  $\Sigma$  point on the Brillouin zone (BZ) edge with  $\vec{Q}_{inc} = (1 \pm \delta \ 0 \ 0)$ ( $\delta = 0.407$ ), while below  $T_0$ , these excitations became gapped

<sup>\*</sup>williamstj@ornl.gov

<sup>2469-9950/2017/95(10)/104440(9)</sup> 

# WILLIAMS, ACZEL, STONE, WILSON, AND LUKE

range, before dropping abruptly. Interestingly, of all of the pure compounds of the family  $UT_2Si_2$ , T = Fe and Os are the only two that are nonmagnetic [9,17]. Furthering the analogy between hydrostatic pressure and Fe/Os doping, the doped systems are also observed to become more conventionally antiferromagnetic with increasing chemical pressure, however no signature of multiple transitions have been observed with transport measurements [15,16]. It was speculated that these systems experience only a gradual crossover between the hidden order and antiferromagnetic states, although this remains an open question.

In this work we use elastic and inelastic neutron scattering to measure the magnetic structure and excitations of various doping concentrations within the  $U(Ru_{1-x}Fe_x)_2Si_2$  series, in an attempt to determine the nature of the hidden order-toantiferromagnetic crossover, as well as whether the doped compounds contain inelastic signatures of the hidden order state and/or signatures of a conventional antiferromagnetic state (spin waves). Recently, neutron diffraction measurements have been carried out on a number of dopings in this series [18], which found that the magnetic moment grows continuously from x = 0 to x = 0.05 and that at dopings above 5% the magnetic moment remains relatively constant at 0.8  $\mu_B$ . This leads the authors to suggest that 5% doping marks the hidden order-to-antiferromagnetic phase transition, analogous to the transition at 0.8 GPa in the parent compound under pressure [18]. This suggests that in order to study the nature of the excitations through the transition, it is important to measure dopings both above and below x = 0.05.

#### **II. EXPERIMENT**

Single crystals of U(Ru<sub>1-x</sub>Fe<sub>x</sub>)<sub>2</sub>Si<sub>2</sub> with x = 0.01, 0.025, 0.05, 0.10, and 0.15 were grown at McMaster University. Stoichiometric amounts of unpurified depleted uranium, Ru (99.95%), Fe (99.99%), and Si (99.9999%) were arc-melted on a water-cooled copper hearth in a mono-arc furnace under an inert Ar atmosphere. The largest impurity in the uranium precursor is elemental Fe at a level of  $\approx$ 50ppm, which is small (<0.01%) when compared to the nominal doping concentrations. The resulting polycrystalline boule was then used to grow the single crystals using the Czochralski method. This was performed in a tri-arc furnace using a water-cooled copper hearth under a continuously gettered Ar atmosphere at 900 °C. After the growths, the single-crystalline nature and sample alignments were confirmed with Laue x-ray diffraction.

These samples were studied using elastic and inelastic neutron scattering at the High-Flux Isotope Reactor (HFIR) and the Spallation Neutron Source (SNS) of Oak Ridge National Laboratory (ORNL). The diffraction measurements were performed on all of the samples using the HB-1A spectrometer at HFIR, while inelastic measurements were done on the HB-1 (for x = 0.01 and 0.05) and HB-3 (for x = 0.025, 0.10, and 0.15) triple-axis instruments at HFIR, as well as the SEQUOIA time-of-flight spectrometer at the SNS (for x = 0.05 and 0.15). For comparison, data on the parent compound have been included where appropriate; this data were measured on the Multi-Axis Crystal Spectrometer (MACS) at the NIST Center for Neutron Research and

# PHYSICAL REVIEW B 95, 104440 (2017)

was published previously [19]. The neutron measurements described in this work were performed using one single crystal of each doping: the x = 0.01 sample had a mass of 5.65(2) g and a mosaic of 4.5°, the x = 0.025 sample had a mass of 1.99(1) g and a mosaic of 1.3°, the x = 0.05 sample had a mass of 2.98(1) g and a mosaic of 10°, the x = 0.10 sample had a mass of 1.85(1) g and a mosaic of 3.0°, and the x = 0.15 sample had a mass of 1.74(1) g and a mosaic of 4.0°. All of these samples were aligned in the [H 0 L] scattering plane for each of the neutron scattering experiments.

The HB-1A measurements were performed in a closedcycle refrigerator with a base temperature of 4.0 K using a fixed incident energy of 14.7 meV. A PG (002) monochromator and analyzer crystals were used with PG filters, and the collimation was 40'-40'-40'-80'. The HB-1 and HB-3 measurements were performed in closed-cycle refrigerators with a base temperature of 4.0 K using a fixed final energy of 14.7 meV. A PG (002) monochromator and analyzer crystals were used with PG filters, and the collimation was 48'-40'-40'-120'. The SEQUOIA measurements were also performed in a closed-cycle refrigerator with a base temperature of 5 K, using a fixed incident energy of 30 meV. The crystals were rotated in the [H 0 L] plane in 1° steps over a 190° range.

# **III. MAGNETIC STRUCTURE DETERMINATION**

The neutron diffraction involved measurements of all of the Bragg peaks for which  $|\vec{Q}| < 4.7 \text{ Å}^{-1}$ , at 4 and 30 K, as well as the temperature dependence of the (1 0 0) and (0 0 1) magnetic Bragg peaks. While the (0 0 1) peaks was found to have a weak magnetic signal, the *c*-axis magnetic contribution was found to be consistent with what would be expected due to multiple scattering for  $E_i = 14.7$  meV, suggesting that the magnetic moments point along the  $\hat{c}$  direction. Multiple scattering was also encountered in the parent material, where the same magnetic structure was refined for the small, intrinsic moments [20].

Figure 1 shows the (1 0 0) magnetic Bragg peak at 4 K in the various Fe-doped samples [Fig. 1(a)] and their temperature dependence [Fig. 1(b)]. This is a disallowed nuclear peak so there is no scattering from the sample above  $T_0$ , as seen in the temperature dependence. We observe the onset of magnetic scattering, and the transition appears to be second order in nature. The temperature dependence of the lowest two dopings, 1% and 2.5%, do not show the same temperature dependence. Previous work using  $\mu$ SR has shown that at these dopings, there is considerable phase separation between magnetic and nonmagnetic regions, likely as a result of the random dopant distribution in these samples [21]. This is a likely origin of the observed temperature dependence of the magnetic Bragg peak. However, the peaks are resolution limited at all dopings, suggesting that the magnetic order is sufficiently long ranged. Using the seven structural and nine magnetic peaks collected on each sample, the magnetic structure and moment can be determined. In agreement with the parent material at ambient pressure and in the pressure-induced antiferromagnetic state, this magnetic structure has magnetic moments aligned along the c axis, with the body-centered moment antiparallel to the moments in the neighboring *ab* planes [20].

HIDDEN ORDER SIGNATURES IN THE ...



FIG. 1. (a) Radial scans through the (1 0 0) magnetic Bragg peaks at T = 4 K in the various samples of  $U(Ru_{1-x}Fe_x)_2Si_2$ . All of the peaks appear resolution limited, indicating long-range magnetic order. This is a disallowed nuclear peak, and so there is no scattering from the sample above  $T_0$ . (b) The temperature dependence of the (1 0 0) magnetic Bragg peak intensity in the various samples. This shows the second-order transition from the paramagnetic state to the antiferromagnetic state at  $T_N$ . The lack of saturation of the moment in the 1% (yellow) and 2.5% (black) samples may be dues to phase separation (see text). In both plots, the error bars lie within the symbols.

The magnetic moment as a function of doping at T = 4 K was extracted from the integrated intensity of the (1 0) magnetic peak normalized by the integrated intensity of the (1 0 1) structural peak, with the proper Lorentz factors taken into account for both Bragg peaks. The (1 0 1) structural peak was chosen for the normalization to minimize the difference in instrumental Q resolution at the two peak positions, since resolution effects were not incorporated in these calculations. This approach is in contrast to the method employed by Das *et al.* [18], who chose the higher order Bragg peak (6 0 0) for the normalization to avoid extinction effects. Neither normalization method accounts for the effect of multiple scattering, which has been noted as significant in URu<sub>2</sub>Si<sub>2</sub>, but that is difficult to calculate directly [11,20]. This may produce differences in the size of the magnetic moments determined.

### PHYSICAL REVIEW B 95, 104440 (2017)

TABLE I. The transition temperatures and extracted moment sizes in the various dopings of  $U(Ru_{2-x}Fe_x)_2Si_2$  measured in this work. The value of  $T_N$  is the transition temperature seen in the measurement of the (1 0 0) Bragg peak [Fig. 1(b)]. Also listed are the values of  $T_0$  and  $T_N$  as determined from the same crystals that were used in the current studies. These values were obtained from susceptibility and  $\mu$ SR measurements as reported in Ref. [21].

Doping (%)	$\mathrm{T}_{N}\left(\mathrm{K}\right)$	Moment $(\mu_B)$	$T_0$ (K) [21]	$T_N$ (K) [21]
1.0%	15.0(5)	0.048(5)	17.5	16.0
2.5%	15.0(5)	0.51(1)		
5.0%	20.0(5)	0.59(1)	21.0	21.0
10.0%	21.0(5)	0.59(2)	21.5	21.0
15.0%	22.5(5)	0.66(2)	25.5	25.0

The moments that were extracted from the neutron diffraction measurements are shown in Table I, along with the values of  $T_N$  and  $T_0$  from  $\mu$ SR in a previous work [21]. The values of  $T_N$  from the measurement of the (1 0 0) magnetic Bragg peak are lower than those found by  $\mu$ SR, likely due to the local probe nature of the  $\mu$ SR measurements. The size of the moments agree well with the values determined from the internal field measurements based on the muon precession frequency, suggesting they are sensitive to the same magnetic ordering. The size of the moment in the Fe-doped samples is comparable to what is seen in the pressure-induced antiferromagnetic state of the parent compound [22], except for the lowest doping (1%). In the lowest-doped sample, the size of the internal field determined by  $\mu$ SR would suggest a moment size of ~0.45  $\mu_B$ , however this was associated with a reduced volume fraction of  $\sim 0.6$  at T = 5 K [21]. The decreased moment seen by the neutron measurements is likely due to the phase separation between antiferromagnetism and the hidden order phase observed by the  $\mu$ SR measurements. This would indicate that the transition from hidden order to antiferromagnetism occurs at a doping between 1% and 2.5%, lower than that suggested by Das et al. [18]. While we speculate that the difference in the moments may result from a different normalization method, the difference in the doping dependence may also be a result of differences in nominal and actual doping concentrations.

### IV. INELASTIC MEASUREMENTS

Figure 2 shows the inelastic time-of-flight measurements of the 5% sample at 30 K [Fig. 2(a)] and at 5 K [Fig. 2(b)], as well as the 15% sample at 5 K [Fig. 2(c)]. Figure 2(a) shows measurements in the paramagnetic state. The inelastic spectrum seen here in the 5%-doped sample is identical to what is seen in the parent material above  $T_0$ : gapless excitations emanating from  $\vec{Q}_{inc} = (0.600)$ , and no excitation at  $\vec{Q}_{com} = (1\ 0\ 0)$ . Figure 2(d) illustrates what happens in the hidden order state of the parent material (this data are adapted from Ref. [19]). The excitation at  $\vec{Q}_{inc}$  becomes gapped, resulting in the entropy change seen by specific heat. Additionally, gapped excitations also appear at  $\vec{Q}_{com}$ , albeit with a smaller gap and less intensity. Figure 2(b) shows the scample. Relative to the parent material, we see that the



FIG. 2. Time-of-flight neutron measurements of various  $U(Ru_{1-x}Fe_x)_2Si_2$  samples. (a) x = 0.05, measured at 30 K in the paramagnetic phase. As is seen in the paramagnetic state of the parent (x = 0) compound, there are gapless excitations at the incommensurate wave vector  $\vec{Q}_{inc} = (1.4 \ 0 \ 0)$ . (b) Below  $T_0$ , these excitations become gapped and their spectral weight increases. (c) At higher Fe dopings (x = 0.15 is shown here), the gap can be seen to increase and broaden in  $\hbar\omega$  and  $\vec{Q}$ . (d) Data from the parent compound (taken from Ref. [19]) below  $T_0$  show similar excitations at  $\vec{Q}_{inc}$ , however the excitations in the parent material are more well defined. Additionally, the commensurate excitations  $\vec{Q}_{com} = (1 \ 0 \ 0)$ , which are clearly present in the parent material, are not as obvious in the Fe-doped samples. Cuts through  $\vec{Q}_{com}$  show these excitations to be substantially weakened, and appear at higher energy than in the parent. Inset: The phase diagram of  $U(Ru_{1-x}Fe_x)_2Si_2$  showing the locations of the measurements for (a) to (d). (a) x = 0.05, T = 30 K; (b) 0.05, T = 5 K; (c) x = 0.15, T = 5 K; (d) x = 0.0, T = 0.5 K.

incommensurate excitation is qualitatively unchanged. The gap appears to be larger, but with little change in the spin wave velocity, similar to what is observed under hydrostatic pressure [19]. The commensurate excitation, however, shows a large change when compared to the pure material in the hidden order state. It is significantly weaker relative to the incommensurate excitation. Furthermore, the scattering that is present at the commensurate point in the 5% doping is only present at much higher energies.

Moving to higher Fe doping [15.0% in Fig. 2(c)], the weakening of these excitations seems to continue at both the commensurate and incommensurate points. Additionally, we observe that the gap at  $\tilde{Q}_{\rm inc}$  is larger than at x = 0.05 or in the parent. This type of trend has been observed under pressure, where an increase in the transition temperature

seems to correlate with an increase in the incommensurate gap, though the magnitude of the gap change in this system is much larger than what has been observed under pressure for the same change in the transition temperature [19,23]. The excitations also appear broadened, both in |Q| and  $\hbar\omega$ . This would suggest that Fe doping distorts the Fermi surface, weakening the nesting that gives rise to the excitations [13]. Furthermore, no additional excitations appear with Fe doping, including any conventional spin waves centered on the (1 0 0) magnetic Bragg peak. To more carefully investigate the changes in the excitations, inelastic triple axis neutron scattering measurements were performed at both  $\vec{Q}_{com}$  and  $\vec{Q}_{inc}$ , above and below  $T_0$ .

The inelastic triple-axis measurements at  $\hat{Q}_{com} = (1 \ 0 \ 0)$  are shown in Fig. 3, at 30 K, above the transition (open circles),



FIG. 3. Commensurate excitation as a function of doping at T = 4 K (filled circles) and T = 30 K (open circles). The solid line is a fit to the low temperature data as described in the text. The data for the parent compound are adapted from Ref. [19].

HIDDEN ORDER SIGNATURES IN THE ...

and at 4 K, below the transition (filled circles) for each of the measured dopings. The data for the 1% [Fig. 3(a)] and 5% [Fig. 3(d)] samples were taken on the HB-1 spectrometer, which had a lower background than the same measurements on the HB-3 spectrometer for the other Fe-doped samples. However, all samples clearly show the opening of the gap in the excitation spectrum below the transition. The same excitation in the parent compound is shown in Fig. 3(a) for comparison (data adapted from Ref. [19]). The solid line is a fit to the data, following the analysis of Refs. [3,19], given by

$$\tilde{I}(\mathbf{Q},\omega) = I \left[ \frac{\hbar\gamma/\pi}{[\hbar\omega - \epsilon(\mathbf{Q})]^2 + (\hbar\gamma)^2} - \frac{\hbar\gamma/\pi}{[\hbar\omega + \epsilon(\mathbf{Q})]^2 + (\hbar\gamma)^2} \right],\tag{1}$$

where *I* is an overall scale factor for the intensity and  $\hbar\gamma$  is the half width at half maximum (HWHM) for the Lorentzian functions. With an energy gap  $\Delta$ , the dispersion relation reads

$$\epsilon(\mathbf{Q}) = \sqrt{\Delta^2 + \hbar^2 (\delta Q_{\perp}^2 v_{\perp}^2 + \delta Q_{\parallel}^2 v_{\parallel}^2)}, \qquad (2)$$

where  $\delta Q_{\perp,\parallel} = |(\mathbf{Q} - \mathbf{Q}_0)_{\perp,\parallel}|$  is the projection of the difference of the wave vector transfer  $\mathbf{Q}$  from the critical wave vector  $\mathbf{Q}_0$  perpendicular and parallel, respectively, to the  $\hat{\mathbf{c}}$  direction. The velocities used were those of the parent compounds, where  $v_H = v_K = v_\perp = 23.7(5) \text{ meV} \hat{\mathbf{A}}$  and  $v_L = v_{\parallel} = 32.5(7) \text{ meV} \hat{\mathbf{A}}$  [19]. Equation (1) was multiplied by a Bose factor and convoluted with the 4D experimental resolution function using RESLIB [24]. This underestimates the elastic peak at (100) in Fig. 3 due to the elastic magnetic Bragg peak at this  $\hat{Q}$ , but more reliably reproduces the quasielastic signal at the incommensurate (1.4 0 0) in Fig. 4. Since these measurements were most concerned with extracting the parameters of the inelastic excitation, no additional terms were

# PHYSICAL REVIEW B 95, 104440 (2017)

TABLE II. Results of fitting the data in Figs. 3 and 4 to Eq. (1), as described in the text. Data for the parent compound (x = 0.0) are taken from Ref. [19].

Doping	Wave vector	I (arb. units)	$\Delta$ (meV)	γ (meV)
0.0% [19]	(1 0 0)	-	2.3(4)	0.9(1)
1.0%	$(1\ 0\ 0)$	1.55(3.77)	2.3(1)	1.2(2)
2.5%	(100)	6.99(2.13)	6.7(1)	8.0(6)
5.0%	$(1\ 0\ 0)$	10.28(3.08)	6.8(1)	7.7(6)
10.0%	$(1\ 0\ 0)$	7.01(1.95)	6.6(1)	6.9(5)
15.0%	(1 0 0)	6.04(1.34)	7.5(1)	6.7(6)
0.0% [19]	(1.4 0 0)	-	4.2(2)	0.7(1)
1.0%	(1.400)	5.12(3.08)	4.18(4)	0.48(9)
2.5%	(1.400)	5.26(2.26)	3.5(1)	2.7(3)
5.0%	(1.400)	2.48(78)	5.21(6)	3.4(3)
10.0%	(1.400)	0.59(26)	5.9(1)	6.1(7)
15.0%	(1.4 0 0)	0.25(25)	7.1(3)	6.4(1.6)

included to model the elastic peak. The values obtained from these fits are given in Table II below.

We see that in the 1% doping, the commensurate excitation is nearly unchanged from the parent material; the gap and width are unchanged within error. However, we notice a dramatic change in the 2.5% doped sample, where the excitation is substantially broadened in energy and is peaked at much higher energies. The excitation is essentially unchanged with further increases in doping, with the gap energy and the width much larger than in the parent compound. This trend is shown in Fig. 5 where we can see the very abrupt changes in the gap [Fig. 5(a)] and the FWHM [Fig. 5(c)], which are relatively constant above 1% doping. It is also notable that the commensurate excitation is qualitatively unchanged across



FIG. 4. Incommensurate excitation as a function of doping at T = 4 K (filled circles) and T = 30 K (open circles). The solid line is a fit to the low temperature data as described in the text. The data for the parent compound are adapted from Ref. [19].

WILLIAMS, ACZEL, STONE, WILSON, AND LUKE





FIG. 5. (a) The gap at  $\vec{Q}_{com}$  (filled circles) and  $\vec{Q}_{inc}$  (open circles) as a function of Fe doping measured at T = 4 K. The values of the gap at 1% doping are nearly unchanged from the parent compound. Above 1% doping, the gap at the commensurate wave vector increases dramatically, while the incommensurate gap increases continuously with Fe doping. (b) The value of the gap at  $\vec{Q}_{com}$  (red circles),  $\vec{Q}_{inc}$  (blue circles), and the gap measured by transport (black triangles) as a function pressure. Figure reproduced with permission from Ref. [23], copyright American Physical Society. (c) The full width at half maximum (FWHM) of the excitations as a function of doping at T = 4 K. Similarly to the behavior of the gaps, the width of the excitations is nearly unchanged at 1% doping. Above 1%, the width of the commensurate excitation is greatly broadens with increasing Fe doping.

the phase transition, despite the emergence of the magnetic Bragg peaks at  $(1 \ 0 \ 0)$ . In agreement with the time-of-flight measurements, no other excitations are present in any of the samples.

Figure 4 shows the excitation that is present below  $T_0$ at  $\vec{Q}_{inc} = (1.4 \ 0 \ 0)$  as a function of doping. This excitation was fit in the same manner as the commensurate excitation, shown by the solid lines in Fig. 4. The values obtained from this fitting are given in Table II. As with the commensurate excitation, the incommensurate excitation shows very little change at 1% doping relative to the parent compound. However, above 1% doping, rather than a discontinuous change, the incommensurate excitation exhibits a continuous broadening and upward shift in energy. As with the doping dependence of the magnetic moment, the incommensurate excitation shows a discontinuous change from the hidden order to antiferromagnetic phases, as well as a continued evolution over the entire range of Fe doping. This is apparent from looking at Figs. 5(a) and 5(c), where the gap and FWHM, respectively, show an increase over the full range of dopings measured. The excitation appears to weaken continuously with increasing Fe doping, but is present in all dopings measured with no additional excitations present.

Comparing these results to the gap measured by inelastic neutron scattering under pressure [shown in Fig. 5(b)], we see that there is a similarity when considering the incommensurate excitation (blue circles). The application of pressure also increases the gap, though it is assumed that under pressure the gap jumps discontinuously at  $P_0 = 0.5$  GPa and is constant above. However, there may not be enough data points to be certain [19,23,25].

Lastly, to more directly probe the relationship between the hidden order and the antiferromagnetic order, we measured the order parameters for both types of ordering simultaneously in the 1% Fe-doped sample, shown in Fig. 6. The black squares denote the peak intensity of the (1 0 0) elastic magnetic Bragg peak, while the blue circles are the scattering intensity at

(1.4 0 0) and an energy transfer of 2 meV. This shows the strength of the scattering at a point within the incommensurate gap, a measurement that was shown to determine the opening of the gap at  $T_0$  in the parent compound [26]. In agreement with the quantitative similarities of the excitations in the 1% sample and the parent compound, as well as the bulk thermodynamic data [15,21], we see the opening of the incommensurate gap at  $T_0 = 17.5$  K. However, in agreement with the  $\mu$ SR measurements [21], the onset of the antiferromagnetic order occurs at a slightly lower temperature,  $T_N = 15$  K. Despite the apparent variation in the transition temperatures, specific heat



FIG. 6. Plots of the order parameters for hidden order and antiferromagnetic phases for the 1% Fe-doped sample. The elastic magnetic Bragg peak (black squares) shows an onset around 15 K, coincident with the transition in the  $\mu$ SR measurements, while the opening of the gap at  $\vec{Q}_{inc}$  (blue circles) onsets at 17.5 K, the same as for the parent compound and where the transition is seen by susceptibility [21].



HIDDEN ORDER SIGNATURES IN THE

FIG. 7. (a) The (1 0 0) magnetic Bragg peak shown at 4, 14, and 16 K, subtracting the same data at 30 K. Here we see the disappearance of the magnetic Bragg peak at a temperature below the hidden order transition at  $T_0 = 17.5$  K. (b) Energy scan at (1.4 0 0) at the same temperatures as in (a), showing the temperature evolution of the gap. The gap is present at all temperatures, though the weak signal and small gap (within the experimental resolution) at 16 K make this less clear than the measurement shown in Fig. 6.

measurements see no entropy change between the hidden order and antiferromagnetic phases, emphasizing that the Fermi surface reconstruction happens at the upper transition [15]. Recent magnetization and thermal expansion measurements also see evidence for the possibility of two transitions, though they suggest that this is also present at higher dopings ( $\sim 5\%$ ) [27]. This may be due to variations in doping concentrations or a difference in sensitivity of the measurement techniques.

To verify the presence of two transitions, constant  $\vec{Q}$  measurements were performed at 4, 14, 16, 18, and 30 K to measure both the (1 0 0) magnetic Bragg peak and the opening of the gap at (1.4 0 0), shown in Fig. 7. It can be seen that the 14 K data show a gap in the (1.4 0 0) excitation spectrum, and there is appreciable scattering at the (1 0 0) magnetic Bragg peak. At 16 K, the magnetic Bragg peak is absent, within error, while the gap in the (1.4 0 0) constant- $\vec{Q}$  measurement had been reduced, it is still present. Both measurements at 18 K are identical within error to the 30 K data. This is consistent with the separation in temperature of the hidden order and magnetic transitions.

PHYSICAL REVIEW B 95, 104440 (2017)

# V. DISCUSSION AND CONCLUSIONS

We have presented a comprehensive set of elastic and inelastic neutron scattering measurements on a range of Fe-doped samples of U(Ru<sub>1-x</sub>Fe<sub>x</sub>)<sub>2</sub>Si<sub>2</sub> with 0.01  $\leq x \leq 0.15$ . We have found that the onset of the antiferromagnetic phase occurs at very low doping, with the 2.5% doped sample showing an ordered moment of 0.51  $\mu_B$ . However, the 1% sample seems to show excitations that are nearly identical to the parent compound, but onsetting at a higher temperature than the antiferromagnetic moment. Combined with previous susceptibility and  $\mu$ SR measurements on these samples [21], there is strong evidence of different transition temperatures for the antiferromagnetic and hidden orders, in agreement with other techniques on different Fe-doped samples [27]. Resistivity and specific heat measurements do not see any signatures of an abrupt phase transition between the hidden order and antiferromagnetic state [15,27]. This is consistent with no observed change in  $\vec{Q}$  for the incommensurate excitation, which remains at the  $\Sigma$  point of the hidden order phase, suggesting no change in the BZ between the antiferromagnetic and hidden order phases. Additionally, the  $\mu$ SR measurements see evidence for phase separation at low dopings, likely a result of the statistically random distribution of Fe dopants [21]. These dopings are also where the (100) magnetic Bragg peak does not show a rapid onset, seen in Fig. 1(b), which would be expected in samples with low doping concentrations.

All of the dopings that were measured show evidence for long-ranged magnetic order, with the moment size increasing as a function of doping. This suggests that even far from the parent compound, there is still an evolution away from hidden order. This increase in the magnetic moment is accompanied by a continuous increase in  $T_N$ , which peaks above the dopings studied at ~40% doping, before being suppressed to a paramagnetic state above ~70% doping. Synthesis of large single crystals becomes difficult above 15% Fe doping [15], but  $\mu$ SR measurements up to 50% Fe doping show that the magnetic moment decreases above 15% Fe substitution [21].

The inelastic time-of-flight and triple-axis measurements show that both sets of excitations observed in the parent compound are present at all dopings measured. However, while the excitations are qualitatively unchanged, there are dramatic changes in the quantitative properties above 1% doping, most noticeably in the reduction of the intensity of the commensurate excitation. The increase in the gap and energy broadening of the excitations at both the commensurate and incommensurate point occurs noticeably in the 2.5% doped sample. Both the magnitude of the gap ( $\Delta$ ) and the width ( $\gamma$ ) evolve continuously with doping, which is most apparent at the incommensurate point. As observed with measurements of the parent compound under pressure, the increase in the gap at  $\vec{Q}_{inc}$  coincides with an increase in  $T_0$ . This also follows the monotonic increase in the magnetic moment with doping, suggesting that the critical doping is between 1% and 2.5%, but that the magnetic moment and the excitations change continuously at higher dopings.

The pressure results have been somewhat unclear about the existence and properties of the commensurate excitation, with work performed at 0.62 GPa reporting its absence [23,25,28], while other work seeing a gap of <1meV at 0.72 GPa

## WILLIAMS, ACZEL, STONE, WILSON, AND LUKE

[29] and a gap of 1.8 meV at 1.02 GPa [19]. This has been interpreted as mode softening at the critical pressure  $P_C = 0.6$  GPa, which may explain the changing value of the gaps as seen in the present case of Fe doping. However, the much larger gap and width in the Fe-doped samples clearly demonstrate that the behavior of the commensurate excitation under Fe doping is not the same as under applied pressure, which may suggest that the effect of Fe doping on the Z point Fermi surface pocket is not strictly analogous to the changes that occur under hydrostatic pressure. Furthermore, the change in the excitations point to evolutions in the Fermi surface with increasing Fe doping; this serves to increase the gap, suggesting that the Fermi surface pockets at the  $\Sigma$ , Z, and/or  $\Gamma$  points distort slightly to change the optimal energy for the nesting. This must occur without any Fermi surface reconstruction, as there is no entropy change across the HO-AF transition [15], nor do we see any change in the location of the incommensurate excitation  $(\Sigma)$ , suggesting that the Fermi surface is not distorted in the antiferromagnetic state. Drawing the analogy to the antiferromagnetic state induced by applied pressure, that transition similarly shows no Fermi surface reconstruction by quantum oscillation measurements [30]. We can make further comparison to the pressure-induced AF state by looking at the excitations seen by neutron scattering. Under pressure, the gap at the incommensurate point similarly shows a slight increase, while the intensity of the excitations also increases [19]. The intensity of the excitations does not increase with Fe doping, but this may be a result of impurities distorting the Fermi surface, serving to weaken the nesting that is undistorted in the case of applied pressure. This can also be seen by comparing the width of the excitations, which are unchanged under pressure [19], but dramatically broadened in the case of Fe doping.

- [1] T. T. M. Palstra, A. A. Menovsky, J. van den Berg, A. J. Dirkmaat, P. H. Kes, G. J. Nieuwenhuys, and J. A. Mydosh, Phys. Rev. Lett. 55, 2727 (1985).
- [2] C. Broholm, J. K. Kjems, W. J. L. Buyers, P. Matthews, T. T. M. Palstra, A. A. Menovsky, and J. A. Mydosh, Phys. Rev. Lett. 58, 1467 (1987).
- [3] C. Broholm, H. Lin, P. T. Matthews, T. E. Mason, W. J. L. Buyers, M. F. Collins, A. A. Menovsky, J. A. Mydosh, and J. K. Kjems, Phys. Rev. B 43, 12809 (1991).
- [4] J. A. Mydosh and P. M. Oppeneer, Rev. Mod. Phys. 83, 1301 (2011).
- [5] J. A. Mydosh and P. M. Oppeneer, Philos. Mag. 94, 3642 (2014).
- [6] Y. J. Jo, L. Balicas, C. Capan, K. Behnia, P. Lejay, J. Flouquet, J. A. Mydosh, and P. Schlottmann, Phys. B: Condens. Matter 403, 749 (2008).
- [7] N. P. Butch, J. R. Jeffries, S. Chi, J. B. Leão, J. W. Lynn, and M. B. Maple, Phys. Rev. B 82, 060408(R) (2010).
- [8] H. Amitsuka and T. Sakakibara, J. Phys. Soc. Jpn. 63, 736 (1994).
- [9] T. Endstra, G. J. Nieuwenhuys, and J. A. Mydosh, Phys. Rev. B 48, 9595 (1993).
- [10] J.-G. Park and B. R. Coles, J. Phys.: Condens. Matter 6, 1425 (1994).

#### PHYSICAL REVIEW B 95, 104440 (2017)

This study serves to illustrate that  $URu_2Si_2$  is ideally placed on the precipice of magnetic states: antiferromagnetism under pressure or Fe doping, and even ferromagnetism under Re doping [31]. In all cases, we see that the excitation spectrum changes quantitatively, but not qualitatively, and is not destroyed by the emergence of the magnetically ordered state [19,32]. Thus this work demonstrates that in the Fe-doped compounds studied here, as with other perturbations, the hidden order state is not incompatible with magnetic order but rather that the electronic correlations are intimately related to magnetism.

## ACKNOWLEDGMENTS

The authors would like to thank C.R. Wiebe for helpful discussions as well as C. Broholm for his input and collaboration on the parent compound [19]. We also note that inelastic neutron scattering work on these compounds was submitted recently during the preparation of this manuscript [33] and we thank N.P. Butch for sharing that work, whose results are consistent with the present study. We acknowledge instrument support from S. Chi, M. Matsuda, L.M. Debeer-Schmitt, and D. Pajerowski. This research at ORNL's High Flux Isotope Reactor and Spallation Neutron Source was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. Work at McMaster University was supported by the Natural Sciences and Engineering Research Council of Canada and the Canadian Foundation for Innovation. T.J.W. acknowledges support from the Wigner Fellowship program at Oak Ridge National Laboratory. M.N.W. acknowledges support from the Alexander Graham Bell Canada Graduate Scholarship program.

- [11] F. Bourdarot, S. Raymond, and L.-P. Regnault, Philos. Mag. 94, 3702 (2014).
- [12] H. Amitsuka, K. Matsuda, I. Kawasaki, K. Tenya, M. Yokoyama, C. Sekine, N. Tateiwa, T. C. Kobayashi, S. Kawarazaki, and H. Yoshizawa, J. Magn. Magn. Mater. 310, 214 (2007).
- [13] N. P. Butch, M. E. Manley, J. R. Jeffries, M. Janoschek, K. Huang, M. B. Maple, A. H. Said, B. M. Leu, and J. W. Lynn, Phys. Rev. B **91**, 035128 (2015).
- [14] C. R. Wiebe, J. A. Janik, G. J. MacDougall, G. M. Luke, J. D. Garrett, H. D. Zhou, Y.-J. Lo, L. Balicas, Y. Qiu, J. R. D. Copley, Z. Yamani, and W. J. L. Buyers, Nat. Phys. 3, 96 (2007).
- [15] N. Kanchanavatee, M. Janoschek, R. E. Baumbach, J. J. Hamlin, D. A. Zocco, K. Huang, and M. B. Maple, Phys. Rev. B 84, 245122 (2011).
- [16] N. Kanchanavatee, B. D. White, V. W. Burnett, and M. B. Maple, Philos. Mag. 94, 3681 (2014).
- [17] L. M. Sandratskii and J. Kübler, Phys. Rev. B 50, 9258 (1994).
- [18] P. Das, N. Kanchanavatee, J. S. Helton, K. Huang, R. E. Baumbach, E. D. Bauer, B. D. White, V. W. Burnett, M. B. Maple, J. W. Lynn, and M. Janoschek, Phys. Rev. B 91, 085122 (2015).

HIDDEN ORDER SIGNATURES IN THE ...

- [19] T. J. Williams, H. Barath, Z. Yamani, J. A. Rodriguez-Riviera, J. B. Leao, J. D. Garrett, G. M. Luke, W. J. L. Buyers, and C. Broholm, arXiv:1607.00967.
- [20] K. A. Ross, L. Harriger, Z. Yamani, W. J. L. Buyers, J. D. Garrett, A. A. Menovsky, J. A. Mydosh, and C. L. Broholm, Phys. Rev. B 89, 155122 (2014).
- [21] M. N. Wilson, T. J. Williams, Y.-P. Cai, A. M. Hallas, T. Medina, T. J. Munsie, S. C. Cheung, B. A. Frandsen, L. Liu, Y. J. Uemura, and G. M. Luke, Phys. Rev. B 93, 064402 (2016).
- [22] H. Amitsuka, M. Sato, N. Metoki, M. Yokoyama, K. Kuwahara, T. Sakakibara, H. Morimoto, S. Kawarazaki, Y. Miyako, and J. A. Mydosh, Phys. Rev. Lett. 83, 5114 (1999).
- [23] F. Bourdarot, E. Hassinger, S. Raymond, D. Aoki, V. Taufour, L.-P. Regnault, and J. Flouquet, J. Phys. Soc. Jpn. 79, 064719 (2010).
- [24] A. Zheludev, *ResLib 3.4* (Oak Ridge National Laboratory, Oak Ridge, TN, 2007).
- [25] A. Villaume, F. Bourdarot, E. Hassinger, S. Raymond, V. Taufour, D. Aoki, and J. Flouquet, Phys. Rev. B 78, 012504 (2008).

# PHYSICAL REVIEW B 95, 104440 (2017)

- [26] C. R. Wiebe, G. M. Luke, Z. Yamani, A. A. Menovsky, and W. J. L. Buyers, Phys. Rev. B 69, 132418 (2004).
- [27] S. Ran, C. T. Wolowiec, I. Jeon, N. Pouse, N. Kanchanavatee, K. Huang, D. Martien, T. DaPron, D. Snow, M. Williamsen, S. Spagna, and M. B. Maple, Proc. Nat. Acad Sci. USA 113, 13348 (2016).
- [28] E. Hassinger, D. Aoki, F. Bourdarot, G. Knebel, V. Taufour, S. Raymond, A. Villaume, and J. Flouquet, J. Phys.: Conf. Ser. 251, 012001 (2010).
- [29] D. Aoki, F. Bourdarot, E. Hassinger, G. Knebel, A. Miyake, S. Raymond, V. Taufour, and J. Flouquet, J. Phys. Soc. Jpn. 78, 053701 (2009).
- [30] E. Hassinger, G. Knebel, T. D. Matsuda, D. Aoki, V. Taufour, and J. Flouquet, Phys. Rev. Lett. 105, 216409 (2010).
- [31] N. P. Butch and M. B. Maple, J. Phys.: Condens. Matter. 22, 164204 (2011).
- [32] T. J. Williams, Z. Yamani, N. P. Butch, G. M. Luke, M. B. Maple, and W. J. L. Buyers, Phys. Rev. B 86, 235104 (2012).
- [33] N. P. Butch, S. Ran, I. Jeon, N. Kanchanavatee, K. Huang, A. Breindel, M. B. Maple, R. L. Stillwell, Y. Zhao, L. Harringer, and J. W. Lynn, Phys. Rev. B 94, 201102 (2016).

# 3.3 Comparison of iron doping results with recent literature

Since we started our work on iron doped URu<sub>2</sub>Si<sub>2</sub>, there have been a number of additional papers published on this subject [166–172]. Synthesizing these works with our own, we can reach some broad consensus about the properties of the magnetic states that appear for URu<sub>2-x</sub>Fe<sub>x</sub>Si<sub>2</sub>.

First, most other reports of Fe doping put the critical doping where antiferromagnetism appears at a higher level than what we observed in Sections 3.1 and 3.2. In particular, the work of Das et al. indicates a critical doping of 5 %, and that of Ran et al. suggests 3 %, both of which are higher than our suggested critical doping of between 1 and 2.5 %. Measurements of  $URu_{2-x}Fe_xSi_2$  under pressure also suggest that iron doping behaves the same as pressure, suggesting a critical doping of 7.5 % Fe [168]. These other works have all been performed on crystals grown by the group of Brian Maple at the University of California San Diego, which suggests some difference between our sample preparation methods compared to his group. One possibility is that our iron doping levels are slightly higher than expected. Iron is a common impurity in uranium, and as we performed the crystal growths using unpurified depleted uranium, it is possible that some additional level of iron was introduced with the uranium. This would increase our actual doping levels and make our critical doping level coincide better with the measurements from the other groups.

Outside of the preparation of these papers, we did energy-dispersive spectroscopy measurements on some of our iron doped samples that can, in principle, determine the doping level of the samples. These were performed at the Canadian Centre for Electron Microscopy in McMaster University using the JEOL 2010 transmission electron microscope. The results for the iron doped samples are detailed in Table 3.1. This data suggests that our lowest doped sample in particular had a higher than nominal iron concentration, which would make our results more consistent with those of the other groups. However, the uncertainty,  $x = 0.07 \pm 0.03$ , is over 40% of the value, which makes it difficult to gain meaningful insight from these measurements.

Nominal doping $x$	Measured doping $x_m$	Uncertainty
0.02	0.07	0.03
0.1	0.14	0.04
0.2	0.14	0.05
0.3	0.27	0.05

Table 3.1: Doping levels for samples of the  $URu_{2-x}Fe_xSi_2$  crystals measured by energy-dispersive spectroscopy.

Setting aside the exact doping level of the transition from hidden order, we can compare the

other facets of our results to the other groups.

Elastic neutron scattering measurements by Das et al. suggest that the magnetic moment is over 0.8  $\mu_B$  / U for URu<sub>1.9</sub>Fe<sub>0.1</sub>Si<sub>2</sub>, and slightly decreases with increasing doping. This is in substantial disagreement with our results from Section 3.2 that show both a much smaller moment of about 0.55  $\mu_B$  / U, and an increase with doping. The results of Das et al furthermore seem unlikely in light of our  $\mu$ SR results from Section 3.1, as a moment of 0.8  $\mu_B$  / U should give an internal field much larger than observed, and our  $\mu$ SR results also show an increase in the internal field with doping. The most likely explanation for these discrepancies is that a different normalization method used by Das et al. to calculate the moment resulted in somewhat erroneous results.

We can also contrast our inelastic neutron scattering measurements with those recently published by Butch et al. [170]. These measurements are quite consistent with our own, showing that at higher doping levels the commensurate excitation at (1 0 0) becomes weakened with a much larger gap, while the incommensurate excitations remain strong. While they do not use their data to determine the gap as a function of doping, their data does show an increasing gap for the incommensurate excitation, and they suggest that the gap is around 7 meV in the antiferromagnetic state, which matches our data for the 15 % doped sample. Measurements of the overall energy gap by optical conductivity [166], specific heat [167], and thermal conductivity [171] also show a sharp increase upon entering the antiferromagnetic state, as would be expected from our neutron scattering results.

Turning to the question of whether some samples can show both hidden order and antiferromagnetism at different temperatures, the phase diagram produced by Ran et al. suggests that this can be the case for samples between doping levels of about x = 0.06 and x = 0.11 [171]. Interestingly, if we consider the doping level of our nominal x = 0.02 sample suggested by the energy-dispersive spectroscopy measurements in Table 3.1 of x = 0.07, this falls directly in the range where Ran et al. would expect the coexistence of hidden order and antiferromagnetism. This is perhaps additional evidence that the true doping levels of our samples were somewhat different from the nominal dopings.

# 3.4 $\mu$ SR studies of Ge-doped URu<sub>2</sub>Si<sub>2</sub>

Doping germanium onto the silicon site of URu<sub>2</sub>Si<sub>2</sub> causes a reduction in the lattice volume of about 0.24% /per 5% doping [173]. Using the bulk modulus,  $\kappa = 5.2 \times 10^{-3}$  GPa<sup>-1</sup>, of pure URu<sub>2</sub>Si<sub>2</sub>, this is equivalent to a negative chemical pressure of about -0.47 GPa per 5% doping [173], which is somewhat larger than that that produced by the osmium doping discussed in Section 3.1. As this doping does not change the ruthenium site at all, it is a way to distinguish whether it is the negative chemical pressure in  $URu_{2-x}Os_xSi_2$  that causes the hidden order to change into antiferromagnetism, or if it is some other effect of changing the ruthenium site as hypothesized above. While germanium doped  $URu_2Si_2$  has been studied before [87,173], these measurements were on polycrystalline samples and did not study the local magnetism of the samples. It is therefore of interest to extend this work by performing  $\mu$ SR on crystals of this doping in order to determine whether the magnetic state at low temperature remains in the hidden order state, becomes antiferromagnetic, or shows some other behaviour.

We grew crystals of  $\text{URu}_2\text{Si}_{2-x}\text{Ge}_x$  using the tri-arc Czochralski method for doping levels between x = 0.1 and x = 0.5. The end member  $\text{URu}_2\text{Ge}_2$  does not exist, and previous work established that germanium concentrations above 40% do not form the I4/mmm structure [87], therefore we did not attempt crystal growths up to higher doping. For each of these growths we started with stoichiometric ratios of the 4 elements (uranium, ruthenium, silicon, germanium) in atomic form, melted them together in our mono-arc furnace to form a boule of 3 - 6.5 grams, and then grew crystals out of the boule in the tri-arc.

For the x = 0.1 and x = 0.2 doping levels, the crystal growths proceeded very smoothly, facets appeared on the edges of the crystals, and they cleaved easily into flat plates to use for further measurements. The x = 0.35 experiment did not show facets during the growth, but also resulted in a good quality single crystal which cleaved easily. However, during the x = 0.4 and x = 0.5 growths, solid was observed floating on top of the molten material until the power was raised significantly above that needed to melt the bulk. This is indicative of a material with a different melting point co-existing with the bulk I4/mmm URu<sub>2</sub>Si<sub>2-x</sub>Ge<sub>x</sub> phase; i.e., phase separation as was expected when approaching higher doping levels. This was also obvious when the crystals were removed from the tri-arc furnace, as, while they did cleave, the cleavage planes were mottled by small regions of other material.

After the growths, we performed SQUID magnetometry measurements on samples of each of the crystals. The samples used for these measurements were aligned with the c-axis (perpendicular to the cleavage plane) parallel to the applied magnetic field. Measurements were taken in the zero field cooled mode under an applied magnetic field of 1000 Oe. Previous measurements on URu<sub>2</sub>Si<sub>2</sub> have shown no difference between field cooled and zero field cooled measurements, therefore we did not perform both. The results of these measurements are shown in Fig. 3.1 for doping levels up to x = 0.35.



Figure 3.1: Magnetization (a) and derivitive of magnetization with respect to temperature dM/dT (b) for URu<sub>2</sub>Si<sub>2-x</sub>Ge<sub>x</sub> with doping levels of x = 0 (green), x = 0.1 (black), x = 0.2 (blue) and x = 0.35 (red). All measurements were performed on warming, after cooling in zero applied magnetic field and applying a field of 1000 Oe at 2 K. Temperature values with arrows on (b) show the transition temperatures inferred based on the dM/dT data.

These measurements show minimal change in the character of the transition, with it still appearing as a kink in the magnetization in all four samples. As the doping level increases, the overall magnitude of the magnetization drops, and the transition temperature, shown by the arrows in Fig. 3.1 (b), shifts to lower temperatures. The decrease in transition temperature seen in these measurements is consistent with that measured by Dhar et al. on polycrystalline samples, suggesting that these crystals have the expected doping levels [173]. Furthermore, the low temperature upturn of the magnetization increases as the doping level increases. This sort of upturn suggests some amount of paramagnetic impurity in the samples that is larger in more heavily doped samples, suggesting that some phase separation occurs at all dopings levels. Powder X-ray diffraction measurements would be useful to determine what this impurity phase is, but these were not performed due to the safety hazards of working with powdered radioactive materials.

Magnetometry measurements on the x = 0.4 and x = 0.5 samples under the same conditions as stated above are shown in Fig. 3.2 along with the data from the x = 0 sample. These higher doped samples show significantly different behaviour. There is still a broad high temperature maximum in the magnetization and some feature near 15 K, but the signal is dominated by a paramagnetic upturn at low temperatures. This suggests that for these doping levels there is a substantial paramagnetic impurity phase, as was expected based on the behaviour of the crystal growth. The dM/dT data still shows a peak for both of these samples that can be used to infer the transition temperature, although picking out the exact value will be somewhat complicated by the background signal caused by the paramagnetic impurities. Nevertheless, the transition temperature for these two samples appears to be quite similar to that of the x = 0.35 sample. This suggests that the behaviour at higher doping is due to hitting a solubility limit of Ge in URu<sub>2</sub>Si<sub>2</sub> and that the excess germanium added for samples above x = 0.35 is not going into the crystal, but rather forming an additional impurity phase that gives the paramagnetic background. This observation of the transition temperature ceasing to change and the apparent large impurity phase means that these heavily doped samples are not of interest for  $\mu$ SR measurements.



Figure 3.2: Magnetization (a) and dM/dT (b) for URu<sub>2</sub>Si<sub>2-x</sub>Ge<sub>x</sub> with doping levels of x = 0 (green), x = 0.4 (purple), and x = 0.5 (gray). All measurements were performed on warming, after cooling in zero applied magnetic field and applying a field of 1000 Oe at 2 K.

We therefore performed  $\mu$ SR measurements only on the x = 0.1, 0.2, and 0.35 doped samples. These measurements were performed at the TRIUMF laboratory using the LAMPF spectrometer and a helium flow cryostat. This instrument gives access to temperatures between 2 and 300 K, fields up to 4000 Oe, and a timing resolution of 0.4  $\mu$ s. Zero field measurements allow determination of the magnetic state of the system. The typical antiferromagnetic state of URu<sub>2</sub>Si<sub>2</sub> has internal fields aligned parallel to the c-axis, and therefore would show oscillations in the  $\mu$ SR asymmetry for muon spins incident perpendicular to the c-axis. We therefore aligned the crystals with the c-axis parallel to the incoming beam, and initially performed zero field  $\mu$ SR measurements in the spin rotated mode: muon spins incident perpendicular to the c-axis. Results from these measurements at 2 K are shown in 3.3 (a) along with a measurement of pure URu<sub>2</sub>Si<sub>2</sub> taken by Dr. Graeme Luke's group in the past.



Figure 3.3: (a) Muon asymmetry spectra of  $URu_2Si_{2-x}Ge_x$  crystals measured at 2 K in zero applied field with the muon spins initially perpendicular to the c-axis. Data for x = 0.1 (black), 0.2 (blue), and 0.35 (red) were measured in this work and the x = 0 sample was measured by past members of Graeme Luke's group. (b) Muon asymmetry spectra measured with muon spins initially parallel to the c-axis. Solid lines in these figures show fits to Eq. 3.1.

This data does not show long lived oscillations that would be evidence of long-range magnetic order. Instead, the data can be described by the exponential Kubo-Toyabe function given by the equation,

$$A = A_T \left( \frac{1}{3} + \frac{2}{3} (1 - \lambda t) e^{-\lambda t} \right) \right),$$
 (3.1)

where  $A_T$  is the maximum asymmetry and  $\lambda$  is the relaxation rate. This function is characteristic of a system of dilute randomly oriented magnetic moments [174]. The data from the pure URu<sub>2</sub>Si<sub>2</sub> sample can also be described by Eq. 3.1, but with a significantly lower relaxation rate. This suggests that the germanium doped samples are in the same magnetic state as the pure URu<sub>2</sub>Si<sub>2</sub>. As a further check that there is no long range magnetic order in these samples, we also performed some ZF  $\mu$ SR measurements with the muon spins aligned parallel to the c-axis and show the data collected at 2 K in Fig. 3.3 (b). These measurements would be sensitive to internal fields that lie perpendicular to the c-axis in the a-a plane and would therefore be substantially different if the observed asymmetry spectra arose from static magnetic order. Instead, we see that, apart from a change in the maximum asymmetry that comes from the different detectors used, the asymmetry spectra are almost identical and can again be fit by Eq. 3.1. This is exactly the expected behaviour for a system of randomly oriented magnetic moments where the  $\mu$ SR measurements should not change with changing incident muon spin direction or crystal orientation.

The relaxation rate as a function of temperature for the germanium doped samples is shown in Fig. 3.4. The relaxation rate falls off to zero at a temperature coincident with the transition temperature measured by magnetometry, indicating that the relaxation is associated with magnetism appearing below the transition.



Figure 3.4: Relaxation rate,  $\lambda$ , extracted from fits of the  $\mu$ SR data in Fig. 3.3 to equation 3.1.

One possible explanation for this behaviour is randomly oriented antiferromagnetic puddles appearing at grain boundaries or other defects. It is well known that in URu<sub>2</sub>Si<sub>2</sub> these puddles do appear in imperfect samples, and are the cause of the original misidentification of the hidden order state as antiferromagnetism [175]. This inhomogeneous antiferromagnetism is thought to arise from defect-induced changes to the lattice causing variations in the c/a axis ratio that favours the antiferromagnetic state over hidden order [80]. Doping the sample would be expected to create more defects, especially with a dopant that we know is not perfectly soluble and may precipitate out some fraction of other phases that would act as defect sites. It is therefore reasonable that the relaxation rate would increase with increasing doping as this would suggest a higher number of these antiferromagnetic puddles, created at the larger number of defect sites.

These results overall indicate that doping URu<sub>2</sub>Si<sub>2</sub> with germanium does not produce an antiferromagnetically ordered state. With this, we can compare these results to what was discussed in Section 3.1 for osmium doped  $\mu$ SR. In the germanium doped case, we see no

antiferromagnetism appearing up to a doping level of x = 0.35, which equates to a chemical pressure of -1.5 GPa. By contrast, antiferromagnetism appears for osmium doping at least down to a doping level of x = 0.1, which equates to a chemical pressure of -0.3 GPa [103]. If chemical pressure was the dominant cause of antiferromagnetism for osmium doping, we would expect to see it also arise for germanium doping at a similar chemical pressure, equating to a doping level of about x = 0.07. That we do not see antiferromagnetism at doping levels 5 times larger than x = 0.07 is strong evidence that chemical pressure does not drive the transition to antiferromagnetism.

One other possible explanation would be to fall back on the c/a axis ratio argument of Yokoyama et al. [80]. However, this too does not suffice, as the c/a axis ratios increase for both germanium [173] and osmium [103] doping, which is what is supposed to favour the antiferromagnetic state. For a change from 0 to 10% doping, germanium increases the c/a ratio by 0.04% compared to an increase of 0.02% for an equivalent osmium doping [103,173]. We would therefore expect, by this argument, that germanium doping should produce antiferromagnetism even more quickly than osmium doping, which is not what is observed.

A different explanation, not arising from changes to the lattice parameters, must therefore be given for the presence of antiferromagnetism in osmium doped URu<sub>2</sub>Si<sub>2</sub>. One explanation was advanced in Section 3.1: larger osmium orbitals promote more hybridization between the d-shells. Again using the temperature of the magnetization maxima as a proxy for the hybridization strength [34], we can clearly see that the temperature of the maximum decreases for increasing germanium doping in Fig. 3.1 (a), compared to the increase seen for osmium doping (Fig. 8 (c) in Section 3.1). The data for germanium doping is therefore consistent with this picture of increasing hybridization driving the antiferromagnetic transition, as germanium doping appears to push the system in the opposite direction and does not show antiferromagnetism. We can attempt to quantify this by plotting the transition temperature,  $T_N$  or  $T_{HO}$ , vs. the temperature of maximum magnetization,  $T_P$ , as was done in Fig. 8 (c) of Section 3.1. This plot is shown in Fig. 3.4, which includes data from Ref. [176] for rhodium doping.

Figure 3.4 demonstrates that the transition temperature and the temperature of the magnetization maximum do scale with one another for the various dopings. However, the slope of the scaling is clearly different for rhodium doping than for the others, and, despite having a smaller hybridization based on this picture, rhodium doped samples do show antiferromagnetic order. The picture of this scaling describing the competition between hidden order and antiferromagnetism is therefore not complete, and must take into account other factors such as the additional charges



Figure 3.5: Transition temperature,  $T_N$  for the transition into antiferromagnetism, or  $T_{HO}$  for the transition into hidden order, plotted against the peak in the magnetization,  $T_p$ . This data is plotted for pure URu<sub>2</sub>Si<sub>2</sub> (orange star), iron doping (red squares), osmium doping (blue circles), germanium doping (black diamonds), and rhodium doping taken from Ref. [176] (green triangles).

added by rhodium doping, compared to isoelectronic osmium, iron, and germanium doping. A full description of these effects will have to wait for future work.

# 3.4.1 Contributions to this work

The  $\mu$ SR work in Section 3.4 was led by myself and benefited from collaboration with the following other scientists: Shengli Guo, Zizhou Gong, Timothy Munsie, and Graeme Luke. The sample growth was performed by myself with the assistance of Yipeng Cai. The remainder of the measurements and analysis in this section were performed by myself under the supervision of Graeme Luke.



# Dichalcogenide Superconductors

# 4.1 Summary of Publication III: $Ir_{0.95}Pt_{0.05}Te_2$

In this paper we present a combined magnetometry and  $\mu$ SR study of the superconducting state in Ir<sub>0.95</sub>Pt<sub>0.05</sub>Te<sub>2</sub>. This material is previously known to superconduct with a  $T_C$  of 3 K [116]. We sought to further investigate the superconducting state by measuring the temperature dependence of the superfluid density in order to infer the symmetry of the superconducting gap. To do this, we used  $\mu$ SR measurements in an applied transverse field that is between  $H_{c1}$  and  $H_{c2}$  to measure the field distribution in the vortex state. These measurements allow us to determine the penetration depth, and hence superfluid density, at a finite field. We also performed reversible magnetization measurements using a SQUID magnetometer, which allow us to fit an effective zero field value for the penetration depth that can again be converted into a superfluid density. The  $\mu$ SR measurements were performed on a polycrystalline sample, giving a directionally averaged penetration depth, while the magnetometry measurements were performed on a single crystal in two different orientations.

Our magnetometry measurements of the penetration depth show an anisotropy in the penetration depth that is relatively small. The low temperature penetration depth measured with a field perpendicular to the c-axis, which is a combination of the penetration depth along the c-axis and that in the a-a planes, is only 37% larger than that measured with the field parallel to the c-axis, a measure of only the penetration depth in the a-a planes. This is, for example, much smaller than the ratio  $\lambda_c/\lambda_{ab} \approx 20$  seen in the highly anisotropic cuprate superconductors [177]. Such a small anisotropy suggests that, despite the layered structure, Ir<sub>0.95</sub>Pt<sub>0.05</sub>Te<sub>2</sub> shows mainly 3D character, which is supported by band structure calculations that show a quasi 3D fermi

surface for the P3m1 structure [178]. The  $\mu$ SR results yield a low temperature penetration depth substantially larger than that measured by the magnetometry. This is expected as the  $\mu$ SR measured the penetration depth at 300 G which is a significant field of about  $0.2H_{c2}$ . The superconducting state will therefore be somewhat suppressed at this field and the penetration depth increased.

The temperature dependence of the superfluid density from both techniques is well fit to the model of Eq. 1.5 that assumes an isotropic gap. The magnetometry data fits to a  $T_C$  of 2.9 K compared to the  $T_C$  from  $\mu$ SR measurements of 2.3 K. This is again the expected behaviour caused by suppression of  $T_C$  at the finite field used in the  $\mu$ SR measurements. Furthermore, fitting the data gives a ratio of the gap to  $T_C$  of  $2\Delta_0 = 3.8k_BT_C$  averaging the two directions from the magnetometry, and  $2\Delta_0 = 4.7k_BT_C$  from the  $\mu$ SR. These numbers are fairly similar to the expected value of  $2\Delta_0 = 3.52k_BT_C$  for a BCS superconductor, and we therefore suggest that Ir<sub>0.95</sub>Pt<sub>0.05</sub>Te<sub>2</sub> is a conventional BCS superconductor with an isotropic BCS gap.

Our results agree with STM results on palladium doped IrTe<sub>2</sub> that show an s-wave gap with a gap to  $T_C$  ratio of  $T_C$  of  $2\Delta_0 = 3.6k_BT_C$ , also indicating weak coupled BCS superconductivity [128]. They also agree with thermal conductivity measurements that suggest a superconducting gap without nodes [129]. The combination of these results and our own paint a consistent picture of s-wave superconductivity in the IrTe<sub>2</sub> system when the structural transition has been suppressed by doping.

Publication III: "μSR and magnetometry study of superconducting 5% Pt-doped IrTe<sub>2</sub>",
M. N. Wilson, T. Medina, T. J. Munsie, S. C. Cheung, B. A. Frandsen, L. Liu, J. Yan, D. Mandrus, Y. J. Uemura, and G. M. Luke. Physical Review B 94, 184504 (2016).
Reproduced from Ref. [3] with permission, copyrighted by the American Physical Society.

# **Author Contributions:**

- Experimental Concept: M.N. Wilson, and G.M. Luke.
- Sample Preparation: J. Yan, and D. Mandrus.
- Magnetometry Experiments: M.N. Wilson, T.J. Munsie, and G.M. Luke.
- μSR Experiments: M.N. Wilson, T. Medina, T.J. Munsie, S.C. Cheung, B.A. Frandsen, L. Liu, Y.J. Uemura and G.M. Luke.
- Data Analysis: M.N. Wilson and G.M. Luke.
- Manuscript: M.N. Wilson, B.A. Frandsen, J. Yan, and G.M. Luke.

PHYSICAL REVIEW B 94, 184504 (2016)

# $\mu$ SR and magnetometry study of superconducting 5% Pt-doped IrTe<sub>2</sub>

M. N. Wilson,<sup>1</sup> T. Medina,<sup>1</sup> T. J. Munsie,<sup>1</sup> S. C. Cheung,<sup>2</sup> B. A. Frandsen,<sup>2</sup> L. Liu,<sup>2</sup> J. Yan,<sup>3,4</sup> D. Mandrus,<sup>3,4</sup> Y. J. Uemura,<sup>2</sup> and G. M. Luke<sup>1,5</sup>

<sup>1</sup>Department of Physics and Astronomy, McMaster University, Hamilton, Ontario L8S 4M1, Canada

<sup>2</sup>Department of Physics, Columbia University, New York, New York 10027, USA

<sup>3</sup>Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, USA

<sup>4</sup>Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

<sup>5</sup>Canadian Institute for Advanced Research, Toronto, Ontario M5G 1Z7, Canada

(Received 11 May 2016; revised manuscript received 19 October 2016; published 11 November 2016)

We present magnetometry and muon spin rotation ( $\mu$ SR) measurements of the superconducting dichalcogenide Ir<sub>0.95</sub>Pt<sub>0.05</sub>Te<sub>2</sub>. From both sets of measurements, we calculate the penetration depth and thence superfluid density as a function of temperature. The temperature dependence of the superfluid densities from both sets of data indicate fully gapped superconductivity that can be fit to a conventional *s*-wave model and yield fitting parameters consistent with a BCS weak coupling superconductor. We therefore see no evidence for exotic superconductivity in Ir<sub>0.95</sub>Pt<sub>0.05</sub>Te<sub>2</sub>.

DOI: 10.1103/PhysRevB.94.184504

# I. INTRODUCTION

Transition metal dichalchogenides have been studied for many years in an effort to understand their diverse properties [1,2]. These materials are layered quasi-two-dimensional systems that frequently exhibit charge density wave (CDW) ordering that is not yet fully understood [2]. Furthermore, the crystal structure of these materials is amenable to substitution and intercalation of a wide variety of dopant atoms to allow tuning through a broad range of electronic properties [3]. In particular, these systems provide a valuable avenue to study the interplay of structural transitions and superconductivity as in many cases superconductivity emerges after the CDW transition is suppressed by doping or applied pressure [4–8].

IrTe<sub>2</sub> is a member of this group of compounds. It undergoes a structural transition at about 270 K [9] from the trigonal P3m1 space group to triclinic P1 [10-12]. Recent work has shown that this structural transition is associated with a charge density wave that has a periodicity six times larger than the underlying lattice [13–15]. Substituting Ir with Pd, Pt, or Rh [7,16–18] or intercalation with Cu [19] suppresses the structural transition and leads to superconductivity with a maximum  $T_C$  of 3 K and  $H_{C2} \approx 0.1$  T. Intercalation with other transition metals also suppresses the structural transition but does not lead to superconductivity, possibly as a result of competing magnetism [20]. Measurements of  $T_C$  as a function of hydrostatic pressure in Pt-substituted IrTe2 have shown that increasing the temperature of the structural transition decreases  $T_C$ , which shows that the appearance of superconductivity is directly related to the disappearance of the structural transition [21].

IrTe<sub>2</sub> is of particular interest as both Ir and Te have high atomic numbers. Spin orbit coupling is therefore expected to be high which may lead to exotic states such as topological superconductivity [22,23]. Determining the superconducting symmetry is important as unconventional (non-*s*-wave) symmetry is required for superconductors to be topologically nontrivial [23].

Previous measurements of the superconducting symmetry by thermal conductivity [24] and STM [25] suggest conventional *s*-wave superconductivity. However, the thermal conductivity measurements cannot conclusively rule out oddparity *p*-wave superconductivity, and STM measurements are inherently a surface technique and so the state they probe may not be representative of the bulk superconductivity. Furthermore, no penetration depth measurements have been conducted on this material. These measurements are important, as the temperature dependence of the penetration depth gives information about the symmetry of the superconducting gap [26].

Muon spin rotation ( $\mu$ SR) is a powerful technique that can be used to study the magnetic penetration depth of type II superconductors in the vortex state [26]. In this technique spin-polarized muons are implanted up to a few hundred  $\mu$ m into the sample where they precess in the local magnetic field and decay, emitting positrons that are detected to gain information about the local magnetic field. Importantly, the muons are implanted far enough into the sample that this can be considered a truly bulk technique. Therefore surface effects that may change the states measured by techniques such as STM will not be a factor in these measurements.

In this paper, we present complementary  $\mu$ SR and SQUID magnetometry measurements of the penetration depth of Ir<sub>0.95</sub>Pt<sub>0.05</sub>Te<sub>2</sub>. These measurements indicate an *s*-wave superconducting state, with gap and  $T_C$  values that are consistent with a conventional BCS weak-coupling superconductor.

# **II. EXPERIMENTAL METHODS**

Single crystals of  $Ir_{0.95}Pt_{0.05}Te_2$  with sizes of a couple mm<sup>3</sup> were grown using the self flux growth method [27]. Muon spin rotation ( $\mu$ SR) experiments were performed at the TRIUMF laboratory in Vancouver, Canada. We used the Pandora dilution refrigerator spectrometer on the M15 surface-muon beam line. This instrument gives access to temperatures between 0.03 and 10 K with the sample mounted on a silver cold finger, magnetic fields up to 5 T with a superconducting magnet to the incoming muon beam direction, and we performed measurements with the muon spin rotated perpendicular to the

2469-9950/2016/94(18)/184504(6)

PHYSICAL REVIEW B 94, 184504 (2016)

# M. N. WILSON et al.

field direction (SR). These experiments were performed on an unaligned collection of small (<1–2 mm) irregularly shaped single crystals mounted on a  $1 \times 2$  cm<sup>2</sup> silver plate using Apiezon N-grease. We used the  $\mu$ SR fit software package to analyze the  $\mu$ SR data [28].

Magnetometry measurements were performed at McMaster University using a Quantum Design XL-5 MPMS with an iHelium He<sup>3</sup> cryostat insert for measurements down to 0.5 K. Magnetization vs. temperature curves were measured both on a subset of unaligned crystals from the  $\mu$ SR sample weighing 238 mg (polycrystalline sample), and on an aligned single-crystal plate weighing 4.72 mg with dimensions 2.4 mm × 1.5 mm × 0.35 mm (C axis). Magnetization versus field curves were measured with fields up to 0.15T and temperatures ranging from 0.5 to 3 K using the single-crystal plate. Alignment of the single crystal was verified with Laue x-Ray diffraction prior to the magnetometry measurements.

## **III. RESULTS AND DISCUSSION**

Figure 1 shows a temperature scan of the magnetization taken with an applied field of 300 Oe after cooling in zero field on the polycrystalline sample for comparison with the  $\mu$ SR data. This data shows strong diamagnetism, indicating that our sample is superconducting with a  $T_c$  of about 2.3 K at  $H_{ext} = 300$  Oe. The inset shows the temperature dependence of the upper critical field ( $H_{C2}$ ) measured by performing magnetization measurements during isothermal field scans. This data shows a linear dependence to the critical field down to the lowest accessible temperature.

Figures 2(a)–2(c) show  $\mu$ SR time spectra measured in an applied external field of 300 Oe <  $H_{C2}$  transverse to the muon spins at 0.03, 1, and 2 K after field cooling the sample to ensure a uniform vortex lattice. These data show a relaxing oscillating signal, with a beat evident in the lower temperatures along with a nonrelaxing signal that persists to large times. This indicates



FIG. 1. Magnetization measurements on a polycrystalline sample of  $Ir_{0.95} Pt_{0.05} Te_2$  measured in a field of 300 Oe after cooling in zero field. (Inset) Upper critical field of the polycrystalline sample. The red line shows a linear fit to the critical field.



FIG. 2. SR  $\mu$ SR time spectra of Ir<sub>0.95</sub>Pt<sub>0.05</sub>Te<sub>2</sub> measured in an applied field of 300 Oe at (a) T = 0.03, (b) 1, and (c) 2 K. (d) Fourier transform of the  $\mu$ SR data collected in an applied field of 300 Oe at T = 0.03 K. The inset in (d) shows the theoretical field distribution of a superconductor using the London model [29].

the presence of more than one component to the signal, and can be more easily visualized by looking at the Fourier transform (FT) of the 0.03 K data found in Fig. 2(d). We interpret the two peaks in the FT as arising from muons missing the sample and landing in the silver sample holder (peak at  $\approx$ 300 G) and those hitting the sample and probing the superconducting state (lower field peak).

Muons that land in a superconducting sample with an applied field between  $H_{C1}$  and  $H_{C2}$  see an asymmetric field distribution arising from the vortex state that will have the form shown in Fig. 2(d) inset. The experimental data from such a measurement, even on an ideal vortex lattice, will always show some broadening of this distribution due to the finite lifespan of the muon and time-window of the experiment. In practice, inhomogeneities in a sample will cause additional broadening of the field distribution that is difficult to rigorously account for. This is particularly important for the case of a polycrystalline sample where varied orientation and possible slight differences between the properties of different grains will broaden the signal. For our sample, we fit the field distribution to a three component model shown in Eq. (1) similar to that used by Khasanov et al. in measurements on high  $T_C$  cuprates [30]. This fit has two Gaussian-relaxing components representing the asymmetric superconducting line shape, and one nonrelaxing component representing the silver background. These fits are made in the time domain to avoid Fourier transform broadening and to properly use the experimental error bars for weighting:

$$A = A_T [F \cos(\gamma_\mu B_{Ag} t) + (1 - F)((1 - C) \cos (\gamma_\mu B_1 t) e^{-0.5(\sigma_1 t)^2} + C \cos(\gamma_\mu B_2 t) e^{-0.5(\sigma_2 t)^2})].$$
(1)

Here, *C* and *F* are temperature independent values giving the ratio of the three components,  $B_{Ag}$  is the temperature independent mean field for the silver site,  $B_1$  and  $B_2$  are the temperature dependent sample fields, and  $\sigma_i$  are the temperature dependent Gaussian relaxation rates.

184504-2

83

PHYSICAL REVIEW B 94, 184504 (2016)



 $\mu$ SR AND MAGNETOMETRY STUDY OF ...

FIG. 3. Parameters used to fit Eq. (1) to the  $\mu$ SR data measured in a field of 300 Oe transverse to the muon spins. (a) and (b) show the individual relaxation rates  $\sigma_1$  and  $\sigma_2$ . (c) shows the average sample internal field. (d) shows the effective total width of the frequency distribution [see Eq. (3)].

These fits gave values of C = 0.405 and F = 0.271, and the temperature dependent values shown in Fig. 3, where  $B_{av} = (1 - F)B_1 + FB_2$ . The temperature dependence of the fit parameters indicate that  $T_C \approx 2.25$  K, consistent with that from our magnetization measurements at the same field. From these fits, we then determined the penetration depth using the analytical approximation appropriate for applied fields 0.25 < b < 1, where  $b = B_{av}/B_{c2}$  [31]:

$$\lambda = \xi \sqrt{(1.94 \times 10^{-2}) \frac{\phi_0}{\xi^2} (1-b) \frac{\gamma_\mu}{\sigma_T}} + 0.069.$$
 (2)

Here,  $\gamma_{\mu} = 2\pi \times 135.538 \text{ MHz/T}$  is the muon gyromagnetic ratio,  $\phi_0 = 2.06783 \times 10^{-15}$  Wb is the flux quantum,  $\xi$  is the coherence length, and  $\sigma_T$  is the overall effective width of the fit frequency distribution. We interpolated  $H_{c2}$  values from the data shown in the inset of Fig. 1 and used the relation  $H_{c2} = \phi_0/(2\pi\xi^2)$  to determine  $\xi$ .  $\sigma_T$  is given by Eq. (3) for the sum of two Gaussian distributions with different means [32]:

$$\sigma_T = \left( (1 - C)(\sigma_1 - \sigma_{bg})^2 + C\sigma_2^2 + C(1 - C)(\gamma_\mu B_1 - \gamma_\mu B_2)^2 \right)^{0.5}.$$
 (3)

Here,  $\sigma_b$  is the high-T background relaxation rate.

The calculated penetration depth is shown in Fig. 4 (blue squares). This penetration depth diverges towards infinity approaching  $T_C$  and at low temperature (T < 0.5 K) has an average value of  $154 \pm 6$  nm with very weak temperature dependence (linear fit slope of  $-1 \pm 4$  nm  $\approx 0$ ). This behavior is consistent with what is expected for a conventional fully gapped superconductor that should asymptote to a constant low temperature value.

To compare with the penetration depth measured by  $\mu$ SR, we also performed magnetization versus field measurements at a range of temperatures below  $T_C$  on a single-crystal plate. As our field in these measurements was applied using a superconducting coil, there will always be some trapped flux in the magnet, resulting in an offset from the expected



FIG. 4. Penetration depth determined from magnetometry and  $\mu$ SR measurements. Green circles are from magnetometry of a single crystal with  $H \parallel C$  axis. Red triangles are from magnetometry with  $H \perp C$  axis. Blue squares are from  $\mu$ SR using a Gaussian fit.

field set by applying current. We corrected for this by doing a linear fit of the low-field MvH data of the ZFC field scans and subtracting the resulting field offset. This indicated a trapped flux of  $\approx 2.5$  Oe for the  $H \parallel C$  axis measurements, and  $\approx 7.5$  Oe for  $H \perp C$  axis.

Magnetization vs. temperature data for this crystal at 50 Oe  $< H_{c1}$  is shown in Fig. 5 and indicates that  $T_C \approx 3$  K at this lower applied field. The magnetization in Fig. 5(b) is significantly larger than 50 G because demagnetization effects increase the effective internal field. We accounted for this in the rest of the analysis by approximating our sample as a rectangular prism of dimensions 2.4 mm  $\times$  1.5 mm  $\times$ 0.35 mm. This gives a demagnetization factor of  $D_{\parallel} = 0.7039$ for the field applied parallel to the C axis, and  $D_{\perp} = 0.1124$ for the field applied perpendicular to the C axis, using the formula found in Ref. [33]. The internal field is then calculated as  $H_{\text{int}} = H_{\text{ext}} - DM$ . This gives low temperature effective ZFC internal fields of 176 G for H || C axis, and 55 G for  $H \perp C$  axi,s which indicate that either 98% or 84% of the volume is superconducting. The discrepancy between these two numbers may indicate some inaccuracy in our estimation of the demagnetization factors, but this uncertainty does not substantially affect the conclusions we have reached.

The magnetization of a type II superconductor in the reversible regime near  $H_{c2}$  can be approximated using the London model as [34]

$$-4\pi M = \frac{\alpha \phi_0}{8\pi \lambda_2} \ln\left(\frac{\beta H_{c2}}{H}\right). \tag{4}$$

Here, *M* is the magnetization in G,  $\phi_0$  is the flux quantum,  $\lambda$  is the effective zero-field penetration depth,  $\alpha$  and  $\beta$  are constants that depend on the field range being fit. We therefore plotted *M* versus ln(*H*) and fit the resulting linear regime to determine  $\lambda$  from the slope (*s*) as

2

$$L = \sqrt{\alpha \frac{\phi_0}{8\pi s}}.$$
 (5)





FIG. 5. Magnetization measurements on a single-crystal sample of  $Ir_{0.95}Pt_{0.05}Te_2$  in a field of 50 Oe applied (a) perpendicular to the C axis and (b) parallel to the C axis. Closed circles show measurements after cooling in zero applied field and open circles show measurements after cooling with the field applied.

We used an  $\alpha$  value of 0.7 in the following analysis, appropriate to higher field ranges [34]. However, it is important to note that changing this value will only result in a rescaling of the penetration depth; it will not affect the temperature dependence. Examples of these linear fits are shown in Figs. 6(c) and 6(d). The resulting penetration depths are plotted alongside that measured by  $\mu$ SR in Fig. 4 (green circles and red triangles).

This analysis gives low-temperature penetration depths of  $\lambda_{\parallel}(0) = 91$  nm and  $\lambda_{\perp}(0) = 125$  nm, which shows that the anisotropy in this material is not large. The low temperature penetration depth measured by  $\mu$ SR (156 nm) is slightly larger than these two values. One would expect that the polycrystalline  $\mu$ SR sample should result in a directional averaging of the two penetration depths, However, as the  $\mu$ SR data is measured at 300 Oe, we would also expect it to have a slightly larger penetration depth compared to the effective zero-field values from the magnetization fitting. It is thus not surprising that the  $\mu$ SR value is above the average of the two zero-field values, and we can say that penetration



FIG. 6. (a) and (b) Magnetization vs internal field curves measured at 0.5 K (black squares) and 2 K (red circles) for (a)  $H \parallel C$  axis and (b)  $H \perp C$  axis. (c) and (d) Magnetization vs ln(H) curves along with linear fits to the high-field region (solid lines) measured at 0.5 K (black squares) and 2 K (red circles) for (c)  $H \parallel C$  axis and (b)  $H \perp C$  axis.

depths measured by our two different techniques seem broadly consistent, giving a true zero-field average penetration depth close to 100 nm.

From the penetration depth, we determined the normalized superfluid density,  $n_s$ , in each case as

$$\frac{n_s(T)}{n_s(0)} = \frac{\lambda^2(0)}{\lambda^2(T)}.$$
 (6)

The resultant superfluid densities are plotted in Fig. 7. This figure allows us to look at the temperature dependencies of the superfluid density in each case without the confounding possible normalization issues discussed above. The inset in Fig. 7 shows these superfluid densities plotted versus normalized temperature  $\left(\frac{T}{T_c}\right)$  and shows that the temperature dependence of the superfluid density measured by the two methods is essentially the same aside from the shift in  $T_C$ . Estimating  $H_{c2}$  from our MvH scans gives approximate values of 300 G for  $H \perp C$  axis and 225 G for  $H \parallel C$  axis at T = 2.3 K, the  $T_C$  measured from  $\mu$ SR at 300 G. From these values we would expect a somewhat lower  $T_C$  at 300 G (closer to 2.1 K), but the discrepancy is not large. The likely explanation is that there is some variation between individual crystal grains, and that the one we used for the single-crystal measurements has a slightly lower  $T_C$  compared to the polycrystalline aggregate used for the  $\mu$ SR measurements.

To determine whether our data matches what would be expected of a fully gapped superconductor, we fit these superfluid densities to the formula [35]

$$n_s(T) = C \left[ 1 - 2 \int_{\Delta}^{\infty} dE \left( -\frac{\partial F}{\partial E} \right) \frac{E}{\sqrt{E^2 - \Delta^2}} \right].$$
(7)

Here, *C* is a scaling constant, *E* is the energy difference above the Fermi energy,  $F = \frac{1}{e^{E/k_BT}+1}$  is the Fermi function,  $k_B$  is the Boltzmann constant, and  $\Delta$  is the gap, which we approximate

184504-4

85



 $\mu$ SR AND MAGNETOMETRY STUDY OF ...

FIG. 7. Normalized superfluid density determined from magnetization and  $\mu$ SR measurements. Red triangles are from magnetometry of a single crystal with  $H \parallel C$  axis. Green circles are from magnetometry with  $H \perp C$  axis. Blue squares are from the  $\mu$ SR data. Solid lines show BCS fits to the data using Eq. (7).

using the interpolation formula [36]

$$\Delta(T) = \Delta_0 \tanh\left(1.742\sqrt{\frac{T_c}{T}} - 1\right).$$
(8)

Here,  $\Delta_0$  is the zero temperature value of the gap, and  $T_c$  is the critical temperature.

The results of these fits are shown as the solid lines in Fig. 7. These data all show good agreement with the fits, therefore our data is consistent with  $Ir_{0.95}Pt_{0.05}Te_2$  being a fully gapped superconductor. In particular, the data show a flat temperature dependence of  $n_s$  at low temperatures, which suggests that there are no nodes in the gap and hence the majority of the carriers are fully gapped. We find no evidence in these fits for unconventional superconductivity, however there are some exotic states such as *p*-wave  $k_x \pm ik_y$  that are fully gapped and would be indistinguishable from *s* wave in our measurements [37].

Furthermore, we can compare the fit values for  $T_c$  and  $\Delta_0$ shown in Table I to the expected constant  $\frac{2\Delta_0}{k_B T_C} = 3.5$  expected for a BCS weak coupling superconductor. The data show a range between 3.68 and 4.7 for this ratio, which is close to the expected ratio. The somewhat larger gap extracted from the  $\mu$ SR data may come from disorder in the vortex lattice during the  $\mu$ SR measurements particularly at higher temperature. Disorder would tend to increase the measured  $\mu$ SR relaxation

PHYSICAL REVIEW B 94, 184504 (2016)

TABLE I. Parameters used for the superfluid density fits to Eq. (7) shown in Fig. 7.

	$\Delta_0 ({\rm meV})$	$T_C$ (K)	$\frac{2\Delta}{k_B T_C}$
μSR	0.467	2.29	4.7
SQUID perpendicular	0.463	2.84	3.9
SQUID parallel	0.463	2.92	3.7

rate and hence the superfluid density. If this occurs most at higher temperature, it would have the effect of sharpening the measured transition, yielding a larger fit gap value. This could be mitigated by future  $\mu$ SR measurements on large single crystals where the effect of disorder may be easier to isolate.

Our data overall give results similar to other groups STM measurements on  $Ir_{0.95}Pd_{0.05}Te_2$  that found a value of  $\frac{2\Delta_0}{k_BT_c}$  = 3.6 [25]. This indicates that differently doped (Pd versus Pt) IrTe<sub>2</sub> display similar superconducting properties.

# **IV. CONCLUSION**

We have presented penetration depth and superfluid density data of Ir<sub>0.95</sub>Pt<sub>0.05</sub>Te<sub>2</sub> determined from SQUID magnetometry and  $\mu$ SR. These data are consistent with conventional BCS weak coupling *s*-wave superconductivity in Ir<sub>0.95</sub>Pt<sub>0.05</sub>Te<sub>2</sub>, with a zero-temperature gap of  $\Delta_0 = 0.46$  meV. We see no evidence for nodes in the gap which suggests that *d*-wave pairing symmetry does not appear in this material. However, we are unable to distinguish *p*-wave and *s*-wave pairing as some *p*-wave states may be fully gapped.

Finally, our work shows that the temperature dependence of the penetration depths measured by two very different techniques ( $\mu$ SR and magnetometry) are consistent with one another. This strengthens the conclusions we can draw from one technique alone, and is to our knowledge the first quantitative comparison of the results of the two techniques on the same material.

## ACKNOWLEDGMENTS

We thank G. D. Morris, B. S. Hitti, and D. J. Arseneau (TRIUMF) for their assistance with the  $\mu$ SR measurements. Work at McMaster University was supported by the Natural Sciences and Engineering Research Council of Canada and the Canadian Foundation for Innovation. M.N.W acknowledges support from the Alexander Graham Bell Canada Graduate Scholarship program. The Columbia University group acknowledges support from NSF DMR-1436095 (DMREF), OISE-0968226 (PIRE), JAEA Reimei project, and Friends of University of Tokyo Inc. Work at ORNL was supported by the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.

- [2] K. Rossnagel, J. Phys.: Condens. Matter 23, 213001 (2011).
- [3] R. H. Friend and A. D. Yoffe, Adv. Phys. 36, 1 (1987).
- [4] T. Yokoya, T. Kiss, A. Chainani, S. Shin, M. Nohara, and H. Takagi, Science 294, 2518 (2001).
- [5] E. Morosan, H. W. Zandbergen, B. S. Dennis, J. W. G. Bos, Y. Onose, T. Klimczuk, A. P. Ramirez, N. P. Ong, and R. J. Cava, Nat. Phys. 2, 544 (2006).
- [6] A. F. Kusmartseva, B. Sipos, H. Berger, L. Forró, and E. Tutiš, Phys. Rev. Lett. **103**, 236401 (2009).

<sup>[1]</sup> J. A. Wilson and A. D. Yoffe, Adv. Phys. 18, 193 (1969).

M. N. WILSON et al.

- [7] J. J. Yang, Y. J. Choi, Y. S. Oh, A. Hogan, Y. Horibe, K. Kim, B. I. Min, and S.-W. Cheong, Phys. Rev. Lett. 108, 116402 (2012).
- [8] B. Sipos, A. F. Kusmartseva, A. Akrap, H. Berger, and L. Forró, Nat. Mater. 7, 960 (2008).
- [9] N. Matsumoto, K. Taniguchi, R. Endoh, H. Takano, and S. Nagata, J. Low Temp. Phys. 117, 1129 (1999).
- [10] H. Cao, B. C. Chakoumakos, X. Chen, J. Yan, M. A. McGuire, H. Yang, R. Custelcean, H. Zhou, D. J. Singh, and D. Mandrus, Phys. Rev. B 88, 115122 (2013).
- [11] G. L. Pascut, K. Haule, M. J. Gutmann, S. A. Barnett, A. Bombardi, S. Artyukhin, T. Birol, D. Vanderbilt, J. J. Yang, S.-W. Cheong, and V. Kiryukhin, Phys. Rev. Lett. **112**, 086402 (2014).
- [12] T. Toriyama, M. Kobori, T. Konishi, Y. Ohta, K. Sugimoto, J. Kim, A. Fujiwara, S. Pyon, K. Kudo, and M. Nohara, J. Phys. Soc. Jpn. 83, 033701 (2014).
- [13] W. Ruan, P. Tang, A. Fang, P. Cai, C. Ye, X. Li, W. Duan, N. Wang, and Y. Wang, Sci. Bull. 60, 798 (2015).
- [14] P. J. Hsu, T. Mauerer, M. Vogt, J. J. Yang, Y. S. Oh, S.-W. Cheong, M. Bode, and W. Wu, Phys. Rev. Lett. 111, 266401 (2013).
- [15] Q. Li, W. Lin, J. Yan, X. Chen, A. G. Gianfrancesco, D. J. Singh, D. Mandrus, S. V. Kalinin, and M. Pan, Nat. Commun. 5, 5358 (2014).
- [16] S. Pyon, K. Kudo, and M. Nohara, J. Phys. Soc. Jpn. 81, 053701 (2012).
- [17] K. Kudo, M. Kobayashi, S. Pyon, and M. Nohara, J. Phys. Soc. Jpn. 82, 085001 (2013).
- [18] D. Ootsuki, Y. Wakisaka, S. Pyon, K. Kudo, M. Nohara, M. Arita, H. Anzai, H. Namatame, M. Taniguchi, N. L. Saini, and T. Mizokawa, Phys. Rev. B 86, 014519 (2012).
- [19] M. Kamitani, M. S. Bahramy, R. Arita, S. Seki, T. Arima, Y. Tokura, and S. Ishiwata, Phys. Rev. B 87, 180501(R) (2013).
- [20] J.-Q. Yan, B. Saparov, A. S. Sefat, H. Yang, H. B. Cao, H. D. Zhou, B. C. Sales, and D. G. Mandrus, Phys. Rev. B 88, 134502 (2013).

### PHYSICAL REVIEW B 94, 184504 (2016)

- [21] A. Kiswandhi, J. S. Brooks, H. B. Cao, J. Q. Yan, D. Mandrus, Z. Jiang, and H. D. Zhou, Phys. Rev. B 87, 121107(R) (2013).
- [22] A. P. Schnyder, S. Ryu, A. Furusaki, and A. W. W. Ludwig, Phys. Rev. B 78, 195125 (2008).
- [23] L. Fu and E. Berg, Phys. Rev. Lett. **105**, 097001 (2010).
- [24] S. Y. Zhou, X. L. Li, B. Y. Pan, X. Qiu, J. Pan, X. C. Hong, Z. Zhang, A. F. Fang, N. L. Wang, and S. Y. Li, Europhys. Lett. 104, 27010 (2013).
- [25] D. J. Yu, F. Yang, L. Miao, C. Q. Han, M.-Y. Yao, F. Zhu, Y. R. Song, K. F. Zhang, J. F. Ge, X. Yao, Z. Q. Zou, Z. J. Li, B. F. Gao, C. Liu, D. D. Guan,w and C. L. Gao, D. Qian, and J.-F. Jia, Phys. Rev. B 89, 100501(R) (2014).
- [26] J. E. Sonier, Rev. Mod. Phys. 72, 769 (2000).
- [27] A. F. Fang, G. Xu, T. Dong, P. Zheng, and N. L. Wang, Sci. Rep. 3, 1153 (2013).
- [28] A. Suter and B. M. Wojek, Phys. Proceedia 30, 69 (2012).
- [29] E. H. Brandt, Phys. Rev. B 37, 2349(R) (1988).
- [30] R. Khasanov, A. Shengelaya, A. Maisuradze, F. La Mattina, A. Bussmann-Holder, H. Keller, and K. A. Müller, Phys. Rev. Lett. 98, 057007 (2007).
- [31] E. H. Brandt, Phys. Rev. B 68, 054506 (2003).
- [32] H. Cramér, Mathematical Methods of Statistics (Princeton University Press, Princeton, 1946), Chap. 15.4.
- [33] A. Aharoni, J. Appl. Phys. 83, 3432 (1998).
- [34] Z. Hao and J. R. Clem, Phys. Rev. Lett. 67, 2371 (1991).
- [35] M. Tinkham, *Introduction to Superconductivity* (Dover, New York, 2004), p. 92.
- [36] F. Gross, B. S. Chandrasekhar, D. Einzel, K. Andres, P. J. Hirschfeld, H. R. Ott, J. Beuers, Z. Fisk, and J. L. Smith, Z. Phys. B 64, 175 (1986).
- [37] G. M. Luke, Y. Fudamoto, K. M. Kojima, M. I. Larkin, B. Nachumi, Y. J. Uemura, J. E. Sonier, Y. Maeno, Z. Q. Mao, Y. Mori, and D. F. Agterberg, Phys. B (Amsterdam, Neth.) 289-290, 373 (2000).

# 4.2 Summary of Publication IV: PbTaSe<sub>2</sub>

In this paper we present  $\mu$ SR measurements in zero field and in an applied field oriented transverse to the muon spin, as well as magnetometry measurements for initial characterization. These measurements are all performed on a single crystal of PbTaSe<sub>2</sub> that is oriented with the field applied parallel to the c-axis. This material is a superconductor with a T<sub>C</sub> of 3.6 K and is noncentrosymmetric, which may lead to exotic behaviour such as mixed parity superconductivity [137]. Zero field  $\mu$ SR measurements allow us to look for evidence of time reversal symmetry breaking in the superconducting state, while transverse field measurements allow us to measure the superfluid density as was done in Section 4.1.

Our initial magnetometry characterization shows a superconducting transition at 3.6 K, as expected, with a low temperature susceptibility of  $\chi = -0.77$ . That  $\chi$  is close to one indicates that our sample is superconducting through mostly the entire bulk of the sample. The remaining discrepancy likely comes from uncertainty in the applied field and/or uncertainty in the demagnetizing factor of the sample.

We performed transverse field  $\mu$ SR measurements at two different fields, 250 G and 400 G, both of which are between  $H_{c1}$  and  $H_{c2}$  and therefore put the sample in the vortex state. Only about 1/3 of the  $\mu$ SR signal comes from muons stopping in the sample, which happens because the crystal used was relatively thin and is mounted on a silver cold finger that will stop any muons that penetrate all the way through the sample. This data shows a decreased diamagnetic shift at 400 G compared with 250 G, consistent with what is expected for a superconductor in a field closer to  $H_{c2}$ . The relaxation rate of the signal also decreases, consistent with an increase in the low temperature penetration depth from 140 nm at 250 G to 180 nm at 400 G.

The temperature dependence of the superfluid density determined from the penetration depth can be reasonably well explained by s-wave BCS behaviour. However, there is some deviation at low temperature for the measurements at 250 G, with a continued upward slope persisting down to 30 mK. This could be taken as evidence for nodes in the gap structure, or as evidence for multi-band behaviour. We fit this data to a two-band model where 91% of the superfluid density comes from a band with a gap of 0.399 meV, and the rest from a band with a smaller gap of 0.109 meV. This two-band fit shows statistically superior agreement to our data compared to the single-band fit for the 250 G data, while the 400 G data can be well described by superconductivity on a single band. The discrepency between the two fields may come from a lower field being required to suppress superconductivity on the band with a lower energy gap.

While we cannot rule out an anisotropic gap as the cause of the low temperature behaviour

from our  $\mu$ SR data alone, previous STM [147] and thermal conductivity [145] measurements suggest that the energy gap has no nodes. Furthermore, the field dependence of the thermal conductivity [145], and the temperature dependence of  $H_{c2}$  [141], are both anomalous and suggest multiband behaviour, which is also consistent with the band structure measured by STM [147] and ARPES [140] that show multiple bands near the Fermi surface that could contribute to the superconductivity. The combination of our results with these other studies suggests that a fully gapped superconducting state exists on multiple bands in PbTaSe<sub>2</sub>.

One study that disagrees with this interpretation is tunnel diode oscillator (TDO) measurements of the penetration depth by Pang et al. [148]. The TDO measurements find a penetration depth that is consistent with a fully gapped superconducting state on a single band. One possible explanation for this discrepancy is that the TDO measurements measure the penetration depth in zero field into the surface of the sample. If there are different properties near the surface, this could modify the results somewhat compared to our  $\mu$ SR measurements which are sensitive to the full bulk of the sample. The different field range could also change the measurements somewhat, although it would be expected that the effect of superconductivity on a second band with smaller field might be more prominent, not less. Further study may be needed to fully understand why these measurements disagree with our own.

Finally, our  $\mu$ SR measurements in zero field show no evidence for time-reversal breaking fields in the superconducting state down to 30 mK. These measurements can rule out such fields with magnitudes greater than 0.05 G, which is smaller than the fields that have been seen in other materials that show triplet superconductivity [179, 180]. The absence of such a time-reversal breaking field, combined with the evidence for an isotropic gap from the superfluid density, suggests that PbTaSe<sub>2</sub> is not a mixed parity superconductor.

Publication IV: "µSR study of the noncentrosymmetric superconductor PbTaSe<sub>2</sub>", M. N.
Wilson, A. M. Hallas, Y. Cai, S. Guo, Z. Gong, R. Sankar, F. C. Chou, Y. J. Uemura, and
G. M. Luke. Physical Review B 95, 224506 (2017).

Reproduced from Ref. [4] with permission, copyrighted by the American Physical Society.

# Author Contributions:

- Experimental Concept: M.N. Wilson, and G.M. Luke.
- Sample Preparation: R. Sankar, and F.C. Chou.

- Magnetometry Experiments: M.N. Wilson
- μ*SR Experiments*: **M.N. Wilson**, A.M. Hallas, Y. Cai, S. Guo, Z. Gong, Y.J. Uemura, and G.M. Luke.
- Data Analysis: M.N. Wilson, and G.M. Luke.
- Manuscript: M.N. Wilson, A.M. Hallas, and G.M. Luke.

PHYSICAL REVIEW B 95, 224506 (2017)

# $\mu$ SR study of the noncentrosymmetric superconductor PbTaSe<sub>2</sub>

M. N. Wilson,<sup>1</sup> A. M. Hallas,<sup>1</sup> Y. Cai,<sup>1</sup> S. Guo,<sup>2</sup> Z. Gong,<sup>3</sup> R. Sankar,<sup>4,5</sup> F. C. Chou,<sup>4</sup> Y. J. Uemura,<sup>3</sup> and G. M. Luke<sup>1,6</sup>

<sup>1</sup>Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, Canada L8S 4M1

<sup>2</sup>Department of Physics, Zhejiang University, Hangzhou, China

<sup>3</sup>Department of Physics, Columbia University, New York, New York 10027, USA

<sup>4</sup>Center for Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan

<sup>5</sup>Institute of Physics, Academia Sinica, Taipei 11529, Taiwan

<sup>6</sup>Canadian Institute for Advanced Research, Toronto, Ontario, Canada M5G 1Z7

(Received 14 March 2017; revised manuscript received 18 May 2017; published 8 June 2017)

We present muon spin rotation and relaxation ( $\mu$ SR) measurements on the noncentrosymmetric superconductor PbTaSe<sub>2</sub>. From measurements in an applied transverse field between  $H_{c1}$  and  $H_{c2}$ , we extract the superfluid density as a function of temperature in the vortex state. These data can be fit with a fully gapped two-band model, consistent with previous evidence from ARPES, thermal conductivity, and resistivity. Furthermore, zero-field measurements show no evidence for a time-reversal symmetry-breaking field greater than 0.05 G in the superconducting state. This makes exotic fully gapped spin-triplet states unlikely, and hence we contend that PbTaSe<sub>2</sub> is characterized by conventional BCS *s*-wave superconductivity in multiple bands.

DOI: 10.1103/PhysRevB.95.224506

# I. INTRODUCTION

Noncentrosymmetric superconductors are materials where the lack of inversion symmetry gives rise to asymmetric spinorbit coupling which splits otherwise degenerate electronic bands [1]. The broken symmetry removes means that the notion of parity can no longer be used to discuss the symmetry of a superconducting state that might emerge. This effectively allows mixed singlet and triplet states in these materials. This mixed-parity superconductivity is theoretically expected to generally give line nodes or partial line nodes in the gap [2–4].

While some noncentrosymmetric superconductors have shown evidence for line nodes, such as CePt<sub>3</sub>Si [5], CeIrSi<sub>3</sub> [6], Mg<sub>10</sub>Ir<sub>19</sub>B<sub>16</sub> [7], Mo<sub>3</sub>Al<sub>2</sub>C [8], and Li<sub>2</sub>Pt<sub>3</sub>B [9], many others display fully gapped states [10–15]. Multigap behavior has also been observed in materials such as La<sub>2</sub>C<sub>3</sub> [16]. Detailed analysis of possible microscopic pairing mechanisms has found that either isotropic or nodal gaps can arise depending on the anisotropy of the pairing interaction [17]; this has also been suggested to depend on the spin-orbit coupling strength of the material [10]. Furthermore, even when the superconducting states appear fully gapped,  $\mu$ SR measurements have found time-reversal symmetry-breaking fields in materials such as La<sub>2</sub>Ir<sub>3</sub> [13] and LaNiC<sub>2</sub> [14]. These varied properties make it valuable to study additional noncentrosymmetric systems in an effort to gain a deeper understanding of their physics.

PbTaSe<sub>2</sub> is a noncentrosymmetric material in the  $P\overline{o}m2$ space group consisting of TaSe<sub>2</sub> layers well separated by Pb interlayers, and was recently found to be superconducting with a  $T_C$  of 3.7 K [18]. This structure is similar to that of transition-metal dichalcogenide (TMD) superconductors such as TaS<sub>2</sub>, IrTe<sub>2</sub>, and TiSe<sub>2</sub>. In these materials, the parent compound typically hosts a charge density wave (CDW) and superconductivity emerges after the CDW is suppressed by applied pressure, doping, or intercalation [19–24]. Pure TaSe<sub>2</sub> has a CDW [25] that is suppressed with Pb doping [26], and so we can view PbTaSe<sub>2</sub> as a stoichiometric version of the doped TMDs, deep inside the superconducting phase, with the novel feature of broken centrosymmetry. ARPES measurements have also provided evidence that the superconductivity in  $PbTaSe_2$  is associated with the presence of a nearby CDW instability [27], which further strengthens the comparison between this compound and the doped TMDs.

The first studies of superconductivity in PbTaSe2 indicated conventional superconductivity as the magnitude of the specific heat jump is consistent with s-wave behavior [18]. However, low-temperature measurements of the upper critical field show an unconventional upward curvature as a function of temperature [28]. As  $H_{C2}(T = 0)$  is still below the Pauli limit, this has been interpreted as evidence of multiband superconductivity rather than exotic pairing symmetry. Furthermore, thermal conductivity measurements are consistent with fully gapped superconductivity as there is no linear term at low temperature, and the field dependence suggests multiband superconductivity [29]. STM [30] and ARPES [31] results support this multiband picture as they both show multiple relevant bands near the Fermi surface. However, despite this broad agreement, tunnel diode oscillator measurements of the penetration depth were found to be consistent with single-band s-wave superconductivity [32]. This apparent contradiction makes it valuable to perform complementary measurements of the penetration depth to gain additional insight into the superconducting state of PbTaSe<sub>2</sub>.

In this paper, we report muon spin rotation and relaxation  $(\mu SR)$  measurements in the superconducting vortex state of PbTaSe<sub>2</sub>. These measurements allow us to extract the temperature dependence of the penetration depth at two different magnetic fields. Zero-field  $\mu SR$  measurements also provide a sensitive test for possible time-reversal symmetry breaking in this material. We find weak temperature dependence to the penetration depth at low temperature that can be characterized by fully gapped superconductivity on two bands. Furthermore, we find no evidence for time-reversal symmetry breaking.

## **II. EXPERIMENTAL METHODS**

The crystal used in this research was prepared by chemical vapor transport at 850 °C using prereacted PbTaSe<sub>2</sub>, and PbCl<sub>2</sub>

2469-9950/2017/95(22)/224506(7)

224506-1

©2017 American Physical Society

# M. N. WILSON et al.

as the transporting agent. Details of the crystal growth can be found in Ref. [33].

Muon spin rotation and relaxation ( $\mu$ SR) experiments were performed at the TRIUMF laboratory in Vancouver, Canada. We used the Pandora dilution refrigerator spectrometer on the M15 surface-muon beam line. This instrument gives access to temperatures between 0.03 and 10 K with the sample mounted on a silver cold finger, magnetic fields up to 50 000 G with a superconducting magnet, and a time resolution of 0.4 ns. The field is applied parallel to the direction of the incoming muon beam, and we performed measurements with the muon spin rotated perpendicular to the field direction. These experiments were performed on a thin crystal aligned with the c axis parallel to the muon beam. We also performed  $\mu$ SR measurements in this cryostat with zero external field using copper coil electromagnets to compensate for ambient magnetic fields. We used the  $\mu$ SRFIT software package to analyze the  $\mu$ SR data [34].

Magnetometry measurements were performed at McMaster University using a Quantum Design XL-5 MPMS with an iHelium He<sup>3</sup> cryostat insert for measurements down to 0.5 K. Magnetization curves were measured as a function of temperature on a 3.55-mg single crystal oriented with H  $\parallel c$  axis. Alignment of the single crystal was verified with Laue x-ray diffraction prior to the magnetometry and  $\mu$ SR measurements.

# III. RESULTS AND DISCUSSION

Figure 1 shows the magnetic susceptibility versus temperature of PbTaSe<sub>2</sub> measured in a 10-G field applied parallel to the *c* axis after cooling in zero field. The susceptibility was calculated by dividing the measured magnetization by the applied field corrected for demagnetizing effects,  $H_{corr} =$ H - NM, where N is the demagnetizing factor, H is the



FIG. 1. Magnetic susceptibility measurements on a 3.55-mg single crystal of PbTaSe<sub>2</sub> with a field of 10 G applied parallel to the *c* axis after cooling in zero field showing a superconducting transition with  $T_c = 3.6$  K. (Inset) Magnetization vs field measurements at 0.5 K showing a lower critical field  $H_{c1} \approx 40$  G.

# PHYSICAL REVIEW B 95, 224506 (2017)

applied field, and M is the magnetization. The crystal we measured had the shape of a thin flat plate with the field applied perpendicular to the plate. We approximate this by an infinitely thin flat sheet, in which case the demagnetizing factor is 1. The susceptibility data show diamagnetism setting in at low temperatures, indicating a superconducting  $T_C$  of 3.6  $\pm 0.1$  K, in agreement with published data [18]. The sharpness of the transition, occurring over about 0.3 K, shows that our sample is reasonably clean, as chemical or structural disorder would broaden the transition. Furthermore, the strength of the diamagnetic response at low temperature can be used to estimate the superconducting volume fraction, as the susceptibility should be 1 for a pure superconductor at low temperature. We therefore estimate the superconducting volume fraction to be 0.77 which demonstrates that our sample is a bulk superconductor. The small difference from one is likely from partial flux penetration that is expected for a thin superconducting plate, or from uncertainty in the applied field caused by flux trapping in the superconducting magnet. The inset of Fig. 1 shows the magnetic moment as a function of applied field at 0.5 K from which we can estimate  $H_{c1} \approx 40$  G and  $H_{c2} \approx 1000$  G.

Figure 2(a) shows a  $\mu$ SR asymmetry spectrum collected at 25 mK in a 250 G >  $H_{c1}$  field applied along the *c* axis of our PbTaSe<sub>2</sub> sample, perpendicular to the muon spin direction. These data show oscillations as expected for muons precessing in an applied field, while also showing a distinct beat in the amplitude. This demonstrates that there are two components contributing to the asymmetry spectra, as can be seen in the Fourier transform of the asymmetry, shown in Fig. 2(b). In these data, the large peak just below 250 G comes from muons



FIG. 2. (a)  $\mu$ SR asymmetry measured at 25 mK in an applied field of 250 G || *c* axis with the muon spins rotated  $\perp$  *c* axis. (b) Fourier transform of the data shown in (a). These data show two peaks, one coming from muons stopping in the superconducting sample and one background peak from muons stopping in the silver sample holder. (c)  $\mu$ SR asymmetry measured at 25 mK in an applied field of 400 G || *c* axis with the muon spins rotated  $\perp$  *c* axis. (d) Fourier transform of the data shown in (c). The superconducting peak is wider and shifted closer to the background peak, indicating a larger penetration depth and smaller diamagnetic shift at 400 G compared to 250 G. The red lines in these figures show fits to the data following Eq. (1).

 $\mu$ SR STUDY OF THE NONCENTROSYMMETRIC ...

stopping in the silver sample holder or nonsuperconducting portions of our sample, while the peak at the lower field comes from muons stopping in the superconducting sample. Similarly, the asymmetry spectra in Fig. 2(c) measured at 25 mK in a field of 400 G and the corresponding Fourier transform in Fig. 2(d) also show two oscillating components. At this higher field, the superconducting peak is narrower and shifted closer to the silver background peak. This indicates a larger penetration depth and a smaller diamagnetic shift at the higher field. While the Fourier transform data are useful to make qualitative observations, it will always contain artifacts such as peak broadening caused by the limited time range, and hence we performed all fitting in the time domain.

Muons implanted into a type II superconductor between the lower  $(H_{C1})$  and upper  $(H_{C2})$  critical fields will see the asymmetric field distribution of the vortex state whose width is related to the London penetration depth ( $\lambda$ ). In our sample,  $H_{c1} \approx 40$  G and  $H_{c2} \approx 1000$  G at low temperature, so 250and 400-G measurements should both be in the vortex state. However, the small relaxation rate makes it difficult to resolve the field distribution and we mainly see a single peak from the sample in the Fourier transform (in addition to the background silver peak). Furthermore, the large background peak overlaps the field region that we would expect to see the tail of the distribution. These factors make fits to the true vortex lattice field distribution difficult and unreliable. Instead, we fit the superconducting data to a single Gaussian damped oscillating term, where the relaxation rate  $\sigma_{SC}$  can be related to the penetration depth, as is commonly done for polycrystalline samples.

We fit the asymmetry data in Figs. 2(a) and 2(c) with Eq. (1),

$$A = A_T \Big[ F \cos(\gamma_{\mu} B_s t + \phi) e^{-0.5(\sigma_s t)^2} + (1 - F) \cos(\gamma_{\mu} B_{Ag} t + \phi) e^{-0.5(\sigma_{Ag} t)^2} \Big], \qquad (1)$$

and show the fits as the red lines in Figs. 2(a) and 2(c) and Fourier transformed as the red lines in Figs. 2(b) and 2(d). This model has two Gaussian damped oscillating terms representing the sample and the silver background. For the fitting, we held the total asymmetry ( $A_T$ ), ratio between components (F), silver field ( $B_{Ag}$ ), silver relaxation rate ( $\sigma_{Ag}$ ), and phase ( $\phi$ ) constant while allowing the sample relaxation rate ( $\sigma_s$ ) and field ( $B_s$ ) to vary and use the constant  $\frac{Y_{te}}{2\pi} = 13.5538$  kHz/G for the muon gyromagnetic ratio. The temperature dependence of  $\sigma_s$  and  $B_s$  for both fields is shown in Fig. 3. Figure 3(a) shows an increase in relaxation rate setting in below 2.5 K, while Fig. 3(c) shows a relaxation rate increase below 1.9 K, compared to the measured  $T_C$  of 3.6 K from Fig. 1. This is consistent with the expected suppression of  $T_C$  by an applied field for a superconductor with a relatively low  $H_{C2} \approx 1000$  G.

From the sample relaxation rate in Figs. 3(a) and 3(c), we determined the superconducting component of this relaxation rate by averaging the rate above  $T_C$  to determine a background rate ( $\sigma_{BG}$ ), and then subtracting this off in quadrature from the total rate to give  $\sigma_{SC} = \sqrt{\sigma_s^2 - \sigma_{BG}^2}$ .

We can relate the width of the field distribution measured by  $\mu$ SR ( $\sigma_{SC}/\gamma_{\mu}$ ) with the penetration depth using the relation given by Eq. (10) in Ref. [35]. This equation gives the variance of the magnetic field for an ideal vortex lattice, accurate for the



FIG. 3. Fit parameters extracted from fits of the  $\mu$ SR data measured in an applied transverse field to Eq. (1). (a)  $\sigma_s$  for 250-G applied field. (b)  $B_s$  for 250-G applied field. (c)  $\sigma_s$  for 400-G applied field. (d)  $B_s$  for 400-G applied field.

range of applied magnetic fields  $0.25 < H/H_{c2} < 1$ , which is valid for our sample with fields down to 250 G. Expressing  $\lambda$  as a function of  $\sigma_{SC}$  yields

$$\lambda = \xi \sqrt{(1.94 \times 10^{-2}) \frac{\phi_0}{\xi^2} (1 - H/H_{c2}) \frac{\gamma_\mu}{\sigma_{\rm SC}} + 0.069.}$$
(2)

Here,  $\phi_0 = 2.06783^{-15}$  Wb is the flux quantum, and  $\xi$  is the coherence length.

In this equation, we used  $H_{c2}$  data from Ref. [29] and the relation  $H_{c2} = \phi_0/(2\pi\xi^2)$  to determine  $\xi$ . The resultant penetration depth is shown in Fig. 4. We fit the low-temperature



FIG. 4. Penetration depth calculated using Eq. (2) from the  $\mu$ SR data measured in 250 G (black) and 400 G (red). The solid lines show fits to the data using Eq. (3) and show that the penetration depth scales as expected for a fully gapped superconductor at low temperature.

M. N. WILSON et al.



FIG. 5. Normalized superfluid density  $n_s(T)/n(0)$  plotted versus reduced temperature  $T/T_C$  from the 250-G  $\mu$ SR data (black circles) and 400-G  $\mu$ SR data (red triangles). The lines correspond to fits to a single-band model [Eq. (4)] and a two-band model [Eq. (6)].

penetration depth  $\lambda$  with the BCS low-temperature limit [36],

$$\lambda(T) = \lambda(0) \left[ 1 + \sqrt{\frac{\pi \Delta_0}{2k_B T}} \exp\left(-\frac{\Delta_0}{k_B T}\right) \right].$$
(3)

Here,  $k_B = 8.617 \times 10^{-5}$  eV K<sup>-1</sup> is Boltzmann's constant, *T* is the temperature,  $\Delta_0$  is the zero-temperature value of the gap that is allowed to vary, and  $\lambda(0)$  is the zero-temperature value of the penetration depth that is also allowed to vary. These fits are shown as the solid lines in Fig. 4 and show that this model fits the data well. This suggests that the superconducting state is fully gapped without any nodes. From these fits we extract the zero-temperature penetration depth values of  $\lambda(0) = 140 \pm 1$  nm at 250 G and  $\lambda(0) = 180 \pm 1$  nm at 400 G.

As a further test of the pairing symmetry of this material, we calculated the normalized superfluid density as  $n_s/n_0 = \lambda^2(0)/\lambda^2(T)$  for both fields, and show these data in Fig. 5. We then used Eq. (4) to fit the full temperature range of this data assuming a fully gapped superconductor:

$$\frac{n_s(T)}{n_0} = \left[1 - 2\int_{\Delta}^{\infty} dE\left(-\frac{\partial F}{\partial E}\right)\frac{E}{\sqrt{E^2 - \Delta^2}}\right].$$
 (4)

In this equation, *E* is the energy difference above the Fermi energy,  $F = \frac{1}{e^{E/k_BT}+1}$  is the Fermi function, and  $\Delta$  is the gap, which we approximate using the interpolation formula [37]

$$\Delta(T) = \Delta_0 \tanh\left(1.742\sqrt{\frac{T_c}{T} - 1}\right).$$
 (5)

To determine the zero-temperature value of the gap  $\Delta_0$ , we use the BCS weak coupling relation  $\frac{2\Delta_0}{k_B T_c} = 3.5$ . This fit is shown as the solid blue line in Fig. 5, where the superfluid density at each field, normalized to the fit zerotemperature superfluid density ( $n_0$ ), is plotted against reduced temperature  $T/T_c$ . The values  $T_c$  (250G) = 2.63 K and  $T_c$  (400G) = 2.04 K were determined from the fit. The fit shows reasonably good agreement at both fields, however,

# PHYSICAL REVIEW B 95, 224506 (2017)

there is a small discrepancy at low temperature for the 250-G data where there is an unexplained increase in the superfluid density. A continuing increase in the superfluid density at low temperature is commonly taken to suggest the presence of nodes in the gap [36], however, another possibility is multiband superconductivity as has notably been observed in MgB<sub>2</sub> [38]. For two uncoupled fully gapped bands, the superfluid density can be described by the sum, scaled by some weighting factor *c*, of the contributions from the different gaps  $\Delta_1$  and  $\Delta_2$  [39]:

$$\frac{n_s(T)}{n_0} = (c) \left[ 1 - 2 \int_{\Delta_1}^{\infty} dE \left( -\frac{\partial F}{\partial E} \right) \frac{E}{\sqrt{E^2 - \Delta_1^2}} \right] + (1 - c) \left[ 1 - 2 \int_{\Delta_2}^{\infty} dE \left( -\frac{\partial F}{\partial E} \right) \frac{E}{\sqrt{E^2 - \Delta_2^2}} \right].$$
(6)

We used this equation to fit the 250-G data and show the fit as the solid green line in Fig. 5. This fit gives values of c = 0.91,  $\Delta_1 = 0.399$  meV, and  $\Delta_2 = 0.109$  meV, suggesting a Fermi surface dominated by a single band, with only a small contribution coming from a second band with smaller gap. The reduced  $\chi^2$  for the two-gap fit at 250 G is 1.01 compared to 1.68 for the single band which demonstrates that it is a statistically superior fit. However, we do not see any evidence for a continued increase in the 400-G superfluid density with decreasing temperature as might be expected. This could be explained by the lower gap on the second band: with a lower gap the field required to suppress the superconducting state is expected to be lower which would reduce the influence of multiband behavior at 400 G compared to 250 G.

The increase at low temperature could also be explained by a contribution from a band with an anisotropic gap, such as a d-wave or p-wave component. While our data alone cannot distinguish the isotropic two-gap state from such a mixed state, comparison with data from other groups makes the fully gapped state most likely. STM measurements show fully gapped superconductivity [30], while thermal conductivity [29] and  $H_{C2}$  measurments [28] are both consistent with multiple fully gapped bands. This picture also matches the theoretical expectations of Samokhin et al. [17] where a noncentrosymmetric superconductor with pairing caused by phonons should exhibit two-band nodeless superconductivity. PbTaSe<sub>2</sub> has no surrounding magnetic phases that might promote pairing by magnetic fluctuations, and ARPES measurements suggest the role of phonon stiffening in PbTaSe2 compared to TaSe2 to explain the appearance of superconductivity [27]. It therefore seems likely that phonon-mediated pairing is the mechanism for superconductivity in PbTaSe2 and thus the model of Samokhin et al., with fully gapped s-wave superconductivity on two bands, would apply, consistent with our fitting.

Some pairing symmetries, notably some spin-triplet p-wave states, have a spontaneous time-reversal symmetrybreaking (TRSB) field in the superconducting state. Most TRSB states are characterized by nodes in the gap which are unlikely based on our preceding analysis. However, in high-symmetry cubic or hexagonal systems TRSB fields can

PHYSICAL REVIEW B 95, 224506 (2017)



# $\mu$ SR STUDY OF THE NONCENTROSYMMETRIC ...

FIG. 6. (a) Example silicon muonium asymmetry spectra at early times in an external field of 5 G. (b) Silicon asymmetry at long times in an external field of 5 G. (c) Early time silicon asymmetry after zeroing the field. Red shows data with the muon spins parallel to momentum, and blue with the muon spins rotated perpendicular to the momentum. (d) Late time spectra corresponding to (c).

appear even for fully gapped states [40] as has been recently reported in La<sub>7</sub>Ir<sub>3</sub> [13] and Re<sub>6</sub>Hf [41]. Such fields have in the past been identified by  $\mu$ SR measurements in zero field across the superconducting state [42,43]. However, as the effect of such a field is very small, significant care must be taken to minimize any stray field at the sample position, lest a relaxation rate change caused by Meissner expulsion of a small field be mistaken for a true time-reversal symmetry-breaking field.

To perform these careful zero-field measurements on our PbTaSe<sub>2</sub> sample following the procedure outlined in Ref. [44], we first loaded a piece of pure silicon in place of the sample and performed measurements at 2 K. At this temperature, a fraction of muons landing in pure silicon bind with electrons to form muonium, which has a gyromagnetic ratio  $\frac{\gamma_{Mu}}{2\pi}$  = 1.394 MHz/G, 103 times larger than that of a bare muon. This gives  $\mu$ SR measurements in low-temperature silicon an extremely high sensitivity to small magnetic fields. Figures 6(a)and 6(b), which show the asymmetry spectra of silicon at 2 K in a field of 5 G, demonstrate this sensitivity. Figure 6(a) shows the early time spectra with the fast oscillations coming from muonium. Figure 6(b) shows the asymmetry out to 8  $\mu$ s and shows the fast oscillations coming from muonium as well as the slower oscillations coming from bare muons. These data are fit with two oscillating components given by Eq. (7),

$$A = A_T \Big[ F_{\text{Mu}} \cos(\gamma_{\text{Mu}} Bt + \phi_{\text{Mu}}) e^{-(\lambda_{\text{Mu}} t)} + (1 - F_{\text{Mu}}) \cos(\gamma_{\mu} Bt + \phi_{\mu}) e^{-(\lambda_{\mu} t)} \Big], \qquad (7)$$

where the field *B* is the same for both components,  $F_{Mu} = 0.16$  is the muonium fraction,  $\lambda_{Mu}$  and  $\lambda_{\mu}$  are the muonium and muon signal relaxation rates, and  $\phi_{Mu}$  and  $\phi_{\mu}$  are phase offsets for the muonium and muon components.

Using this silicon sample, we zeroed the field by adjusting the currents in copper coil electromagnets arranged in three



FIG. 7. (a)  $\mu$ SR asymmetry measured in zero applied field at 0.025 K (blue), 1 K (green), 2 K (yellow), 3 K (orange), and 5K (red). (b) Fit relaxation rate for  $\mu$ SR data measured in zero field. The red line shows a fit to a mean field order parameter with  $T_C = 3.6$  K approximated by Eq. (8).

perpendicular directions. In this procedure, we measured spectra with the muon spin parallel and perpendicular to the beam momentum, ensuring that the field in all directions was minimized. Figures 6(c) and 6(d) show the silicon spectra at 2 K after performing this zeroing procedure with the muon spins in both possible orientations. No oscillations are observed in these data, and the field fits to a value of  $0^{+0.3}_{-0.3}$  G indicating that a good zero-field condition was produced.

Once we arrived at this zero-field condition, we reloaded the PbTaSe<sub>2</sub> single-crystal sample in place of the silicon and performed zero-field  $\mu$ SR measurements with the muon spins parallel to the c axis. Figure 7 shows these data for representative temperatures between 0.025 and 5 K. The asymmetry in this figure represents the signal coming only from the sample. The background signal coming from muons stopping in the silver sample holder is time independent and we have allowed the baseline shift parameter ( $\alpha$ ), commonly used in  $\mu$ SR to account for varying detector efficiencies and geometric effects, to also account for the baseline shift caused by the silver background. This results in a total asymmetry which is comparable to the sample component of the transverse field measurements. The relaxation of this asymmetry in zero field will come from nuclear magnetic moments or from electronic magnetism. As the nuclear moments will not be much affected by temperature, and there are no known structural transitions which would modify the muon stopping site, any significant change in the relaxation rate with temperature is expected to signal the onset of electronic magnetism.

Figure 7 shows no visible difference between the asymmetry spectra at all temperatures. Fitting the data to a single exponentially relaxing component  $A = A_T e^{-\lambda t}$ , we extract the relaxation rate ( $\lambda$ ) and plot it in Fig. 7(b). This figure shows no significant change in relaxation rate down to 0.025 K. To estimate an upper limit on the internal field of the sample, we fit Fig. 7(b) to a mean field order parameter, approximated by Eq. (8):

$$\lambda = c \tanh\left(1.742\sqrt{\frac{T_c}{T} - 1}\right) + \lambda_0. \tag{8}$$

Here,  $\lambda$  is the relaxation rate,  $\lambda_0$  is a background relaxation rate, c is the order parameter, and  $T_C$  is fixed at 3.6 K. The fit yields  $c = 0 \pm 0.004 \ \mu s^{-1}$ , which gives an upper limit on the internal field of 0.05 G. Typical stray fields for time-reversal symmetry breaking in triplet superconductors are between

# M. N. WILSON et al.

0.1 and 0.5 G [42,45], substantially larger than our upper limit. We therefore suggest that there is no time-reversal symmetry breaking in PbTaSe<sub>2</sub> coming from triplet pairing. In certain noncentrosymmetric systems, smaller TRSB fields of around 0.08 G [13,41] have been reported in fully gapped superconducting states. These fields are still larger than our fitting limit, but we cannot rule out a slightly smaller TRSB field existing in our system.

#### **IV. CONCLUSION**

Our results suggest that PbTaSe<sub>2</sub> is not purely a conventional *s*-wave superconductor as the superfluid density is not flat at low temperatures. Zero-field  $\mu$ SR measurements find no evidence for a TRSB field, and are of sufficient precision to rule out the field magnitudes seen in other noncentrosymmetric and centrosymmetric superconductors. These features are overall consistent with describing PbTaSe<sub>2</sub> as a multiband

- Noncentrosymmetric Superconductors: Introduction and Overview, edited by E. Bauer and M. Sigrist (Springer, Berlin, 2012).
- [2] N. Hayashi, K. Wakabayashi, P. A. Frigeri, and M. Sigrist, Phys. Rev. B 73, 024504 (2006).
- [3] M. Sigrist, D. F. Agterberg, P. A. Frigeri, N. Hayashi, R. P. Kaur, A. Koga, I. Milat, K. Wakabayashi, and Y. Yanase, J. Magn. Magn. Mater. **310**, 536 (2007).
- [4] T. Takimoto and P. Thalmeier, J. Phys. Soc. Jpn. 78, 103703 (2009).
- [5] I. Bonalde, W. Brámer-Escamilla, and E. Bauer, Phys. Rev. Lett. 94, 207002 (2005).
- [6] H. Mukuda, T. Fujii, T. Ohara, A. Harada, M. Yashima, Y. Kitaoka, Y. Okuda, R. Settai, and Y. Onuki, Phys. Rev. Lett. 100, 107003 (2008).
- [7] I. Bonalde, R. L. Ribeiro, W. Bramer-Escamilla, G. Mu, and H. H. Wen, Phys. Rev. B 79, 052506 (2009).
- [8] E. Bauer, G. Rogl, X.-Q. Chen, R. T. Khan, H. Michor, G. Hilscher, E. Royanian, K. Kumagai, D. Z. Li, Y. Y. Li, R. Podloucky, and P. Rogl, Phys. Rev. B 82, 064511 (2010).
- [9] M. Nishiyama, Y. Inada, and G.-q. Zheng, Phys. Rev. Lett. 98, 047002 (2007).
- [10] H. Q. Yuan, D. F. Agterberg, N. Hayashi, P. Badica, D. Vandervelde, K. Togano, M. Sigrist, and M. B. Salamon, Phys. Rev. Lett. 97, 017006 (2006).
- [11] M. Isobe, M. Arai, and N. Shirakawa, Phys. Rev. B 93, 054519 (2016).
- [12] V. K. Anand, A. D. Hillier, D. T. Adroja, A. M. Strydom, H. Michor, K. A. McEwen, and B. D. Rainford, Phys. Rev. B 83, 064522 (2011).
- [13] J. A. T. Barker, D. Singh, A. Thamizhavel, A. D. Hillier, M. R. Lees, G. Balakrishnan, D. McK. Paul, and R. P. Singh, Phys. Rev. Lett. 115, 267001 (2015).
- [14] A. D. Hillier, J. Quintanilla, and R. Cywinski, Phys. Rev. Lett. 102, 117007 (2009).
- [15] Y. Iwamoto, Y. Iwasaki, K. Ueda, and T. Kohara, Phys. Lett. A 250, 439 (1998).

# PHYSICAL REVIEW B 95, 224506 (2017)

superconductor, with isotropic fully gapped superconductivity existing on both bands.

# ACKNOWLEDGMENTS

We thank G. D. Morris, B. S. Hitti, and D. J. Arseneau for their assistance with the  $\mu$ SR measurements. Work at Mc-Master University was supported by the Natural Sciences and Engineering Research Council of Canada and the Canadian Foundation for Innovation. M.N.W. acknowledges support from the Alexander Graham Bell Canada Graduate Scholarship program. The Columbia University group acknowledges support from NSF Grant No. DMR-1436095 (DMREF), NSF Grants No. DMR-1610633, No. OISE-0968226 (PIRE), JAEA Reimei project, and Friends of Univ. of Tokyo Inc. F.C.C. acknowledges support funded by the Ministry of Science and Technology (MOST), Taiwan, under Project No. 103-2119-M-002-020-MY3.

- [16] K. Sugawara, T. Sato, S. Souma, T. Takahashi, and A. Ochiai, Phys. Rev. B 76, 132512 (2007).
- [17] K. V. Samokhin and V. P. Mineev, Phys. Rev. B 77, 104520 (2008).
- [18] M. N. Ali, Q. D. Gibson, T. Klimczuk, and R. J. Cava, Phys. Rev. B 89, 020505(R) (2014).
- [19] L. Fang, Y. Wang, P. Y. Zou, L. Tang, Z. Xu, H. Chen, C. Dong, L. Shan, and H. H. Wen, Phys. Rev. B 72, 014534 (2005).
- [20] R. Morosan, H. W. Zandergen, B. S. Dennis, J. W. G. Bos, Y. Onose, T. Klimczuk, A. P. Ramirez, N. P. Ong, and R. J. Cava, Nat. Phys. 2, 544 (2006).
- [21] T. Yokoya, T. Kiss, A. Chainani, S. Shin, M. Nohara, and H. Takagi, Science 294, 2518 (2001).
- [22] A. F. Kusmartseva, B. Sipos, H. Berger, L. Forró, and E. Tutiš, Phys. Rev. Lett. **103**, 236401 (2009).
- [23] J. J. Yang, Y. J. Choi, Y. S. Oh, A. Hogan, Y. Horibe, K. Kim, B. I. Min, and S-W. Cheong, Phys. Rev. Lett. **108**, 116402 (2012).
- [24] B. Sipos, A. F. Kusmartseva, A. Akrap, H. Berger, and L. Forró, Nat. Mater. 7, 960 (2008).
- [25] K. Horiba, K. Ono, J. H. Oh, T. Kihara, S. Nakazono, M. Oshima, O. Shiino, H. W. Yeom, A. Kakizaki, and Y. Aiura, Phys. Rev. B 66, 073106 (2002).
- [26] A. Aharafeev, R. Sankar, A. Glamazada, K.-Y. Choi, R. Bohle, P. Lemmens, and F. Chou, arXiv:1505.00748.
- [27] T.-R. Chang, P.-J. Chen, G. Bian, S.-M. Huang, H. Zheng, T. Neupert, R. Sankar, S.-Y. Xu, I. Belopolski, G. Chang, B. K. Wang, F. Chou, A. Bansil, H.-T. Jeng, H. Lin, and M. Z. Hasan, Phys. Rev. B 93, 245130 (2016).
- [28] J. Wang, X. Xu, N. Zhou, Li. X. Cao, J. Yang, Y. Li, C. Cao, J. Dai, J. Zhang, Z. Shi, B. Chen, and Z. Yang, J. Supercond. Nov. Magn. 28, 3173 (2015).
- [29] M. X. Wang, Y. Xu, L. P. He, J. Zhang, X. C. Hong, P. L. Cai, Z. B. Wang, J. K. Dong, and S. Y. Li, Phys. Rev. B 93, 020503(R) (2016).
- [30] S.-Y. Guan, P.-J. Chen, M.-W. Chu, R. Sankar, F. Chou, H.-T. Jeng, C.-S. Chang, and T.-M. Chuang, Sci. Adv. 2, e1600894 (2016).
$\mu$ SR STUDY OF THE NONCENTROSYMMETRIC ...

- [31] G. Bian, T.-R. Chang, R. Sankar, S.-Y. Xu, H. Zhang, T. Neupert, C.-K. Chiu, S.-M. Huang, G. Chang, I. Belopolski, D. S. Sanchez, M. Neupane, N. Alidoust, C. Lie, B. K. Wang, C.-C. Lee, H.-T. Jeng, C. Zhang, Z. Yuan, S. Jia, A. Bansil, F. Chou, H. Lin, and M. Z. Hasan, Nat. Commun. 7, 10556 (2016).
- [32] G. M. Pang, M. Smidman, L. X. Zhao, Y. F. Wang, Z. F. Weng, L. Q. Che, Y. Chen, X. Lu, G. F. Chen, and H. Q. Yuan, Phys. Rev. B 93, 060506(R) (2016).
- [33] R. Sankar, G. S. Rao, I. P. Muthuselvam, T.-R. Chang, H. T. Jeng, G. S. Murugan, W.-L. Lee, and F. C. Chou, J. Phys.: Condens. Matter 29, 095601 (2017).
- [34] A. Suter and B. M. Wojek, Phys. Proc. 30, 69 (2012).
- [35] E. H. Brandt, Phys. Rev. B 68, 054506 (2003).
- [36] R. Prosorov and R. W. Giannetta, Supercond. Sci. Technol. 19, R41 (2006).
- [37] F. Gross, B. S. Chandrasekhar, D. Einzel, K. Andres, P. J. Hirschfeld, H. R. Ott, J. Beuers, Z. Fisk, and J. L. Smith, Z. Phys. B 64, 175 (1986).
- [38] A. A. Golubov, A. Brinkman, O. V. Dolgov, J. Kortus, and O. Jepsen, Phys. Rev. B 66, 054524 (2002).

#### PHYSICAL REVIEW B 95, 224506 (2017)

- [39] M.-S. Kim, J. A. Skinta, T. R. Lemberger, W. N. Kang, H.-J. Kim, E.-M. Choi, and S.-I. Lee, Phys. Rev. B 66, 064511 (2002).
- [40] D. F. Agterberg, V. Barzykin, and L. P. Gor'kov, Phys. Rev. B 60, 14868 (1999).
- [41] R. P. Singh, A. D. Hillier, B. Mazidian, J. Quintanilla, J. F. Annett, D. McK. Paul, G. Balakrishnan, and M. R. Lees, Phys. Rev. Lett. **112**, 107002 (2014).
- [42] G. M. Luke, Y. Fudamoto, K. M. Kojima, M. I. Larkin, J. Merrin, B. Nachumi, Y. J. Uemura, Y. Maeno, Z. Q. Mao, Y. Mori, H. Nakamura, and M. Sigrist, Nature (London) **394**, 558 (1998).
- [43] M. Smidman, M. B. Salamon, H. Q. Yuan, and D. F. Agterberg, Rep. Prog. Phys. 80, 036501 (2017).
- [44] G. D. Morris and R. F. Heffner, Phys. B (Amsterdam) 326, 252 (2003).
- [45] G. M. Luke, A. Keren, L. P. Le, W. D. Wu, Y. J. Uemura, D. A. Bonn, L. Taillefer, and J. D. Garrett, Phys. Rev. Lett. 71, 1466 (1993).

# Chapter 5

## Conclusions and Future Directions

### 5.1 URu<sub>2</sub>Si<sub>2</sub>

#### 5.1.1 Conclusions on various dopings

These works on the three different dopings of  $URu_2Si_2$  all come together to paint a picture of how chemical pressure affects the magnetic ground state of  $URu_2Si_2$ , and the extent to which it can, and can not, be considered the most important tuning parameter for isoelectronic doping.

First, the measurements on  $URu_{2-x}Fe_xSi_2$  show that iron doping produces an antiferromagnetic state with small doping levels that is similar to that of pure URu<sub>2</sub>Si<sub>2</sub> under hydrostatic pressure [74, 75]. Particularly if we consider that the doping levels of some of the samples may be somewhat higher than the nominal values, the phase diagram as a function of doping can, through converting the doping to effective chemical pressure, be mapped closely to the hydrostatic pressure phase diagram. However, despite the similarity of these phase diagrams, the doping dependence of both the moment measured by neutron scattering, and the internal field measured by  $\mu$ SR, are quite different in iron doping. Both of these parameters, which ideally are sensitive to the same quantity, increase with iron concentration up to a doping level of about x = 0.3, after which point they turn over and begin to decrease. This is significantly different from hydrostatic pressure where both the magnetic moment measured by neutron scattering [75] and the internal field measured by  $\mu$ SR [74] are pressure independent above a critical pressure. Furthermore, our inelastic neutron scattering measurements suggest that the excitation spectra are different for the antiferromagnetic state induced by iron doping and for that under hydrostatic pressure, although it is possible that some of this apparent difference comes from the difficulties of doing scattering experiments under hydrostatic pressure.

Measurements of the osmium doped samples show a similar antiferromagnetic state to that seen in the iron doped samples, despite inducing negative chemical pressure. The internal field measured by  $\mu$ SR in these samples also increases with doping. This constasts with the case of germanium doping, where a similar negative chemical pressure does not change the hidden order state into antiferromagnetism. This difference suggests that the hidden order state is not a finely tuned state that can be pushed away toward antiferromagnetism through a perturbation in either direction in chemical pressure, but rather is somewhat more robust, and is instead forced toward antiferromagnetism by some other feature shared by both iron and osmium doping. We suggest that this feature may be increased hybridization of the ruthenium site electrons and the uranium f-electrons for both osmium and iron doping, compared to a decrease for germanium doping, although more work is necessary to better understand this effect.

#### 5.1.2 Future Directions

It would be interesting to do a more thorough characterization of the magnetic state of germanium doped URu<sub>2</sub>Si<sub>2</sub>. In particular, the lack of magnetic order suggests that the hidden order state persists in these samples, but it would be useful to have inelastic neutron scattering measurements that could probe the excitations to answer this question more clearly. Furthermore, it would potentially be interesting to look at positive chemical pressure in another way by doping the silicon site with carbon. This may allow an antiferromagnetic state more analagous to that under pressure to be produced, without the effects we see in iron doping that appear to set it apart from the pressure-induced antiferromagnetism. However, as the melting point of carbon is very high, and the ionic radius is small, the growth of such carbon doped samples may prove difficult, and techniques such as high pressure synthesis may be needed.

Finally, it would be useful to more thoroughly address the question of whether the increasing hybridization for both iron and osmium doped samples is the cause of the antiferromagnetic state, or if some other factor is causing it. One way to look at this would be to attempt direct measurement of the electronic hybridization by using a technique such as STM on the doped samples that has been successful at measuring these properties in pure URu<sub>2</sub>Si<sub>2</sub> [52]. Another possibility is looking at the osmium doped samples under hydrostatic pressure. If the antiferromagnetism is brought about by changes to the lattice parameters, then applied hydrostatic pressure should suppress the transition temperature and change it back to hidden order. In contrast, if it is hybridization, then one might expect an enhancement of the antiferromagnetism with applied pressure.

### 5.2 Dichalcogenides

#### 5.2.1 Conclusions

This thesis considered two different chemically modified dichalcogenides,  $Ir_{0.95}Pt_{0.05}Te_2$  and PbTaSe<sub>2</sub>. While these share a common material class, it is not necessarily expected for their properties to be similar as the different atoms and slightly different crystal structures can have a large impact on electronic properties. Both of these materials become superconducting at low temperatures; this thesis sought to determine what the gap symmetry of these superconducting states was through measurement of the penetration depth.

We measured the penetration depth of  $Ir_{0.95}Pt_{0.05}Te_2$  using magnetometry and transverse field  $\mu$ SR measurements. These data show that the penetration depth in this material is not strongly anisotropic, and increases slightly with increasing field, as would be expected. Converting the penetration depths to normalized superfluid densities, the temperature dependence of the data taken from  $\mu$ SR and that from magnetometry are quite similar, aside from a change in  $T_C$ resulting from the  $\mu$ SR measurement being at 300 G compared to effectively zero field for the magnetometry. This temperature dependence can be well fit assuming a isotropic fully gapped superconducting state, with a gap to  $T_C$  ratio close to that of the expected BCS weak coupling value. We therefore suggest that  $Ir_{0.95}Pt_{0.05}Te_2$  is a conventional BCS superconductor.

For PbTaSe<sub>2</sub>, we measured the penetration depth using  $\mu$ SR at two different fields, 250 G and 400 G. These again show an increase in the penetration depth with field, as expected. At low temperatures, the superfluid density calculated from the penetration depth at 250 G shows a continuing increase with decreasing temperature. This could be evidence either for multi-band behaviour, or an anisotropic superconducting gap. Due to other measurements from the literature suggesting a fully gapped state with possible multi-band behaviour [141, 145, 147], we fit this data with a two-band model and find good agreement.

Furthermore, we took zero field  $\mu$ SR measurements on PbTaSe<sub>2</sub> to look for possible timereversal symmetry breaking in the superconducting state that would be evidence for spin-triplet superconductivity. These measurements show no change in the relaxation rate down to 30 G and therefore suggest that there is no time-reversal symmetry breaking. We can put a limit on the possible size of time-reversal symmetry breaking fields of 0.05 G, which is smaller than the field seen in other materials that have triplet superconductivity [179, 180]. Therefore, from these measurements, and the penetration depth measurements, we infer that PbTaSe<sub>2</sub> is a spin-singlet superconductor with isotropic fully gapped superconductivity existing on two different bands.

#### 5.2.2 Future Directions

As the evidence presented in this thesis for the multi-band nature of  $PbTaSe_2$  is not conclusive, it would be interesting to continue with a more extensive set of penetration depth measurements on this compound. In particular, measuring the penetration depth as a function of field at multiple temperatures would in principle distinguish between different types of gap symmetry that might be present, as has been suggested from measurements on other multi-band superconductors such as MgB<sub>2</sub> [30].

Finally, recent work by other groups on PbTaSe<sub>2</sub> have shown that there is a change in the superconductivity under relatively modest pressures of about 0.2 GPa [141,144]. This second superconducting phase coincides with the point where substantial changes to the bulk Fermi surface occur as a result of a structural transition [144]. It therefore may be interesting to do penetration depth measurements in this second pressure-induced superconducting phase to determine whether unconventional superconductivity appears, possibly as a result of fluctuations surrounding this structural transition.

# Bibliography

- M. N. Wilson, T. J. Williams, Y. P. Cai, A. M. Hallas, T. Medina, T. J. Munsie, S. C. Cheung, B. A. Frandsen, L. Liu, Y. J. Uemura, and G. M. Luke. *Physical Review B*, 93 (6): 064402 (2016).
- [2] T. J. Williams, A. A. Aczel, M. B. Stone, M. N. Wilson, and G. M. Luke. *Physical Review B*, 95 (10): 104440 (2017).
- M. N. Wilson, T. Medina, T. J. Munsie, S. C. Cheung, B. A. Frandsen, L. Liu, J. Yan,
   D. Mandrus, Y. J. Uemura, and G. M. Luke. *Physical Review B*, 94 (18): 184504 (2016).
- [4] M. N. Wilson, A. M. Hallas, Y. Cai, S. Guo, Z. Gong, R. Sankar, F. C. Chou, Y. J. Uemura, and G. M. Luke. *Physical Review B*, 95 (22): 224506 (2017).
- [5] H. K. Onnes. Proc. K. Ned. Akad. Wet., 13: 1274 (1911).
- [6] R. F. Broom. *Nature*, **190**: 992 (1961).
- [7] W. Meissner and R. Ochsenfeld. Naturwissenschaften, 21 (44): 787 (1933).
- [8] L. N. Cooper. *Physical Review*, **104** (4): 1189 (1956).
- [9] J. Bardeen, L. N. Cooper, and J. R. Schrieffer. *Physical Review*, **106** (5): 1175 (1957).
- [10] M. Tinkham. Introduction to Superconductivity. Dover Publications, New York, second edition (1996).
- [11] A. A. Abrikosov. Soviet Physics JETP, 5 (6): 1174 (1957).
- [12] J. E. Sonier. Journal of Physics: Condensed Matter, 16: S4499 (2004).

- [13] Y. J. Uemura, V. J. Emery, A. R. Moodenbaugh, M. Suenaga, D. C. Johnston, A. J. Jacobson, J. T. Lewandowski, J. H. Brewer, R. F. Kiefl, S. R. Kreitzman, G. M. Luke, T. Riseman, C. E. Stronach, W. J. Kossler, J. R. Kempton, X. H. Yu, D. Opie, and H. E. Schone. *Physical Review B*, **38** (1): 909 (1988).
- [14] F. Gross, B. S. Chandrasekhar, D. Einzel, K. Andres, P. J. Hirschfeld, H. R. Ott, J. Beuers,
   Z. Fisk, and J. L. Smith. Zeitschrift für Physik B Condensed Matter, 64 (2): 175 (1986).
- [15] W. L. McMillan. *Physical Review*, **331 344** (2): 166 (1968).
- [16] J. Bednorz and K. Muller. Zeitschrift für Physik B: Condensed Matter, 64: 189 (1986).
- [17] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu. *Physical Review Letters*, 58 (9): 908 (1987).
- [18] E. Dagotto. Reviews of Modern Physics, 66 (3): 763 (1994).
- [19] C. Pfleiderer. Reviews of Modern Physics, 81: 1551 (2009).
- [20] G. R. Stewart. Reviews of Modern Physics, 83 (4): 1589 (2011).
- [21] R. Prozorov and R. W. Giannetta. Superconductor Science and Technology, 19 (8): 57 (2006).
- [22] T. Yokoya, T. Kiss, A. Chainani, S. Shin, M. Nohara, and H. Takagi. Science, 294 (December): 2518 (2001).
- [23] F. Bouquet, Y. Wang, R. A. Fisher, D. G. Hinks, J. D. Jorgensen, A. Junod, and N. E. Phillips. *European Physics Letters*, 56: 856 (2001).
- [24] R. Khasanov, D. V. Evtushinsky, A. Amato, H. Klauss, H. Luetkens, C. Niedermayer,
  B. Büchner, G. L. Sun, C. T. Lin, J. T. Park, D. S. Inosov, and V. Hinkov. *Physical Review Letters*, **102** (May): 187005 (2009).
- [25] A. Maeda, Y. Iino, T. Hanaguri, N. Motohira, K. Kishio, and T. Fukase. *Physical Review Letters*, 74: 1202 (1995).
- [26] S. K. Yip and J. A. Sauls. *Physical Review Letters*, **69**: 2264 (1992).
- [27] T. Hanaguri, Y. Iino, A. Maeda, and T. Fukase. *Physica C: Superconductivity*, **246** (3-4): 223 (1995).

- [28] A. Maeda, T. Hanaguri, Y. Iino, S. Masuoka, Y. Kokata, J.-i. Shimoyama, K. Kishio, H. Asaoka, Y. Matsushita, M. Hasegawa, and H. Takei. *Journal of the Physical Society of Japan*, 65 (11): 3638 (1995).
- [29] J. E. Sonier, R. F. Kiefl, J. H. Brewer, J. Chakhalian, S. R. DUnsiger, W. A. MacFarlane, R. I. Miller, A. Wong, G. M. Luke, and J. W. Brill. *Physical Review Letters*, **79**: 1742 (1997).
- [30] R. Kadono. Journal of Physics: Condensed Matter, 16 (40): S4421 (2004).
- [31] J. E. Sonier, J. H. Brewer, and R. F. Kiefl. Reviews of Modern Physics, 72: 769 (2000).
- [32] A. Carrington and F. Manzano. *Physica C*, **385**: 205 (2003).
- [33] J. D. Fletcher, A. Carrington, P. Diener, P. Rodière, J. P. Brison, R. Prozorov, T. Olheiser, and R. W. Giannetta. *Physical Review Letters*, **98** (5): 057003 (2007).
- [34] G. R. Stewart. Reviews of Modern Physics, 56 (4): 755 (1984).
- [35] L. Taillefer, R. Newbury, G. G. Lonzarich, Z. Fisk, and J. L. Smith. Journal of Magnetism and Magnetic Materials, 63 & 64: 372 (1987).
- [36] S. Kondo, D. C. Johnston, C. A. Swenson, F. Borsa, A. V. Mahajan, L. L. Miller, T. Gu, A. I. Goldman, M. B. Maple, D. A. Gajewski, E. J. Freeman, N. R. Dilley, R. P. Dickey, J. Merrin, K. Kojima, G. M. Luke, Y. J. Uemura, O. Chmaissem, and J. D. Jorgensen. *Physical Review Letters*, **78** (19): 3729 (1997).
- [37] P. Coleman. arXiv, **1509.05769** (2015).
- [38] M. A. Ruderman and C. Kittel. *Physical Review*, **96** 1: 99 (1954).
- [39] K. T. Ko, K. Kim, S. B. Kim, H.-D. Kim, J. Y. Kim, B. I. Min, J.-H. Park, F.-H. Chang,
   H. J. Lin, A. Tanaka, and S-W. Cheong. *Physical Review Letters*, **107**: 247201 (2011).
- [40] *Heavy Fermions: Electrons at the Edge of Magnetism.* Handbook of Magnetism and Advanced Magnetic Materials (2007).
- [41] R. Jullien, J. N. Fields, and S. Doniach. *Physical Review B*, **16** 11: 4889 (1977).
- [42] Z. Fisk, H. R. Ott, T. M. Rice, and J. L. Smith. Nature, **320** (6058): 124 (1986).

- [43] F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schriefer. *Physical Review Letters*, 43 (25): 1892 (1979).
- [44] J. A. Mydosh and P. M. Oppeneer. Reviews of Modern Physics, 83 (4): 1301 (2011).
- [45] T. T. M. Palstra, A. A. Menovsky, J. van der Berg, A. J. Dirkmaat, P. H. Kes, G. J. Nieuwenhuys, and J. A. Mydosh. *Physical Review Letters*, 55: 2727 (1985).
- [46] C. Broholm, J. K. Kjems, W. J. L. Buyers, P. Matthews, T. T. M. Palstra, A. A. Menovsky, J. A. Mydosh, P. Mathews, T. T. M. Palstra, A. A. Menovsky, and J. A. Mydosh. *Physical Review Letters*, 58 (14): 1467 (1987).
- [47] M. B. Maple, J. W. Chen, Y. Dalichaouch, T. Kohara, C. Rossel, M. S. Torikachvili, M. W. McElfresh, and J. D. Thompson. *Physical Review Letters*, 56 (2): 185 (1986).
- [48] D. E. MacLaughlin, D. W. Cooke, R. H. Heffner, R. L. Hutson, M. W. McElfresh, M. E. Schillaci, C. Boekema, R. L. Lichiti, J. Oostens, H. D. Rempp, J. L. Smith, J. O. Willis, E. Zirngiebl, C. Boekema, R. L. Lichti, and J. Oostens. *Physical Review B*, **37** (7): 3153 (1988).
- [49] C. Broholm, H. Lin, P. T. Matthews, T. E. Mason, W. J. L. Buyers, M. F. Collins, A. A. Menovsky, J. A. Mydosh, and J. K. Kjems. *Physical Review B*, 43 (16): 12809 (1991).
- [50] C. R. Wiebe, J. A. Janik, G. J. MacDougall, G. M. Luke, J. D. Garrett, H. D. Zhou, Y.-J. Jo, L. Balicas, Y. Qiu, J. R. D. Copley, Z. Yamani, and W. J. L. Buyers. *Nature Physics*, **3** (2): 96 (2007).
- [51] D. A. Bonn, J. D. Garrett, and T. Timusk. *Physical Review Letters*, **61**: 1305 (1988).
- [52] A. R. Schmidt, M. H. Hamidian, P. Wahl, F. Meier, A. V. Balatsky, J. D. Garrett, T. J. Williams, G. M. Luke, and J. C. Davis. *Nature*, **465** (7298): 570 (2010).
- [53] T. Shibauchi, H. Ikeda, and Y. Matsuda. Philosophical Magazine, 94 (32-33): 3747 (2014).
- [54] J. G. Rau and H. Y. Kee. *Physical Review B*, **85** (24): 245112 (2012).
- [55] H. Ikeda, M.-T. Suzuki, R. Arita, T. Takimoto, T. Shibauchi, and Y. Matsuda. Nature Physics, 8 (7): 528 (2012).
- [56] P. Chandra, P. Coleman, and R. Flint. *Nature*, **493** (7434): 621 (2013).

- [57] K. A. Ross, L. Harriger, Z. Yamani, W. J. Buyers, J. D. Garrett, A. A. Menovsky, J. A. Mydosh, and C. L. Broholm. *Physical Review B*, 89: 155122 (2014).
- [58] R. Okazaki, T. Shibauchi, H. J. Shi, Y. Haga, T. D. Matsuda, E. Yamamoto, Y. Onuki, H. Ikeda, and Y. Matsuda. *Science*, **331** (6016): 439 (2011).
- [59] H.-H. Kung, R. E. Baumbach, E. D. Bauer, V. K. Thorsmolle, W.-L. Zhang, K. Haule, J. A. Mydosh, and G. Blumberg. *Science*, **347** (6228): 1339 (2015).
- [60] S. Tonegawa, K. Hashimoto, K. Ikada, Y. H. Lin, H. Shishido, Y. Haga, T. D. Matsuda, E. Yamamoto, Y. Onuki, H. Ikeda, Y. Matsuda, and T. Shibauchi. *Physical Review Letters*, 109: 036401 (2012).
- [61] S. Tonegawa, K. Hashimoto, K. Ikada, Y. Tsuruhara, Y. H. Lin, H. Shishido, Y. Haga, T. D. Matsuda, E. Yamamoto, Y. Onuki, H. Ikeda, Y. Matsuda, and T. Shibauchi. *Physical Review B*, 88: 245131 (2013).
- [62] S. Kambe, Y. Tokunaga, H. Sakai, T. D. Matsuda, Y. Haga, Z. Fisk, and R. E. Walstedt. *Physical Review Letters*, **110**: 246406 (2013).
- [63] S. C. Riggs, M. C. Shapiro, A. V. Maharaj, S. Raghu, E. D. Bauer, R. E. Baumbach, P. Giraldo-Gallo, M. Wartenbe, and I. R. Fisher. *Nature Communications*, 6 (May 2014): 6425 (2014).
- [64] S. Tonegawa, S. Kasahara, T. Fukuda, K. Sugimoto, N. Yasuda, Y. Tsuruhara, D. Watanabe, Y. Mizukami, Y. Haga, T. D. Matsuda, E. Yamamoto, Y. Onuki, H. Ikeda, Y. Matsuda, and T. Shibauchi. *Nature Communications*, 5 (May): 1 (2014).
- [65] C. Tabata, T. Inami, S. Michimura, M. Yokoyama, H. Hidaka, T. Yanagisawa, and H. Amitsuka. *Philosophical Magazine*, 94 (32-33): 3691 (2014).
- [66] Y. Chihiro Tabata, Masashi Tokunaga, Makoto Yokoyama, Hiroyuki Hidaka, Tatsuya and H. Amitsuka. Proc. Int. Conf. Strongly Correlated Electron Systems, 3: 011062 (2014).
- [67] N. P. Butch, M. E. Manley, J. R. Jeffries, M. Janoschek, K. Huang, M. B. Maple, A. H. Said, B. M. Leu, and J. W. Lynn. *Physical Review B*, **91**: 035128 (2015).
- [68] A. F. Santander-Syro, M. Klein, F. L. Boariu, A. Nuber, P. Lejay, and F. Reinert. Nat Phys, 5 (9): 637 (2009).

- [69] J. Q. Meng, P. M. Oppeneer, J. A. Mydosh, P. S. Riseborough, K. Gofryk, J. J. Joyce,
  E. D. Bauer, Y. Li, and T. Durakiewicz. *Physical Review Letters*, **111**: 1270021 (2013).
- [70] H. Ohkuni, Y. Inada, Y. Tokiwa, K. Sakurai, R. Settai, T. Honma, Y. Haga, E. Yamamoto,
  Y. [Obar]nuki, H. Yamagami, S. Takahashi, and T. Yanagisawa. *Philosophical Magazine* Part B, **79** (7): 1045 (1999).
- [71] D. Aoki, G. Knebel, I. Sheikin, E. Hassinger, L. Malone, T. D. Matsuda, and J. Flouquet. Journal of the Physical Society of Japan, 81: 074715 (2012).
- [72] E. Hassinger, G. Knebel, T. D. Matsuda, D. Aoki, V. Taufour, and J. Flouquet. *Physical Review Letters*, 105: 216409 (2010).
- [73] F. Bourdarot, S. Raymond, and L.-P. Regnault. Philosophical Magazine, 94 (32-33): 3702 (2014).
- [74] A. Amato, M. J. Graf, A. de Visser, H. Amitsuka, D. Andreica, and A. Schenck. Journal of Physics: Condensed Matter, 16: S4403 (2004).
- [75] N. P. Butch, J. R. Jeffries, S. Chi, J. B. Leão, J. W. Lynn, and M. B. Maple. *Physical Review B*, 82: 060408(R) (2010).
- [76] T. J. Williams, H. Barath, Z. Yamani, J. A. Rodriguez-Riviera, J. B. Leão, J. D. Garrett, G. M. Luke, W. J. Buyers, and C. Broholm. *Physical Review B*, 95: 195171 (2017).
- [77] F. Bourdarot, E. Hassinger, S. Raymond, D. Aoki, V. Taufour, L.-P. Regnault, and J. Flouquet. Journal of the Physical Society of Japan, 79 (6): 064719 (2010).
- [78] A. Villaume, F. Bourdarot, E. Hassinger, S. Raymond, V. Taufour, D. Aoki, and J. Flouquet. *Physical Review B*, 78: 012504 (2008).
- [79] H. Amitsuka, K. Matsuda, I. Kawasaki, K. Tenya, M. Yokoyama, C. Sekine, N. Tateiwa, T. C. Kobayashi, S. Kawarazaki, and H. Yoshizawa. *Journal of Magnetism and Magnetic Materials*, **310**: 214 (2007).
- [80] M. Yokoyama, H. Amitsuka, K. Tenya, K. Watanabe, S. Kawarazaki, H. Yoshizawa, and J. A. Mydosh. *Physical Review B*, **72**: 214419 (2005).
- [81] J.-G. Park, S. B. Roy, and B. R. Coles. Journal of Physics: Condensed Matter, 6: 5937 (1994).

- [82] N. Patrikios, M. de Podesta, S. B. Roy, and K. A. McEwen. Journal of Magnetism and Magnetic Materials, 108: 95 (1992).
- [83] H. Amitsuka, K. Tateyama, C. Paulsen, T. Sakakibara, and Y. Miyako. Journal of Magnetism and Magnetic Materials, 194-107: 60 (1992).
- [84] M. Ocko and J.-G. Park. Physica B: Condensed Matter, 230-232: 71 (1997).
- [85] A. L. de la Torre, P. Visani, Y. Dalichaouch, B. W. Lee, and M. B. Maple. Physica B: Physics of Condensed Matter, 179 (3): 208 (1992).
- [86] M. Yokoyama, H. Amitsuka, K. Watanabe, S. Kawarazaki, H. Yoshizawa, and J. A. Mydosh. Journal of the Physical Society of Japan Suppl., 71: 264 (2002).
- [87] J. G. Park. Journal of Physics Condensed Matter, 6 (18): 3403 (1994).
- [88] F. Wastin, E. Bednarczyk, J. Rebizant, S. Zwirner, and G. Lander. Journal of Alloys and Compounds, 262-263: 124 (1997).
- [89] S. Zwirner, J. C. Waerenborgh, F. Wastin, J. Rebizant, J. C. Spirlet, W. Potzel, and G. M. Kalvius. *Physica B*, 230-232: 80 (1997).
- [90] E. Lidström, D. Mannix, A. Hiess, J. Rebizant, F. Wastin, G. H. Lander, I. Marri, P. Carra, C. Vettier, and M. J. Longfield. *Physical Review B*, 61 (2): 1375 (2000).
- [91] T. Mito, M. Hattori, G. Motoyama, Y. Sakai, T. Koyama, K. Ueda, T. Kohara, M. Yokoyama, and H. Amitsuka. *Journal of the Physical Society of Japan*, 82 (12): 1 (2013).
- [92] A. Gallagher, K.-W. Chen, C. M. Moir, S. K. Cary, F. Kametani, N. Kikugawa, D. Graf, T. E. Albrecht-Schmitt, S. C. Riggs, A. Shekhter, and R. E. Baumbach. *Nature Communications*, 7: 10712 (2016).
- [93] M. R. Wartenbe, K.-W. Chen, A. Gallagher, N. Harrison, R. D. McDonald, G. S. Boebinger, and R. E. Baumbach. *Physical Review B*, 96: 085141 (2017).
- [94] K. R. Shirer, M. Lawson, T. Kissikov, B. T. Bush, A. Gallagher, K.-W. Chen, R. E. Baumbach, and N. J. Curro. *Physical Review B*, 95: 041107 (2017).
- [95] Y. Dalichaouch, M. B. Maple, J. W. Chen, T. Kohara, C. Rossel, M. S. Torikachvili, and A. L. Giorgi. *Physical Review B*, 41: 1829 (1990).

- [96] Y. Dalichaouch, M. B. Maple, M. S. Torikachvili, and A. L. Giorgi. *Physical Review B*, **39**: 2423 (1989).
- [97] M. Torikachvili, L. Rebelsky, K. Motoya, S. M. Shapiro, Y. Dalichaouch, and M. Maple. *Physical Review B*, 45 (5): 2262 (1992).
- [98] Y. Kohori, Y. Noguchi, T. Kohara, Y. Dalichaouch, M. A. L. Delatorre, and M. B. Maple. *Physica B-Condensed Matter*, **186-88**: 792 (1993).
- [99] N. P. Butch, M. B. Maple, A. L. de la Torre, P. Visani, Y. Dalichaouch, B. W. Lee, M. B. Maple, M. Yokoyama, K. Tenya, H. Amitsuka, N. P. Butch, and M. B. Maple. *Journal of Physics: Condensed Matter*, **22** (3): 164205 (2010).
- [100] Y. Dalichaouch, M. Maple, R. Guertin, M. Kuric, M. Torikachvili, and A. Giorgi. *Physica B*, 163: 113 (1990).
- [101] M. Yokoyama, H. Amitsuka, S. Itoh, I. Kawasaki, K. Tenya, and H. Yoshizawa. Journal of the Physical Society of Japan, 73 (3): 545 (2004).
- [102] N. Kanchanavatee, M. Janoschek, R. E. Baumbach, J. J. Hamlin, D. A. Zocco, K. Huang, and M. B. Maple. *Physical Review B*, 84: 245122 (2011).
- [103] N. Kanchanavatee, B. D. White, V. W. Burnett, and M. B. Maple. *Philosophical Magazine*, 94 (32-33): 3681 (2014).
- [104] J. Wilson and A. D. Yoffe. Advances in Physics, 18 (73): 193 (1969).
- [105] R. H. Friend and A. D. Yoffe. Advances in Physics, 36: 1 (2006).
- [106] J. A. Wilson, F. J. Di Salvo, and S. Mahajan. *Physical Review Letters*, **32** (16): 882 (1974).
- [107] J. M. Harper, T. H. Geballe, and F. J. DiSalvo. *Physical Review B*, **15** (6): 2943 (1977).
- [108] J. M. Harper, T. H. Geballe, and F. J. Di Salvo. *Physics Letters A*, **54** (1): 27 (1975).
- [109] F. J. Di Salvo, D. E. Moncton, and J. V. Waszczak. *Physical Review B*, **14** (10): 4321 (1976).
- [110] J. J. Yang, Y. J. Choi, Y. S. Oh, A. Hogan, Y. Horibe, K. Kim, B. I. Min, and S.-w. Cheong. *Physical Review Letters*, **108** (March): 116402 (2012).
- [111] A. D. Yoffe. Solid State Ionics, 9-10 (PART 1): 59 (1983).

- [112] E. Revolinsky, E. Lautenschalger, and C. Armitage. Solid state Communications, 1: 59 (1963).
- [113] E. A. Antonova, S. A. Medvedev, and I. Y. Shebalin. Soviet Physics JETP, **30** (2): 181 (1970).
- [114] C. Berthier, P. Molinie, and D. Jerome. Solid State Communications, 18: 1393 (1976).
- [115] B. Sipos, A. F. Kusmartseva, A. Akrap, H. Berger, L. Forró, and E. Tutiš. Nature Materials, 7 (12): 960 (2008).
- [116] S. Pyon, K. Kudo, and M. Nohara. Journal of the Physical Society of Japan, 81 (5): 1 (2012).
- [117] E. Morosan, H. W. Zandbergen, B. S. Dennis, J. W. G. Bos, Y. Onose, T. Klimczuk, A. P. Ramirez, N. P. Ong, and R. J. Cava. *Nature Physics*, 2 (8): 544 (2006).
- [118] L. J. Li, Y. P. Sun, X. D. Zhu, B. S. Wang, X. B. Zhu, Z. R. Yang, and W. H. Song. Solid State Communications, 150: 2248 (2010).
- [119] N. Masumoto, K. Taniguchi, T. Endoh, H. Takano, and S. Nagata. Journal of Low Temperature Physics, 117: 1129 (1999).
- [120] P. J. Hsu, T. Mauerer, M. Vogt, J. J. Yang, Y. S. Oh, S. W. Cheong, M. Bode, and W. Wu. *Physical Review Letters*, **111** (26): 1 (2013).
- [121] Q. Li, W. Lin, J. Yan, X. Chen, A. G. Gianfrancesco, D. J. Singh, D. Mandrus, S. V. Kalinin, and M. Pan. Nat. Commun., 5: 5358 (2014).
- [122] K. Kudo, M. Kobayashi, S. Pyon, and M. Nohara. Journal of the Physical Society of Japan, 82 (8): 1 (2013).
- [123] D. Ootsuki, Y. Wakisaka, S. Pyon, K. Kudo, M. Nohara, M. Arita, H. Anzai, H. Namatame, M. Taniguchi, N. L. Saini, and T. Mizokawa. *Physical Review B*, 86: 014519 (2012).
- [124] M. Kamitani, M. S. Bahramy, R. Arita, S. Seki, T. Arima, Y. Tokura, and S. Ishiwata. *Physical Review B*, 87 (18): 2 (2013).
- [125] J.-Q. Yan, B. Saparov, A. S. Sefat, H. Yang, H. B. Cao, H. D. Zhou, B. C. Sales, and D. G. Mandrus. *Physical Review B*, 88 (13): 134502 (2013).

- [126] Y. Oh, J. Yang, Y. Horibe, and S.-W. Cheong. *Physical Review Letters*, **110** (12): 127209 (2013).
- [127] a. Kiswandhi, J. Brooks, H. Cao, J. Yan, D. Mandrus, Z. Jiang, and H. Zhou. *Physical Review B*, 87 (12): 121107 (2013).
- [128] D. J. Yu, F. Yang, L. Miao, C. Q. Han, M.-Y. Yao, F. Zhu, Y. R. Song, K. F. Zhang, J. F. Ge, X. Yao, Z. Q. Zou, Z. J. Li, B. F. Gao, C. Liu, D. D. Guan, C. L. Gao, D. Qian, and J.-f. Jia. *Physical Review B*, 89 (10): 100501 (2014).
- [129] S. Y. Zhou, X. L. Li, B. Y. Pan, X. Qiu, J. Pan, X. C. Hong, Z. Zhang, A. F. Fang, N. L. Wang, and S. Y. Li. *EPL (Europhysics Letters)*, **104** (2): 27010 (2013).
- [130] S. Pyon, K. Kudo, and M. Nohara. *Physica C*, **494**: 80 (2013)
- [131] S. L. Zhang, I. Stasinopoulos, T. Lancaster, F. Xiao, A. Bauer, F. Rucker, A. A. Baker, A. I. Figueroa, Z. Salman, F. L. Pratt, S. J. Blundell, T. Prokscha, A. Suter, J. Waizner, M. Garst, D. Grundler, G. van der Laan, C. Pfleiderer, and T. Hesjedal. *Scientific Reports*, 7 (1): 123 (2017).
- [132] G. Cao, W. Xie, W. A. Phelan, J. F. Ditusa, and R. Jin. Physical Review B, 95: 035148 (2017).
- [133] A. P. Schnyder, S. Ryu, A. Furusaki, and A. W. Ludwig. AIP Conference Proceedings, 1134: 10 (2009).
- [134] L. Fu and E. Berg. *Physical Review Letters*, **105**: 097001 (2010).
- [135] K. I. Yokota, G. Kurata, T. Matsui, and H. Fukuyama. *Physica B: Condensed Matter*, 284: 551 (2000).
- [136] A. Sharafeev, R. Sankar, A. Glamazda, K.-Y. Choi, R. Bohle, P. Lemmens, and F. Chou. arXiv, 1505.00748 (2015).
- [137] M. N. Ali, Q. D. Gibson, T. Klimczuk, and R. J. Cava. Physical Review B, 89: 020505(R) (2014).
- [138] a. Bauer and C. Pfleiderer. *Physical Review B*, **85** (21): 1 (2012).

- [139] T. R. Chang, P. J. Chen, G. Bian, S. M. Huang, H. Zheng, T. Neupert, R. Sankar, S. Y. Xu, I. Belopolski, G. Chang, B. Wang, F. Chou, A. Bansil, H. T. Jeng, H. Lin, and M. Z. Hasan. *Physical Review B*, 93: 245130 (2016).
- [140] G. Bian, T.-R. Chang, R. Sankar, S.-Y. Xu, H. Zheng, T. Neupert, C.-K. Chiu, S.-M. Huang, G. Chang, I. Belopolski, D. S. Sanchez, M. Neupane, N. Alidoust, C. Liu, B. Wang, C.-C. Lee, H.-T. Jeng, C. Zhang, Z. Yuan, S. Jia, A. Bansil, F. Chou, H. Lin, and M. Z. Hasan. *Nature communications*, 7: 10556 (2016).
- [141] J. Wang, X. Xu, N. Zhou, L. Li, X. Cao, J. Yang, Y. Li, C. Cao, J. Dai, J. Zhang, Z. Shi, B. Chen, and Z. Yang. *Journal of Superconductivity and Novel Magnetism*, 28 (11): 3173 (2015).
- [142] C. L. Zhang, Z. Yuan, G. Bian, S. Y. Xu, X. Zhang, M. Z. Hasan, and S. Jia. *Physical Review B*, 93: 054520 (2016).
- [143] U. S. Kaluarachchi, Y. Deng, M. F. Besser, K. Sun, L. Zhou, M. C. Nguyen, Z. Yuan, C. Zhang, J. S. Schilling, M. J. Kramer, S. Jia, C. Z. Wang, K. M. Ho, P. C. Canfield, and S. L. Bud'Ko. *Physical Review B*, **95**: 224508 (2017).
- [144] C. Q. Xu, R. Sankar, W. Zhou, B. Li, Z. D. Han, B. Qian, J. H. Dai, H. Cui, A. F. Bangura, F. C. Chou, and X. Xu. *Physical Review B*, **96**: 064528 (2017).
- [145] M. X. Wang, Y. Xu, L. P. He, J. Zhang, X. C. Hong, P. L. Cai, Z. B. Wang, J. K. Dong, and S. Y. Li. *Physical Review B*, 93: 020503(R) (2016).
- [146] J. G. Rodrigo and S. Vieira. Physica C: Superconductivity and its Applications, 404 (1-4): 306 (2004).
- [147] S.-Y. Guan, P.-J. Chen, M.-W. Chu, R. Sankar, F. Chou, H.-T. Jeng, C.-S. Chang, and T.-M. Chuang. *Science Advances*, 2 (11): e1600894 (2016).
- [148] G. M. Pang, M. Smidman, L. X. Zhao, Y. F. Wang, Z. F. Weng, L. Q. Che, Y. Chen,
   X. Lu, G. F. Chen, and H. Q. Yuan. *Physical Review B*, 93 (6): 060506 (2016).
- [149] R. Sankar, G. N. Rao, I. P. Muthuselvam, T.-R. Chang, H. T. Jeng, G. S. Murugan, W.-L. Lee, and F. C. Chou. Journal of Physics: Condensed Matter, 29 (9): 095601 (2017).
- [150] J. Czochralski. Zeitschrift für Physikalische Chemie, 92: 219 (1918).

- [151] G. Dhanaraj, K. Byrappa, V. Prasad, and M. Dudley, editors. Springer Handbook on Crystal Growth. Springer-Verlag, Berlin Heidelberg (2010).
- [152] T. B. Reed and E. R. Pollard. Journal of Crystal Growth, 2: 243 (1968).
- [153] B. Josephson. *Physics Letters*, **2** (7): 251 (1962).
- [154] S. Shapiro. *Physical Review Letters*, **11** (2): 80 (1963).
- [155] J. A. Osborn. *Physical Review*, **67** (11): 351 (1945).
- [156] A. Aharoni. Journal of Applied Physics, 83 (6): 3432 (1998).
- [157] A. Yaouanc and P. Dalmas De Réotier. Muon Spin Rotation, Relaxation and Resonance: Applications to Condensed Matter. Oxford University Press, New York (2011).
- [158] S. Blundell. Magnetism in Condensed Matter. Oxford University Press, New York (2001).
- [159] A. E. Pifer, T. Bowen, and K. R. Kendall. Nuclear Instruments and Methods, 135: 39 (1976).
- [160] J. S. Möller, P. Bonfà, D. Ceresoli, F. Bernardini, S. J. Blundell, T. Lancaster, R. D. Renzi, N. Marzari, I. Watanabe, S. Sulaiman, and M. I. Mohamed-Ibrahim. *Physica Scripta*, 88 (6): 068510 (2013).
- [161] Y. Uemura. In "Muon Science: Muons in Physics, Chemistry, and Materials," Inst of Physics Pub (1998).
- [162] G. Shirane, S. M. Shapiro, and J. M. Tanquada. Neutron Scattering with a Triple-Axis Spectrometer. Cambridge University Press, Cambridge (2004).
- [163] V. F. Sears. *Neutron News*, **3** (3): 26 (2006).
- [164] W. L. Bragg. Cambridge Philosophical Society, 17: 43 (1913).
- [165] H. Amitsuka, M. Sato, N. Metoki, M. Yokoyama, K. Kuwahara, T. Sakakibara, H. Morimoto,
   S. Kawarazaki, Y. Miyako, and J. A. Mydosh. *Physical Review Letters*, 24: 5114 (1999).
- [166] J. S. Hall, M. R. Movassagh, M. N. Wilson, G. M. Luke, N. Kanchanavatee, K. Huang, M. Janoschek, M. B. Maple, and T. Timusk. *Physical Review B*, **92** (19): 1 (2015).

- [167] P. Das, N. Kanchanavatee, J. S. Helton, K. Huang, R. E. Baumbach, E. D. Bauer, B. D. White, V. W. Burnett, M. B. Maple, J. W. Lynn, and M. Janoschek. *Physical Review B*, 91: 085122 (2015).
- [168] C. T. Wolowiec, N. Kanchanavatee, K. Huang, S. Ran, and M. B. Maple. *Physical Review B*, 94: 085145 (2016).
- [169] H. H. Kung, S. Ran, N. Kanchanavatee, V. Krapivin, A. Lee, J. A. Mydosh, K. Haule, M. B. Maple, and G. Blumberg. *Physical Review Letters*, **117**: 227601 (2016).
- [170] N. P. Butch, S. Ran, I. Jeon, N. Kanchanavatee, K. Huang, A. Breindel, M. B. Maple, R. L. Stillwell, Y. Zhao, L. Harriger, and J. W. Lynn. *Physical Review B*, 94: 201102(R) (2016).
- [171] S. Ran, C. T. Wolowiec, I. Jeon, N. Pouse, N. Kanchanavatee, B. D. White, K. Huang, D. Martien, T. DaPron, D. Snow, M. Williamsen, S. Spagna, P. S. Risenborough, and M. B. Maple. *Proceedings of the National Academy of Sciences*, **113** (47): 13348 (2016).
- [172] S. Ran, I. Jeon, N. Pouse, A. J. Breindel, N. Kanchanavatee, and K. Huang. Proceedings of the National Academy of Sciences, 114 (37): 9826 (2017).
- [173] S. K. Dhar, R. J. Begum, P. Raj, P. Suryanarayana, L. C. Gupta, and R. Vijayaraghavan. Solid State Communications, 83: 965 (1992).
- [174] R. S. Hayano, Y. J. Uemura, J. Imazato, N. Nishida, T. Yamazaki, and R. Kubo. *Physical Review B*, **20** (3): 850 (1979).
- [175] K. Matsuda, Y. Kohori, T. Kohara, K. Kuwahara, and H. Amitsuka. *Physical Review Letters*, 87: 87203 (2001).
- [176] H. Amitsuka, T. Sakakibara, and Y. Miyako. Journal of Magnetism and Magnetic Materials, 90-91: 517 (1990).
- [177] T. Shibauchu, H. Kitano, and K. Uchinokura. Physical Review Letters, 72 (14): 2263 (1994).
- [178] S. F. Blake, M. D. Watson, A. McCollam, S. Kasahara, R. D. Johnson, A. Narayanan, G. L. Pascut, K. Haule, V. Kiryukhin, T. Yamashita, D. Watanabe, T. Shibauchi, Y. Matsuda, and A. I. Coldea. *Physical Review B*, **91**: 121105(R) (2015).

- [179] G. M. Luke, A. Keren, L. P. Le, W. D. Wu, Y. J. Uemura, D. A. Bonn, L. Taillefer, and J. D. Garrett. *Physical Review Letters*, **71**: 1466 (1993).
- [180] G. M. Luke, Y. Fudamoto, K. M. Kojima, M. I. Larkin, J. Merrin, B. Nachumi, Y. J. Uemura, Y. Maeno, Z. Q. Mao, Y. Mori, H. Nakamura, and M. Sigrist. *Nature*, **394**: 558 (1998).