NMR STUDY OF POTASSIUM IRON SELENIDE SUPERCONDUCTIVITY

NMR STUDY OF THE POTASSIUM IRON SELENIDE HIGH-TEMPERATURE SUPERCONDUCTOR

By

DAVID TORCHETTI, B.A. & Sc.

A Thesis Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements for the Degree Master of Science

McMaster University ©Copyright by David Torchetti, 2012. M.Sc. Thesis - D. A. Torchetti

McMaster U. — Physics & Astronomy

MASTER OF SCIENCE (2012) (Physics)

McMaster University Hamilton, Ontario

TITLE: NMR Study of the Potassium Iron Selenide High-Temperature Superconductor AUTHOR: David Torchetti, B.A. & Sc.(McGill University) SUPERVISOR: Takashi Imai NUMBER OF PAGES: xi, 82

Abstract

In this thesis we present a ⁷⁷Se NMR study of the iron selenide based high-temperature superconductor $K_x Fe_{2-y}Se_2$ ($T_c = 33$ K). We observe NMR lineshapes as narrow as ~ 4.5 kHz with an applied field along the crystal *c*-axis, and find no evidence for the co-existence of magnetic order with superconductivity. With an applied field along the *ab* plane, however, the lineshape splits into two peaks of equal intensities at all temperatures, suggesting that the tetragonal fourfold symmetry of the average structure may be locally lowered by vacancy superstructure. Knight shift data indicate that spin susceptibility decreases progressively with temperature, similar to other iron arsenide high- T_c systems. In the nuclear spin-lattice relaxation rate $1/T_1$ we observe no Hebel-Slichter coherence peak, nor any enhancement in low frequency antiferromagnetic spin fluctuations in $1/T_1T$. We also report on the effects of sulphur (S) substitution on the selenium sites in this system by conducting ⁷⁷Se NMR measurements on $K_xFe_{2-y}Se_{2-z}S_z$ (z = 0.8, 1.6). We find that both spin susceptibility and low frequency spin fluctuations are suppressed with increasing S content along with T_c .

Acknowledgements

I would like to first and foremost thank my supervisor, Dr. Takashi Imai, for his academic support over the last two years. He has inspired in me, through the example he sets, a tremendous work ethic, thoroughness, and passion for new discoveries in the field, without which my scientific abilities would not have developed or been pushed so far. Many helpful discussions and explanations are also owed to my colleague, Ms. Mingxuan Fu.

I would also like to thank the members of my thesis defense committee, Dr. Graeme Luke and Dr. David Venus, for their valuable questions, comments, and insights throughout the review process. Many thanks go to our collaborators, Dr. Hechang Lei, Dr. Cedmoir Petrovic, and their colleagues at Brookhaven National Laboratory for providing our single crystal samples. I would like to express gratitude to the manager of our helium reliquifier facility, Dr. Paul Dube, who not only provided the cryogens necessary for our research, but also much advice, information, and assistance with all things cryogenic - especially our very own reliquifier.

Finally, I would like to thank my friends and loved ones, especially my parents, for the unconditional love and support they have given me throughout my academic career. Though they may no longer be able to directly assist in my research, certainly all of my accomplishments are owed in no small part to everything they've done and given me.

David Torchetti

CONTENTS

1	Intr	roduction 1				
	1.1	Iron Based Superconductivity	1			
	1.2	Basic Properties of $K_x Fe_{2-y} Se_2$ and $K_x Fe_{2-y} Se_{2-z} S_z$	5			
		1.2.1 Crystal Structure	5			
		1.2.2 Electronic Band Structure	6			
		1.2.3 Magnetism and Parent Phases	9			
		1.2.4 Sulphur Substitution	11			
	1.3	Samples and Their Preparation	11			
	1.4	Motivations and Organization of Thesis	14			
2	NM	IR Basics and Techniques	15			
	2.1	Basic Resonance Theory	15			
	2.2	Methods and Equipment	18			
		2.2.1 NMR Electronics	19			
		2.2.2 Pulse Sequences	21			
	2.3	Knight Shift	23			
	2.4	Nuclear Spin-Lattice Relaxation Rate, $1/T_1$	26			
3	Sup	\mathbf{p} or $\mathbf{K}_x \mathbf{F} \mathbf{e}_{2-y} \mathbf{S} \mathbf{e}_2$	29			
	3.1	\mathbf{T}_c and Superconductivity	29			
	3.2	$^{77}\mathrm{Se}$ NMR Lineshapes \ldots	31			
	3.3	⁷⁷ K Knight Shift	35			
	3.4	Nuclear Spin-lattice Relaxation Rate, $^{77}(1/T_1)$	38			

4	$\textbf{Sulphur Substituted K}_{x}\textbf{Fe}_{2-y}\textbf{Se}_{2-z}\textbf{S}_{z}$				
	4.1	NMR Lineshapes	45		
4.2 ⁷⁷ K Knight Shift					
4.3 Nuclear Spin-Lattice Relaxation Rate $^{77}1/T_1$					
	4.4	Probing the Microscopic Inhomogeneity of the $^{77}\mathrm{Se}$ Magnetic Environment $\ \ .$	52		
5	Sun	nmary and Conclusions	55		
\mathbf{A}	Appendices				
A	A Cryomech PTS 410 Helium Reliquifier				
в	B NMR Probe Design for 16 Tesla Magnet 6				

LIST OF FIGURES

1.1	Superconducting phase diagram for $Ba(Fe_{1-x}Co_x)_2As_2$ [10] as a function of Co doping, x.	
	Optimal superconductivity takes place at x \sim 0.08, the peak of the dome. Note also that	
	superconductivity vanishes near $x \ge 0.14$, as overdoping suppresses T_c .	3
1.2	FeSe electronic phase diagram as a function of pressure [16]	4
1.3	Layered crystal structure for $K_x Fe_{2-y} Se_2$ from Guo <i>et al.</i> [17]. Iron and selenium form edge-	
	sharing tetrahedra, and potassium cations are spaced in between the FeSe-layers	5
1.4	Tabulated summary of crystallographic data for $K_x Fe_{2-y} Se_2$ [17]	6
1.5	Temperature dependence of resistivity for $K_x Fe_{2-y} Se_2$ both within the <i>ab</i> plane and along the	
	c-axis [25]	7
1.6	Electronic band structure summary for $K_x Fe_{2-y} Se_2$ [29]. Important to note is the absence	
	of any holelike band at the center of the Brillouin zone. Electronlike bands are found at the	
	corners of the BZ.	8
1.7	Magnetic structure and iron vacancy order from Wei Bao <i>et al.</i> [37]. In a $\sqrt{5} \ge \sqrt{5} \ge 1$ unit	
	cell, magnetic moments are aligned antiferromagnetically and form a "checkerboard" pattern	
	in their superstructure. Iron vacancy order is established in the same unit cell. \ldots	10
1.8	A summary of the effect of S substitution on lattice parameters. Both the a and c lattice	
	parameters are systematically shortened with S substitution, which mimics the effect of applied $% \mathcal{S}^{(1)}$	
	external pressure	12
1.9	Superconducting transition temperature, T_c , as a function of sulphur concentration, z. Filled	
	circles represent current samples used for NMR, measured $in \ situ$ in zero magnetic field, while	
	open triangles represent data at the source of crystal growth [20]. Solid and dashed lines are	
	a 'guide-to-eye'	13
2.1	Schematic of the classical precession of a magnetic moment in a static applied field	16
<u></u>	Energy level deniction of the Zeeman interaction for the simple edge of nuclear spin $I = 1/2$	17

2.2 Energy level depiction of the Zeeman interaction for the simple case of nuclear spin I = 1/2. 17

2.3	Schematic of the precession of a magnetic moment about B_1 in a rotating reference frame	18
2.4	Schematic of the electronics involved in our NMR circuit.	19
2.5	A depiction of the 'dephasing' and subsequent spin echo. In a) The magnetization is oriented along z (k'), b) A $\pi/2$ pulse flips it 90° into the xy-plane, c) Faster and slower components of M ₀ begin to dephase, and d) A 180° π pulse is applied, and the dephased components refocus.	22
2.6	Pulse sequence schematic for the spin echo method. Ringdown is indicated by the shaded segments toward the end of each pulse, and the FID and echo signals are depicted as a function of time.	22
2.7	Graphic representation of the use of adding/subtracting pulse sequences to eliminate ringdown. In practice there is ringdown from both 90° and 180° pulses, requiring 4 sequences to eliminate	0.0
2.8	Schematic of the phase sensitive detection (PSD) apparatus using a reference signal to elimi- nate the frequency components of the r.f. pulse from our NMR signal.	23 24
2.9	Representative ⁷⁷ Se NMR lineshape at 290 K to illustrate the shift in frequency from expected resonance f_0 .	25
2.10	Some example recovery curves for the magnetization $M(t)$ for ⁵⁹ Co (red) and ⁷⁵ As (blue) in $Ba(Fe_{1-x}Co_x)_2As_2$ following an inversion π -pulse [12]. Lines represent exponential fits used	2.0
	to determine the relaxation rate $1/T_1$	26
2.11	Diagram of the inversion π -pulse and subsequent relaxation of nuclear spins	27
3.1	The change in tuning frequency, $-\Delta f_{tune}(T)$ of our NMR tank circuit caused by superconduct- ing Meissner effects. Data are normalized with the value of $f_{tune}(T_c) \sim 67.7$ MHz	30
3.2	The change in tuning frequency, $-\triangle f_{tune}(T)$ of our NMR circuit with an external magnetic field of $B_{ab} = 8.3$ Tesla applied within the <i>ab</i> -plane.	31
3.3	Representative ⁷⁷ Se NMR lineshapes observed in an external magnetic field B_c Tesla applied along the crystal <i>c</i> -axis.	32
3.4	Temperature dependence of the full width at half maximum (FWHM), $\triangle f_{NMR}$, of the ⁷⁷ Se NMR lineshapes in $B_c = 8.3$ Tesla. Note the enhancement below T_c , induced by the Abrikosov	
	lattice of superconducting vortices and proportional to the in-plane penetration depth λ_{ab}	33
3.5	A representative FFT lineshape observed at 50 K with the external magnetic field $B_{ab} = 8.3$ Tesla applied within the <i>ab</i> -plane. The <i>c</i> -axis lineshape at 50 K is plotted as well for comparison.	35
3.6	Temperature dependence of the ⁷⁷ Se NMR Knight shift, reflecting the local spin susceptibility, χ_{spin} , near the Se sites. Results with the field applied both in the <i>c</i> -axis direction and within the <i>ab</i> -plane show the same qualitative behaviour. Notice the sharp drop below T as well as	
	a slight change in curvature in the normal state near 200 K	36

3.7	$^{77}K_{ab}$ with both <i>ab</i> -plane peak positions plotted as a function of $^{77}K_c$ with temperature as the	
	implicit parameter. The linear fit is good, implying a nearly identical temperature dependence	
	of χ^{ab}_{spin} and χ^{c}_{spin} , with a slope of 1.21 \pm 0.02. The dashed vertical line denotes our estimate	
	for $K_{chem} \sim 0.11$ %, and the arrow denotes T_c .	38
3.8	Temperature dependence of the nuclear spin-lattice relaxation rate $1/T_1$ for 77 Se sites in	
	$K_x Fe_{2-y}Se_2$. We compare with the relaxation rate observed at ⁷⁷ Se sites in FeSe (T _c =	
	9 K) [15] and at ${}^{75}As$ sites in Ba(Fe _{0.92} Co _{0.08}) ₂ As ₂ (T _c = 25 K) [12]. Arrows mark the	
	superconducting transition temperature in each sample.	39
3.9	The temperature dependence of $^{77}(1/T_1T)$ observed in $K_xFe_{2-y}Se_2$ with $B_c = 8.3$ T. Results	
	for FeSe in ambient pressure (T $_c = 9$ K) as well as 0.7 GPa (T $_c = 14$ K) are presented as well	
	for comparison [15]	40
3.10	The temperature dependence of $^{75}(1/T_1T)$ observed in Ba(Fe _{1-x} Co _x) ₂ As ₂ at two representa-	
	tive concentrations. The optimally doped $x = 0.08$ concentration exhibits a large enhancement	
	of low frequency antiferromagnetic spin fluctuations, while the over-doped $\mathbf{x} = 0.14$ concen-	
	tration shows no enhancement [10]	41
3.11	The normal state data for $^{77}(1/T_1T)^{0.5}$ and $^{77}(1/T_1T)$ plotted vs $^{77}K_c$ with temperature as	
	the implicit parameter. A linear relationship between $^{77}(1/T_1T)^{0.5}$ and $^{77}K_c$ would indicate	
	a Korringa relation, represented by the dashed line. The solid lines are free parameter fits for	
	$^{77}(1/T_1T) = (^{77}K_c - K_{chem})^n$, which gives a value of $n \sim 1.6$ instead of the Fermi liquid value	
	of 2. The horizontal intercept in this plot represents K_{chem} , the temperature independent	
	chemical shift. Extrapolating a linear fit yields a ${\rm K}_{chem}$ estimate of \sim 0.04 %, much smaller	
	than the 0.11 % value obtained from the temperature dependence of $^{77}{\rm K}$ in Fig. 3.6	43
4.1	Representative ⁷⁷ Se NMR FFT lineshapes for $K_{\sigma}Fe_{2-\sigma}Se_{2-\sigma}S_{\sigma}$ at 50 K with $B_{\sigma} = 8.33$ Tesla	
	applied along the c-axis. The non-substituted $z = 0$ lineshape is presented for comparison	
	as well, with the lineshapes normalized for an equal integrated instensity. In addition to the	
	broadening in the S substituted lineshapes, note the systematic lowering of the NMR peak	
	frequency with increased S content.	46
4.2	Temperature dependence of the ⁷⁷ Se NMR Knight shift, ⁷⁷ K, for $K_x Fe_{2-y} Se_{2-z} S_z$ with z	
	= 0.8 and 1.6 and $B_c = 8.33$ Tesla along the <i>c</i> -axis. $K_x Fe_{2-y} Se_2$ is presented as well for	
	comparison, and arrows mark T_c for the two superconducting compositions: $z = 0$ ($T_c = 25$	
	K) and $z = 0.8$ (T _c = 13 K). The dashed curve is a phenomenological fit with a pseudo-gap,	
	77 K ~ $\alpha + \beta \exp(-\Delta/k_B T)$, with $\Delta/k_B = 435$ K for all samples. Note the overall suppression	
	of 77 K with S substitution.	48
4.3	Representative T_1 recovery curves measured at the center of the FFT lineshapes presented	
	in Fig. 4.1 at 50 K. Signal intensity is normalized for clarity, and solid lines represent single	
	exponential fits through each data set, the argument of which gives our T_1 value. The strong	

4.4	$1/T_1T$ as a function of temperature for S substituted samples measured in $B_c = 8.33$ Tesla	
	applied along the c-axis. The $z = 0$ composition is again presented alongside for comparison.	
	Relaxation rate and therefore spin excitations systematically slow with S substitution. Neither	
	of the two superconducting samples exhibits an enhancement toward T_c	51
4.5	$1/\sqrt{T_1T}$ vs 77 K(%) with temperature as the implicit parameter for all three compositions. A	
	constant slope would indicate a Korringa relation, an indicator for Fermi liquid theory. The	
	extrapolated horizontal intercept corresponds to K_{chem} .	53
		<u> </u>

4.6 Variation of the relaxation rate, $1/T_1$ as measured across the $K_x Fe_{2-y}Se_{1.2}S_{0.8}$ lineshape. . . 54

M.Sc. Thesis - D. A. Torchetti

LIST OF TABLES

2.1	Representative Nuclear Gyromagnetic Ratios	17
2.2	Phase sensitive detection pulse sequences	21

M.Sc. Thesis - D. A. Torchetti

CHAPTER 1

INTRODUCTION

High transition temperature (T_c) superconductivity became a driving force for research in condensed matter physics when it was discovered in the copper oxide superconductors (cuprates) more than 25 years ago. High- T_c superconductors provide not only a wealth of potential practical applications, but also interesting and in many cases enigmatic many-body physics. The conventional metallic and alloy superconductors can be well described by the Bardeen-Cooper-Schrieffer (BCS) theory [1], but a complete understanding of the unconventional high- T_c mechanism remains, to this day, elusive. The prescription, then, is to search for and study as many of these unconventional high- T_c systems as possible. The hope is that a diverse set of superconductors which share similar aspects will collectively provide the clues we need to understand high- T_c superconductivity as a whole. For 22 years the cuprates dominated - with some exceptions, including e.g. MgB₂ ($T_c = 39$ K) [2] - the high- T_c scene. Several families of cuprates, such as the YBCO, LSCO, and BSCCO systems, provided physicists with important information, including the fact that superconductivity is facilitated in the weakly coupled copper-oxide layers. None of these superconductors, however, were sufficient to pinpoint the high- T_c superconducting mechanism.

1.1 Iron Based Superconductivity

In 2008, Hideo Hosono's group at the Tokyo Institue of Technology reported that an *iron* based compound, LaO_{1-x}F_xFeAs, exhibits superconductivity with a T_c as high as 26 K [3]. This discovery initiated frenzied research into similar systems, and within months the family of iron based high-T_c superconductors was growing rapidly. With the new family of unconventional high temperature superconductors came new clues regarding the superconducting mechanism. Like the layers of copper and oxygen in the cuprates, the typically tetrahedral structure of iron and arsenic seems crucial to the exhibition of superconductivity in these systems. Shortly after the initial discovery it was found that replacing La with Sm or Pr in the Hosono group's compound raised T_c higher still (~ 52 K [4,5]). In addition to these '1111' systems, superconductivity is also exhibited in the simpler '122' family with BaFe₂As₂, the simpler still '11' family including FeSe, and several others. Very unlike the cuprates, the doping (or "substitution") of transition metals like cobalt into the FeAs layers can induce superconductivity; in the cuprates it is detrimental. Another key comparison between the cuprates and iron-based superconductors is found in their parent materials. Both families exhibit antiferromagnetic order in their parent materials, however the type of antiferromagnetic ordering differs markedly between the two. The cuprates have spins that align in an antiparallel arrangement and the parent material is a Mott insulator. Conversely many iron based systems are "spin density wave" (SDW) metals, where the spins on the iron atoms modulate periodically in space with a specific magnetic phase [6]. As magentic order is destroyed, e.g. by doping [3,7] or by application of pressure [8,9], optimal superconductivity emerges. These are just some examples of the new avenues through which researchers were able to pursue the high-T_c superconducting mechanism, thanks to the wealth of new information provided by the iron superconductors.

By adjusting the level of dopant as a kind of 'tuner' for superconductivity, physicists are able to pinpoint in many systems where superconductivity is optimized and where it is destroyed. Figure 1.1 depicts a typical and representative superconducting phase diagram for $Ba(Fe_{1-x}Co_x)_2As_2$, where the peak of the 'dome' indicates optimal superconductivity, and its boundaries show where superconductivity vanishes [10]. Studying the various properties of iron based superconductors at these points and observing how they change shows much promise in revealing information about the superconducting mechanism.

One such property is the aforementioned magnetic order and its destruction. By following the evolution of the antiferromagnetic order in the parent material as it disappears and superconductivity emerges, we can try to establish signatures of optimal superconductivity. Early studies, for example, suggested that the optimal doping level is that which places the system in the vicinity of magnetic instability, as evidenced by the largest enhancement of antiferromagnetic spin fluctuations (AFSF) near T_c [10–14]. Some natural follow up questions to ask are what causes these fluctuations, and how can they be enhanced so as to maximize T_c ?

In many iron-arsenide systems, the AFSF may be connected to the effects induced by Fermi surface nesting. In families of iron based superconductors, band theory predicts a metal with several Fermi surfaces separated by a wave vector that is nearly commensurate with the magnetic ordering. With electron bands near the Brillouin zone edge and hole bands at the zone center, these "nesting effects" between them may be associated with the AFSF. This may, in turn, lead to Cooper pairing and superconductivity. In this scenario overdoping would suppress nesting effects via the filling of hole bands, leading to supression of the AFSF and T_c as well. Our group recently reported that in the optimally doped phase of Ba(Fe_{1-x}Co_x)₂As₂, the maximum enhancement of low frequency AFSF near T_c is observed [10]. The overdoped Ba(Fe_{1-x}Co_x)₂As₂ phases indeed exhibit a systematic suppression of the low frequency AFSF enhancement near T_c , lending further evidence to the connection between these fluctuations and the superconducting mechanism.

In addition, our group reported that AFSF enhance in direct correlation with the enhancement of T_c



Figure 1.1: Superconducting phase diagram for $Ba(Fe_{1-x}Co_x)_2As_2$ [10] as a function of Co doping, x. Optimal superconductivity takes place at $x \sim 0.08$, the peak of the dome. Note also that superconductivity vanishes near $x \ge 0.14$, as overdoping suppresses T_c .

and the application of pressure in the simple 11 iron-selenide superconductor, FeSe [15]. Application of pressure alone was enough to raise T_c from ~ 9 K to as high as 37 K [16]. The T_c -pressure phase diagram for FeSe is presented in Fig. 1.2. Similar to the case of an overdoped material (e.g. $Ba(Fe_{1-x}Co_x)_2As_2$), overpressuring can cause T_c to decrease. This provides further evidence for the connection between AFSF and the superconducting mechanism, and while we have studied the electronic properties of overdoped iron-arsenides [10], the evolution of electronic properties in overpressured FeSe is not well understood because extremely high pressures of \geq 9 GPa are required [16]. Rather than explore these potentially difficult experimental conditions, the bulk of this thesis focuses on two materials that provide an alternate route to study the 'right-hand side' of the superconducting dome in the electronic phase diagram of the iron selenides. The first, $K_x Fe_{2-y}Se_2$ discovered by Guo *et al.* in 2010, intercalates potassium into the simple FeSe to raise T_c as high as 33 K [17]. Building on our study of this system we also explore the effects of substituting sulphur on the selenium sites in $K_x Fe_{2-y}Se_2 - zS_z$ [18–20].



Figure 1.2: FeSe electronic phase diagram as a function of pressure [16].



Figure 1.3: Layered crystal structure for $K_x Fe_{2-y}Se_2$ from Guo *et al.* [17]. Iron and selenium form edgesharing tetrahedra, and potassium cations are spaced in between the FeSe-layers.

1.2 Basic Properties of $K_x Fe_{2-y} Se_2$ and $K_x Fe_{2-y} Se_{2-z} S_z$

1.2.1 Crystal Structure

Guo *et al.*'s report of a 33 K transition temperature in $K_x Fe_{2-y}Se_2$ was the highest to date for an FeSe-layered material with alkali metal intercalation (K, Rb, Cs) under ambient pressure. The nominal composition $K_{0.8}Fe_2Se_2$ is produced by intercalating the alkali metal potassium in between the FeSe layers. The system belongs to the I4/mmm space group and, as indicated in Fig. 1.3, its crystal structure consists of layers of edge-sharing tetrahedra of FeSe₄ interspaced with K cations [17]. This is identical to the well known ThCr₂Si₂ structure in other 122 materials such as BaFe₂As₂ [21], and the heavy Fermion superconductors CeCu₂Si₂ [22] and URu₂Si₂ [23]. In comparison with FeSe, the potassium cations in $K_xFe_{2-y}Se_2$ act to separate the distance between FeSe layers to the point where two neighboring Fe square planes are 7.0184 Å apart, the largest discovered in these materials at the time [17]. Chemical analyses are also consistent with

Formula	KFe ₂ Se ₂
Temperature (K)	297
Space group	I4/mmm
Fw	212.03
a (Å)	3.9136(1)
<i>c</i> (Å)	14.0367(7)
V (Å ³)	214.991(3)
Ζ	2
R_p	3.26%
R_{wp}	5.15%
R _{exp}	2.22%
χ^2	5.38
Atomic parameters	
K	2a (0, 0, 0)
Fe	4d (0, 0.5, 0.25)
Se	4e(0, 0, z)
	z = 0.3539(2)
Bond length (Å)	
K-Se	3.4443(4)×8
Fe-Se	$2.4406(4) \times 4$
Fe-Fe	$2.7673(5) \times 4$
Bond angles (deg)	
	110.926(4) × 4
	$106.600(4) \times 2$

Figure 1.4: Tabulated summary of crystallographic data for $K_x Fe_{2-y} Se_2$ [17].

both potassium and iron deficiencies, and there has been reported evidence for Fe vacancy order forming in these systems [24]. The crystallographic data is tabulated in Fig. 1.4.

Figure 1.5 displays data for the resistance within the *ab*-plane and along the *c*-axis for a $K_x Fe_{2-y}Se_2$ crystal sample [25]. The resistance exhibits semiconducting behaviour in the temperature range above the broad 105 K peak, and metallic characteristics below. Resistance drops abruptly at about 30 K, indicating a superconducting transition, and exhibits a transition width of ~ 3 K. The crystallographic and resistive properties are altogether not unexpected for this system, given the comparable results for related 122 systems.

1.2.2 Electronic Band Structure

The Fermi surface (FS), however, distinguishes the $K_x Fe_{2-y}Se_2$ material from its cousins. In BaFe₂As₂, angle-resolved photoemission spectroscopy (ARPES) reveals a FS with hole pockets at the center of the Brillouin zone and electron pockets at the corners [26, 27]. It is the *inter-band* (hole and electron) nesting effects that are believed to be related to AFSF and the superconducting mechanism. Further support for



Figure 1.5: Temperature dependence of resistivity for $K_x Fe_{2-y}Se_2$ both within the *ab* plane and along the *c*-axis [25].

this scenario is found in ARPES reports on cobalt doping in $Ba(Fe_{1-x}Co_x)_2As_2$. Cobalt has one additional valence electron compared with iron, so doping it into the Fe sites would result in the donation of an extra electron. Measurements revealed that the hole pockets at the zone center become smaller with electron doping [27,28], as one would expect, and that they nearly disappear in the heavily electron-doped (x = 0.15) sample [26].

T. Qian, H. Ding *et al.* reported that in $K_x Fe_{2-y}Se_2$ ARPES measurments point to an absence of a holelike FS at the zone center, implying that the inter-band nesting effects are absent as well [29]. They observe clear band dispersion, and if their local density approximation (LDA) band calculations are renormalized by a factor of 2.5, they are consistent with several dispersion features that are observed experimentally. They suggest this indicates relatively strong correlation effects are present. Their summary of the electronic band structure is reproduced in Fig. 1.6. An electronlike band evidently crosses the Fermi energy, forming a circular FS at the (π ,0) point (M point). The holelike band at the zone center, however, is found to sink ~ 90 meV below the Fermi energy, with a band gap of 30 meV to the bottom of the electronlike band. Some calculations suggest that it is iron vacancy disorder that can inhibit or supress sections of the Fermi surface required for nesting effects to induce AFSF [30]. Could it be that this superconductor is a counterexample to the evidence provided by many other iron systems that AFSF induced by nesting effects are key to the superconducting mechanism?



Figure 1.6: Electronic band structure summary for $K_x Fe_{2-y} Se_2$ [29]. Important to note is the absence of any holelike band at the center of the Brillouin zone. Electronlike bands are found at the corners of the BZ.

1.2.3 Magnetism and Parent Phases

One of the features in common between iron-based superconductors and the cuprates that generated initial excitement was the magnetically ordered ground state of the parent material without doping. In the cuprates, spins will align antiparallel to their neighbors, in a Mott insulating parent material, whereas the commensurate SDW ground state seems to be shared by metallic parent materials of the FeAs-based systems [31–33]. One line of research has thus been into the evolution of magnetism and its competition with the superconducting phase as one tunes a "control" parameter such as doping or applied pressure. In both classes of superconductors, the antiferromagnetic order (magnetism) must be suppressed in order for bulk-phase optimal superconductivity to emerge.

The ground state of BaFe₂As₂, for example, was confirmed by Kitagawa *et al.* to be a commensurate SDW, with a discrete hyperfine field $B_{hf}^c \sim \pm 1.4$ Tesla at As sites at 4.2 K [33]. Well-defined values for the hyperfine field are characteristic of the commensurate SDW state in this case. As Co is doped into the Ba(Fe_{1-x}Co_x)₂As₂ system it approaches a quantum critical point; the magnetic SDW state is suppressed and eventually vanishes at $x \sim 0.06$, allowing for optimal superconductivity at $x \sim 0.08$. In the family of K_xFe_{2-y}Se₂ superconductors, however, there has been reported electronic identification of two antiferromagnetic *insulating* parent phases and one semiconducting parent phase, with the insulating phases exhibiting "Mott-like physics" [34]. Moreover, the superconducting phase is not adjacent to or near any metallic SDW states like its FeAs relatives, but rather it borders an insulating, antiferromagnetically ordered parent material, attention turned naturally to the interplay, if any, between magnetic order and superconductivity in the superconductivity phase.

Wei Bao et al. performed a neutron diffraction study on $K_x Fe_{2-y} Se_2$ in which they reported evidence for the co-existence of superconductivity and atiferromagnetic order [37]. They in fact found that the ordered magnetic moment is 3.31 μ_B/Fe atom and that the magnetic transition occurs at $T_N \sim 559$ K - both record high values among iron pnictide (P, As) and chalcogenide (S, Se, Te) superconductors. They also found evidence for an Fe vacancy order with transition at $T_S \sim 578$ K. The magnetic and iron vacancy structure is reproduced in Fig. 1.7. Both types of order are determined in a $\sqrt{5} \ge \sqrt{5} \ge 1$ unit cell, which contains a pair of Fe-Se layers related by inversion symmetry. According to the report from Bao et al., the magnetic moments of the Fe atoms align to form an antiferromagnetic structure, with the *c*-axis as the magnetic easy axis. While this seems like compelling evidence for the co-existence of superconductivity and antiferromagnetic order, a "microscopic phase separation" between magnetically ordered domains and superconducting domains can easily account for the same results. As we will discuss in sections to follow, nuclear magnetic resonance (NMR) measurements have yet to find any evidence for this co-existence. The neutron diffraction report nonetheless sparked a debate amongst condensed matter physicists, and at the very least highlighted the importance of stoichiometry via the iron vacancy ordering. In addition, it was found that the state of $K_x Fe_{2-y} Se_2$ could be altered simply by aging or an annealing process [38]. An insulating sample was tuned into the superconducting state by post-annealing followed by quenching. Conversely,



Figure 1.7: Magnetic structure and iron vacancy order from Wei Bao *et al.* [37]. In a $\sqrt{5} \ge \sqrt{5} \ge 1$ unit cell, magnetic moments are aligned antiferromagnetically and form a "checkerboard" pattern in their superstructure. Iron vacancy order is established in the same unit cell.

aging a superconducing sample for ~ 20 days reverses the process, producing the insulating sample upon post-annealing and quenching at 673.15 K (400 °C). These results seem to suggest that the superconducting phase has disordered vacancies, and that vacancy ordering tends to favour the antiferromagnetically ordered phase. Evidently researchers must be careful about the phase purity of a particular $K_x Fe_{2-y}Se_2$ sample, despite what the *average* x and y contents may be, when very small changes can have substantial effects.

1.2.4 Sulphur Substitution

Yet another useful way to tune superconductivity is through isovalent substitution, which can alter structural parameters but does not contribute any additional valence to the carrier density. It was discovered that $K_x Fe_{2-y}S_2$, isostructural to $K_x Fe_{2-y}Se_2$, is a small gap semiconductor and exhibits spin-glass behaviour below 32 K [20]. Sulphur is isovalent to selenium and has an ionic radius of only 1.84 Å compared to 1.98 Å for Se; S substituted into Se sites then tends to generate a chemical pressure on the lattice without directly altering the electronic properties, as it is not a dopant. A report on the full evolution of structural parameters and physical properties of $K_x Fe_{2-y}Se_{2-z}S_z$ single crystals was made, and contraction of the lattice was confirmed [18]. Fig. 1.8 summarizes the change in lattice parameters with increasing z content. Both the *a* and *c* lattice parameters decrease monotonically with z ranging from 0 to 2.0. Also important to note is that while the sum of Se and S stoichiometry in the single crystals is near 2.0, both iron and potassium are revealed to have deficiencies, which will facilitate comparison with the 'z = 0' non-substituted sample.

 T_c is also systematically suppressed with increasing z content, and superconductivity vanishes altogether at z ~ 1.6. In Fig. 1.9 we explicitly plot this suppression, including T_c measured both *in situ* in our NMR lab [39] as well as at the source of crystal growth [20]. This is analogous to the situation in FeSe, where overpressurizing results in suppression of T_c [16]. The evolution in electronic properties of FeSe, however, is relatively poorly explored due to the extremely high pressures (≥ 9 GPa) required. A microscopic investigation of the S-substituted $K_x Fe_{2-y} Se_{2-z} S_z$ may provide an alternative path to investigate any possible correlations between pressure, AFSF, and the superconducting transition temperature.

1.3 Samples and Their Preparation

All of our samples for both the $K_xFe_{2-y}Se_2$ and $K_xFe_{2-y}Se_{2-z}S_z$ systems were grown and characterized by Dr. Hechang Lei, Dr. Cedomir Petrovic, and their colleagues at Brookhaven National Laboratory [18–20, 25, 40]. Single crystals were grown using the self-flux method, and characterized by powder X-ray diffraction (XRD) on ground samples. Lattice and structural parameters were refined with the Rietica software [41] in the case of $K_xFe_{2-y}Se_2$, and the General Structure Analysis System [42, 43] for $K_xFe_{2-y}Se_{2-z}S_z$. Average stoichiometries for both materials were determined using energy-dispersive X-ray spectroscopy (EDX) in a JEOL JSM-6500 scanning electron microscope. In the non-substituted system, results showed stoichiometry consistent with both K and Fe deficiency: $K_{0.65(3)}Fe_{1.41(4)}Se_{2.00(4)}$. In the



Figure 1.8: A summary of the effect of S substitution on lattice parameters. Both the a and c lattice parameters are systematically shortened with S substitution, which mimics the effect of applied external pressure.



Figure 1.9: Superconducting transition temperature, T_c , as a function of sulphur concentration, z. Filled circles represent current samples used for NMR, measured *in situ* in zero magnetic field, while open triangles represent data at the source of crystal growth [20]. Solid and dashed lines are a 'guide-to-eye'.

S-substituted system, we examined two concentrations, z = 0.8 (40 % substitution) and z = 1.6 (80 % substitution), and note that both K and Fe defect content increase slightly as we have $K_{0.7}Fe_{1.55}Se_{1.2}S_{0.8}$ and $K_{0.8}Fe_{1.64}Se_{0.4}S_{1.6}$ in our two representative concentrations, respectively.

Qualitatively the crystals were black, with shiny surfaces, and cleaved well along the crystal *ab*-plane, forming rectangular 'slab-like' shapes. Each crystal selected for measurements weighed approximately 30 mg. Due to the samples' sensitivity to oxidation, as well as the above mentioned phase changes induced by aging, the samples were stored in vacuum sealed quartz tubes. During our preparation of the samples for NMR measurements, their exposure to the air was limited to several minutes. For the non-substituted $K_x Fe_{2-y}Se_2$ we conducted our ⁷⁷Se NMR measurements by applying an external magnetic field of 8.3 Tesla along the *c*-axis or within the *ab*-plane. In the case of $K_x Fe_{2-y}Se_{2-z}S_z$ we applied an 8.33 Tesla magnetic field along the *c*-axis.

1.4 Motivations and Organization of Thesis

NMR measurements [44, 45] have added to the body of knowledge for this system as an invaluable local probe of the electronic properties. The bulk of this thesis will focus on our NMR measurements, and their implications, on these iron selenide superconducting systems. $K_x Fe_{2-y}Se_2$ proves interesting for two main reasons: it maintains high-T_c superconductivity despite an apparent lack of nesting effects, and exhibits interesting magnetic order in its parent phase which some argue co-exists with superconductivity. The sulphur substituted $K_x Fe_{2-y}Se_{2-z}S_z$ on the other hand, provides an interesting anologue to externally applied pressure and will be useful to compare with $K_x Fe_{2-y}Se_2$.

The remainder of this thesis will be organized as follows. Chapter 2 will introduce the reader to the experimental techniques as well as theoretical background of NMR required to interpret our results. In chapter 3 we will summarize our ⁷⁷Se results for the superconducting $K_x Fe_{2-y}Se_2$ with some discussion of their implications [39]. Chapter 4 will present our measurements on the two S-substituted $K_x Fe_{2-y}Se_{2-z}S_z$ samples, comparing both static and dynamic magnetic properties of the z = 0, 0.8, and 1.6 concentrations [46]. We will summarize and conclude our research in chapter 5. The appendices contain information regarding laboratory instrumentation projects that are aimed at improving our NMR research capabilities. Appendix A contains some basic instructions and test results for our PTS 410 Helium Reliquifier by Cryomech, a closed-cycle system for producing liquid helium, essential for low temperature NMR measurements. Appendix B contains design schematics for a cryogenic NMR probe we have been developing for use in conjunction with our 16 Tesla magnet.

CHAPTER 2

NMR BASICS AND TECHNIQUES

Nuclear magnetic resonance (NMR) is a powerful experimental technique and a cornerstone of condensed matter physics research. In addition to its commercial offspring, magnetic resonance imaging (MRI), NMR spectrometry has been providing physicists with subtle details of the electronic properties in solids for decades, including numerous contributions to superconductivity. After verifying different aspects of BSC theory and the conventional superconductors [47–49], physicists had every reason to suspect that the technique would also make great strides in probing the unconventional superconductors. In fact, the absence of a coherence peak in the temperature dependence of the nuclear spin relaxation rate - directly measureable by NMR - was one of the earliest established distinguishing traits of the unconventional high-T_c superconductors [50,51], and today remains a benchmark characteristic of a superconductor's unconventional nature. This chapter will present the reader with information needed to understand exactly where our NMR results come from and how they are interpreted. It will begin with a brief introduction to basic NMR theory, followed by a description of the electronics needed to apply said theory and the methods or pulse sequences employed in data collection. We will then focus on two important measurables that NMR data can provide: static magnetic properties from the NMR Knight shift, and dynamical magnetic properties from the nuclear spin-lattice relaxation rate, $1/T_1$.

2.1 Basic Resonance Theory

The term 'resonance' itself implies the response of a system to a specific frequency. In this case the system is a magnetic moment in an external magnetic field. In a classical picture (Fig. 2.1), the frequency is the gyroscopic precession of the magnetic moment about the axis along which the external field is oriented, known as the *Larmor* precession (frequency). By tuning to the Larmor precession of nuclear spins in solids, NMR can probe at the level of atomic sites of interest. Since nuclear spins are under the influence of electrons



Figure 2.1: Schematic of the classical precession of a magnetic moment in a static applied field.

in their vicinity, this makes NMR an excellent local probe of electronic properties in solids, and is one of the main reasons it has proven invaluable in the study of strongly correlated electron systems like high- T_c superconductors.

Quantum mechanically, the external magnetic field lifts the degeneracy of the nuclear spin states through the Zeeman interaction. The Zeeman energy for a moment in a magnetic field is

$$E_z = -\gamma_n \hbar B I, \tag{2.1}$$

where I is the nuclear spin (1/2 for Se), \hbar is Planck's constant divided by 2π , and γ_n is the nuclear gyromagnetic ratio. For the simplest case of I = 1/2, the Zeeman energy splitting is depicted in Fig. 2.2. The energy difference, then, is $\Delta E = E_2 - E_1 = \gamma_n \hbar B$, and photons with a frequency of $\omega_0 = \gamma_n B$ may be absorbed by the nuclear spins. These frequencies typically fall in the radio frequency (r.f.) region of the electromagnetic spectrum. Table 2.1 presents data for representative atoms studied in NMR, including their nuclear spins, gyromagnetic ratios, and natural abundances. Our ⁷⁷Se atom allows for relatively easy NMR detection. It has a gyromagnetic ratio of $\frac{\gamma_n}{2\pi} = 8.118$ MHz/T, and spin I = 1/2, which generally produces a sharp NMR line; there is only one transition and no additional splitting from the nuclear quadrupole interaction. It also has a fairly large γ_n and hence large NMR frequency, which tends to make NMR measurements easier thanks to a large signal intensity, and less "ringdown". To detect resonance in ⁷⁷Se or any other atom, one needs the spectroscopic equipment to accomplish two main tasks: provide the r.f. photons that interact with the nuclear spins, and properly collect and amplify the resulting NMR signal. The next section describes the equipment and procedures we employ to perform these tasks.



Figure 2.2: Energy level depiction of the Zeeman interaction for the simple case of nuclear spin I = 1/2.

Atom	Spin, I	$\gamma_n/2\pi \; (\mathrm{MHz/T})$	Natural Abundance (%)
$^{1}\mathrm{H}$	1/2	42.574	99.98
$^{13}\mathrm{C}$	1/2	10.705	1.108
$^{17}\mathrm{O}$	5/2	5.772	0.037
$^{63}\mathrm{Cu}$	3/2	11.285	69.09
$^{65}\mathrm{Cu}$	3/2	12.089	30.91
^{75}As	3/2	7.2919	100
$^{77}\mathrm{Se}$	1/2	8.118	7.58

 Table 2.1: Representative Nuclear Gyromagnetic Ratios



Figure 2.3: Schematic of the precession of a magnetic moment about B_1 in a rotating reference frame.

2.2 Methods and Equipment

To produce and observe an NMR signal in a sample, it must, in addition to being placed in an external magnetic field B, be irradiated with a radio-frequency magnetic field B₁, produced by an NMR coil surrounding the sample. If this applied r.f. field B₁ is alternating (rotating) with the Larmor frequency ω_0 , then in a rotational frame of the same frequency, B₁ becomes static and the moment precesses about the axis of B₁ only (see Fig. 2.3). If a sample (i.e. an ensemble of $\gtrsim 10^{18}$ atoms) possesses a net nuclear magnetization vector M₀ in the z direction, and a rotational magnetic field B₁ is applied for a time duration t₉₀ satisfying

$$\gamma_n B_1 t_{90} = \omega_1 t_{90} = \frac{\pi}{2},\tag{2.2}$$

where ω_1 is the precession frequency about B_1 , then M_0 will be 'pulled' by 90° entirely into the *xy*-plane the rotational plane of B_1 . The magnetization vector now undergoes Larmor precession in the plane of the NMR coil, and induces a voltage across it known as the free induction decay (FID) signal. To provide the r.f. B_1 pulses that manipulate the nuclear spins requires careful timing and a pulse amplifier that provides peak to peak voltages on the order of 100's of volts. To adequately collect the extremely weak induced voltage signal (on the order of μV) requires a high gain system of amplifiers in conjunction with an analog to digital converter. These electronics together constitute our NMR spectrometer.



Figure 2.4: Schematic of the electronics involved in our NMR circuit.

2.2.1 NMR Electronics

All of the NMR measurements we conducted and present in this thesis were taken using the spectrometer developed and constructed by previous group members (Dr. Allen Hunt and Dr. Kent Thurber) as well as by Dr. Takashi Imai, using commercially available components. The external magnetic field is provided by our 9 Tesla superconducting magnet from Oxford Instruments. In Fig 2.4 we present a block diagram schematic of the spectrometer, and the general flow of its processes are described in this section.

The PTS 310 (or 500) is our radio-frequency source and generates continuous r.f. waves ranging from 1-310 (or 500) MHz. The continuous r.f. signal is fed into a power splitter (ZFSC-2-1W by Mini Circuits) which splits it into two, identically phased signals, one that will be a *reference* signal dedicated to *detection* following resonance, and the other dedicated to r.f. *pulse generation*. The signal dedicated to generating

pulses goes through a series of attenuators to adjust the output voltage from the Kalmus power amplifier, which provides +60 dB gains. The output of the Kalmus amplifier must not exceed the specific limit set by the breakdown voltage of the variable capacitors in our resonance circuit. This is done to prevent "arcing" from occurring - that is the electrical discharge of our pulse in helium gas. From the attenuators, the continuous r.f. signal feeds into a homemade protection box, which serves two purposes. The first is to take TTL (transistor-transistor logic) signals from our Aries spectrometer (by TecMag), which is controlled via computer, to gate the r.f. signal into r.f. pulses. The second purpose is to use homemade logic elements to monitor and control the trigger line to the amplifier. This ensures that only the desired signal is sent for amplification, and safeguards against not only the destruction of an expensive amplifier, but also the burning of precious samples in the event that the wrong signal is amplified (e.g. due to computer malfunction or a power surge). Protected r.f. pulses are then amplified by a factor of ~ 1000 via a power amplifier by Kalmus before being sent into our NMR probe.

The NMR probe consists mainly of two adjustable, r.f. capacitors and an inductive coil surrounding our sample. The capacitors allow us to tune the NMR circuit to the desired r.f. frequency as well as match the 50 Ω impedance of the circuit. The coil subjects the sample to the oscillating magnetic field B₁ created by the r.f. pulses, and detects the resonant response of the system via induced voltage. During the course of writing this thesis we are also constructing a new NMR probe to be used with our 16 Tesla magnet, which requires a much smaller cross-sectional diameter (~ 30 mm). Details on its design and assembly can be found in appendix B.

The detection components of our spectrometer must simultaneously amplify the extremely weakly induced NMR signal while isolating it from any stray or unwanted voltage. Immediately upon leaving the coil and probe, the signal passes through a "lambda over four" ($\lambda/4$) cable, chosen to be of length 45/f₀ meters, where f₀ is the frequency of the pulse in MHz (expected resonance), and used to create a standing wave which will help eliminate unwanted voltage leaking into the pre-amplifiers by decoupling the transmission and receiving sections of our circuit. Then a series of diodes short any voltage above the threshold of ~ 0.5 V before the signal is sent through a series of cascaded signal pre-amplifiers. After being sufficiently amplified, the NMR signal is split by a power splitter.

The continuous r.f. *reference* signal, meanwhile, goes through a 90° phase splitter, producing a continuous sine wave reference signal and continuous cosine wave reference signal. Each of these is mixed in double-balanced-mixers (DBMs) for phase sensitive detection (PSD), to be discussed in the next section. After PSD the DC signal is further amplified by a DC amp. The Aries spectrometer then digitizes the information before sending it to the computer for visual display. The overall process of the r.f. pulse production and subsequent signal acquisition contains some logistical obstacles that must be overcome both by clever choice of pulse timing and manipulation of signal phase (i.e. PSD).

90_{+x}	180_{x}	$Echo_{+y}$	Add
90_{-x}	180_{x}	$Echo_{-y}$	Subtract
90_{-x}	180_{y}	$Echo_{+y}$	Add
$90 \pm r$	180.	Echo_"	Subtract

 Table 2.2: Phase sensitive detection pulse sequences

2.2.2 Pulse Sequences

One of the main obstacles NMR spectrometers must overcome is the phenomenon known as *ringdown*. When we apply our r.f. pulse to excite the nuclear spins, the voltage in the impedance matched LC tank circuit is on the order of $1\sim2$ kV. It generally takes $\gtrsim 5 \ \mu$ s for this high voltage to decay because of the finite Q-value of our resonance circuit, and so it inevitably enters the pre-amplifier, which is designed to amplify a comparatively tiny NMR signal on the order of μ V. Despite the fact that diodes inside the the pre-amplifier ground the high voltage, a small leak on the order ~ 0.5 V nonetheless enters the amplifying circuits. The leaked voltage is several orders of magnitude larger than the NMR signal intensity, and hence saturates the amplifier. The pre-amplifier "rings" with the large, unwanted voltage, leading us to insert a DBM - triggered by TTL signals by the spectrometer - to minimize the ringdown in the signal leaving the pre-amplifier. The ringdown, however, typcially lasts longer than 10 μ s, and often is superimposed over the NMR signal. To further eliminate this problem, we use the phase cycling technique in conjuction with the spin-echo pulse sequence, as described below.

In NMR spectrometry the "spin echo" method of r.f. pulses is often used as a technique that helps eliminate ringdown. As described in the previous section, the nuclear spins are first polarized by an external field $B_{ext} \parallel z$ so that the nuclear magnetization M_0 is along the z-axis, and then with a rotating r.f. pulse, B_1 , applied for t_{90} (the 90°- or $\pi/2$ -pulse), M_0 is flipped to the *xy*-plane. As FID takes place, some elements of M_0 precess faster or slower due to the distribution in strength (inhomogeneity) of the external B-field, and nuclear spins begin to "dephase" accordingly (see Fig. 2.5). The homogeneity of our magnets are 10 ppm (sweepable magnet without shim coils) and 1 ppm (non-sweepable high resolution magnet with 4 shim coils) over a sphere of 1 cm diameter. If, however, after a time τ we apply a pulse for duration t_{180} satisfying

$$\gamma_n B_1 t_{180} = \omega_1 t_{180} = \pi, \tag{2.3}$$

called a 180°-pulse or π -pulse, then the dephased nuclear spins will invert, and refocus within the *xy*-plane at time 2τ . This refocusing is the "spin echo", and in the time domain it is essentially two FID signals appearing back to back as shown in Fig. 2.6. The pulse sequence used here is called the 90°-180° pulse sequence. Since our NMR spectrometer is capable of phase sensitive detection (PSD), we employ the technique of phase cycling within this spin echo procedure to eliminate as much ringdown as possible. Phase cycling involes alternating the phases of both the $\pi/2$ and π pulse to control the phase of the resulting echo. By clever selection of the phase of the irradiating pulses, and appropriate addition of the echo, we can cancel the ringdown while constructively adding the echo signal (see table 2.2). In the first and third sequences, for



Figure 2.5: A depiction of the 'dephasing' and subsequent spin echo. In a) The magnetization is oriented along z (k'), b) A $\pi/2$ pulse flips it 90° into the xy-plane, c) Faster and slower components of M₀ begin to dephase, and d) A 180° π pulse is applied, and the dephased components refocus.



Figure 2.6: Pulse sequence schematic for the spin echo method. Ringdown is indicated by the shaded segments toward the end of each pulse, and the FID and echo signals are depicted as a function of time.


Figure 2.7: Graphic representation of the use of adding/subtracting pulse sequences to eliminate ringdown. In practice there is ringdown from both 90° and 180° pulses, requiring 4 sequences to eliminate the ringdown from both.

example, the $\pi/2$ rotation takes place about the +x and -x axis (in the rotating frame), respectively. By changing the phase of the π pulse as well, the resulting echo for these two sequences will have the same +y phase. Addition of the first and third sequence then will cancel the ringdown from the $\pi/2$ pulse(+x + (-x)) while constructively doubling the echo signal (y + y), as shown in Fig. 2.7. To eliminate the ringdown from the π pulse we use two more sequences and subtract them (x + y - x - y), resulting in a quadrupling of the echo and cancellation of ringdown from both pulses. PSD is an effective technique that permits better signal averaging, and helps significantly in acheiving a clear signal, especially at short τ .

Figure 2.8 depicts the phase sensitive detection apparatus mentioned above. We use continuous reference sine and cosine waves to eliminate the frequency components of the NMR signal associated with the pulses. This allows us to observe only the envelope of the FID or spin echo signal, and by taking the Fast Fourier Transformation (FFT) of the enevelope we obtain our FFT spectrum or NMR lineshape in the frequency domain (see p.179ff of [52]).

2.3 Knight Shift

With the basics of NMR data collection covered, we now turn our attention to some of the meaningful information that can be obtained by NMR. The NMR Knight shift provides rich information on the static magnetic properties at the nuclear site. Though the resonant frequency of bare nuclei is given by $f_0 = \gamma_n B_{ext}$, nuclear sites in solids (or other samples) are under the influence of electrons in their vicinity, which requires



Figure 2.8: Schematic of the phase sensitive detection (PSD) apparatus using a reference signal to eliminate the frequency components of the r.f. pulse from our NMR signal.

us to replace B_{ext} with an effective field at the nucleic site, $B_{eff} = B_{ext}(1+K)$. The equation for frequency then becomes

$$f = \gamma_n B_{ext}(1+K), \tag{2.4}$$

where the Knight shift, K, is a fractional shift in the resonance frequency and is conventionally written as a percentage of the bare frequency. In $K_x Fe_{2-y}Se_2$ at 290 K, for example, we found a shift in frequency of $\Delta f \sim 0.493$ MHz in $B_{ext} = 8.3$ Tesla, as shown in Fig. 2.9. With a bare expected frequency of $f_0 =$ $^{77}\gamma_n B_{ext} = (8.118 \text{ MHz/T})(8.3 \text{ T}) = 67.379 \text{ MHz}$, this yields a Knight shift of $K = \Delta f/f_0 = 0.493/67.379$ = 0.73 %. The Knight shift is useful because it provides information on the spin susceptibility of electrons in the vicinity of atomic sites via their interaction with the atomic nuclei. It includes both the chemical shift and the electron spin shift, so that $K = K_s + K_{chem}$. K_{chem} arises from the coupling between the nuclear spin and the magnetic field induced by the orbital motion of electrons, associated with the Van Vleck (orbital) paramagnetic susceptibility, $\chi_{vv}(\chi_{orb})$, and the diamagnetic susceptibility of inner core electrons [53]. Furthermore, perturbation theory gives us $\chi^2_{orb} \propto \Sigma_n \frac{|\langle 0|L_z|n \rangle|^2}{E_0 - E_n}$, where L_z is the electron orbital angular momentum operator [54]. E_0-E_n is the energy separation and is ~ 1 eV = 11,600 K, much larger than the temperature in our NMR experiments ($\lesssim 300$ K), and accordingly χ_{orb} usually does not have any significant T-dependence.

We can then turn our focus to the electron spin shift, K_s , which arises from hyperfine coupling between the nuclear spin and the electron spin, polarized by the static applied magnetic field B. Since the polarization is proportional to electron spin susceptibility, K_s provides information about the local χ_s . This can be temperature dependent in strongly correlated electron systems, and results from two main types of hyperfine interactions - the Fermi contact, and dipole-dipole interaction. The Fermi contact is the interaction between nuclear spins and s-electrons only, since non-s-electrons have wavefunctions which vanish at the nucleus



Figure 2.9: Representative 77 Se NMR lineshape at 290 K to illustrate the shift in frequency from expected resonance f_0 .

(origin). Unless the s-orbitals contribute conduction electrons, the Fermi contact interaction does not directly contribute to K_s , but through a process called "inner core polarization" it can indirectly contribute. In this process outer orbital electrons polarized by B_{ext} polarize the inner s orbitals through a direct exchange interaction, which in turn have a Fermi contact term with the nuclear spins. The dipole-dipole interaction between nuclear spin I and non-s-electron spin S also gives rise to hyperfine coupling, and for the Se²⁻ atom in $(K^+)_x(Fe^{2+})_{2-y}(Se^{2-})_2$, for example, partially filled 4p orbital electrons may contribute to the hyperfine field.

Moreover, we can probe the spin susceptibility of Fe in $K_x Fe_{2-y}Se_2$ with ⁷⁷Se Knight shift thanks to orbital hybridization. The Fe electron spins are polarized by the external B field. Through hybridization between the Fe and Se orbitals (nearest neighbours), this small spin polarization is transferred to the Se electrons, which in turn exert hyperfine fields on the Se nuclear spins through the aforementioned interactions.

Whatever the manner by which the nuclear and electron spins are coupled, it is the hyperfine coupling A_{hf} which quantifies how large the interaction is, or more importantly, how much magnetic field is produced at the nuclear sites. In the context of $K_x Fe_{2-y} Se_2$ we therefore write

$$^{77}K = \frac{A_{hf}}{g\mu_B}\chi_{spin} + K_{chem},\tag{2.5}$$

where A_{hf} is the coupling constant and K_{chem} the temperature independent shift, and interpret our results



Figure 2.10: Some example recovery curves for the magnetization M(t) for ⁵⁹Co (red) and ⁷⁵As (blue) in Ba(Fe_{1-x}Co_x)₂As₂ following an inversion π -pulse [12]. Lines represent exponential fits used to determine the relaxation rate $1/T_1$.

accordingly.

2.4 Nuclear Spin-Lattice Relaxation Rate, $1/T_1$

One of the most important quantities NMR can extract is the nuclear spin relaxation rate of the crystal lattice. This rate characterizes the lattice's ability to absorb and dissipate energy from a nuclear spin. When we want to measure the nuclear spin-lattice relaxation rate $1/T_1$, the pulse sequence we use is not very different. Before applying the 90°-180° pulse sequence, we first invert M₀ with a 180° pulse. After a short period, we then collect the spin echo signal as a function of time, observing the recovery to equilibrium of M₀. By fitting the recovery data to a single exponential curve, calculated for transitions of a particular nuclear spin (exemplified in Fig. 2.10), we can determine the relaxation rate of the nuclear spins. Fig. 2.11 describes the relaxation process through energy level diagrams. The applied π -pulse ($\hbar\omega$) inverts the population of our nuclear spin ensemble in thermal equilibrium by exciting nuclear spins, which then relax back to equilibrium after a time, T₁. Relaxation takes place as the nuclear spins give energy ($\hbar\omega$) back to the lattice. The lattice absorbs this energy by generating *low energy excitations* via, for example, lattice vibrations, conduction electrons, and magnons. T₁ then probes the low energy excitations or fluctuations of the lattice, and the more low energy excitations that are generated, the faster T₁ will be.



Figure 2.11: Diagram of the inversion π -pulse and subsequent relaxation of nuclear spins.

Furthermore, one can use the fluctuation-dissipation theorem [55], and rewrite the electron spin-spin correlation function in terms of its space-time Fourier component $S(\mathbf{q},\omega_0)$, where electron spins produce hyperfine magnetic fields through

$$B^{\pm} = A_{hf}(S_x \pm iS_y) \tag{2.6}$$

to derive, in the low frequency limit, the relation

$$\frac{1}{T_1} = \frac{\gamma_n^2 k_B T}{2\mu_B^2} \sum_{\mathbf{q} \in B.Z.} |A(\mathbf{q})|^2 \frac{\chi''(\mathbf{q}, \omega_0)}{\omega_0}.$$
(2.7)

 $A(\mathbf{q})$ in this case is the wavevector dependent hyperfine form factor introduced by Moriya [56], where $A(\mathbf{q}) = \sum_i A_i e^{i\mathbf{q}\cdot\mathbf{r}_i}$, a summation over electron spins *i* at position \mathbf{r}_i relative to the nucleus. Equation 2.7 indicates that by dividing the relaxation rate by temperature, i.e. $1/T_1T$, we can measure the summation over \mathbf{q} -modes within the first Brillouin zone of the imaginary part of the dynamical electron-spin susceptibility, at an energy scale set by the NMR frequency ω_0 . We utilize this relation to probe $K_xFe_{2-y}Se_2$ and $K_xFe_{2-y}Se_{2-z}S_z$ for low frequency spin fluctuations, as they may be associated with the high- T_c mechanism.

The relaxation rate T_1 provides the NMR researcher with yet another test. In a canonical Fermi liquid, one can show using the 'golden rule' that $1/T_1T$ is proportional to the square of the density of states at the chemical potential [52], $1/T_1T \propto [N(E_F)]^2$. Since $K_{spin} \propto [N(E_F)]$ from Pauli spin susceptibility in a Fermi liquid scenario, we then have

$$\sqrt{\frac{1}{T_1 T}} \propto K_{spin},\tag{2.8}$$

known as the Korringa relation - an excellent test for the applicability of a Fermi liquid picture. We probe $K_x Fe_{2-y}Se_2$ and $K_x Fe_{2-y}Se_{2-z}S_z$ both for low frequency spin fluctuations as well as the Korringa relation in our NMR results and discussions, presented in the next chapters.

CHAPTER 3

SUPERCONDUCTING $K_x Fe_{2-y} Se_2$

This chapter presents our ⁷⁷Se NMR measurements on $K_x Fe_{2-y}Se_2$, along with discussions of the results, interpreting and comparing them to similar iron based systems. All of our data was collected with an external magnetic field of 8.3 Tesla applied along the crystal *c*-axis, or, where specified, within the *ab*-plane. We will first briefly summarize preliminary measurements made to further characterize our sample, and then delve into the details of our NMR lineshapes. We will then describe our ⁷⁷K Knight shift results, providing information on the spin susceptibility, χ_{spin} , of electrons near the ⁷⁷Se sites, followed by a discussion of the relaxation rate $1/T_1$ and the spin dynamics of this system.

3.1 T_c and Superconductivity

By changing the capacitance in our variable tuning capacitor (achieved by changing the position of the capacitor's two concentric cylinders), we may tune our NMR tank circuit to a particular frequency. The tuning frequency of our NMR circuit varies as

$$f_{tune} \sim \frac{1}{\sqrt{LC}},\tag{3.1}$$

where L and C are the inductance and capacitance of the circuit, respectively. Additionally, the total inductance is given by $L = L_0(1 + \eta \chi_{bulk})$, where L_0 is the bare inductance without a sample present in the coil, χ_{bulk} is the bulk magnetic susceptibility of our sample, and η is the filling factor of the sample. When doing NMR measurements we normally tune the tank circuit to the same frequency of our r.f. pulse B_1 at the desired NMR resonant frequency f_0 . With a gyromagnetic ratio, γ_n , of 8.118 MHz/Tesla, the expected bare frequency for the ⁷⁷Se atom is $f_0 = 67.379$ MHz in an 8.3 Tesla magnetic field. We can also use a network analyzer, however, to monitor the tuning frequency f_{tune} as we vary temperature while maintaining constant C. When the $K_x Fe_{2-y}Se_2$ crystal crosses T_c and undergoes a superconducting phase transition,



Figure 3.1: The change in tuning frequency, $-\Delta f_{tune}(T)$ of our NMR tank circuit caused by superconducting Meissner effects. Data are normalized with the value of $f_{tune}(T_c) \sim 67.7$ MHz.

 χ_{bulk} will suddenly become negative because of superconducting Meissner effects. By tuning our circuit to a frequency of $f_{tune}(T_c) \sim 67.7$ MHz at a temperature slightly above T_c (~ 35 K) and observing f_{tune} as we sweep temperature down to ~ 6 K, we determine the T_c of our sample. This is an effective technique for determining T_c , as shown in our group's earlier NMR study of FeSe [15], and has the additional advantage of being done *in-situ*, eliminating any risk of sample decomposition by additional exposure to air. Another merit of this technique over standard SQUID measurements is that we can determine T_c at a high magnetic field - over 5 T - which is typically the upper bound of the magnetic field of SQUID measurements.

In Fig. 3.1 we plot $-\Delta f_{tune}(T)/f_{tune}(T_c)$, the change in frequency as a function of temperature, normalized by dividing by the tuning frequency at the transition temperature. We plot the data for both 0 and 8.3 Tesla applied external magnetic field along the crystal *c*-axis. The zero field data display a fairly sharp superconducting transition, with an onset as high as $T_c = 33$ K. The overall change in frequency we observe is relatively small $(-\Delta f_{tune}(T)/f_{tune}(T_c) \sim 0.015)$, and may be attributed to the relatively small filling factor η of the crystal with respect to the total volume of our NMR coil. Because of the limited oxygen exposure time imposed by our sample, we were unable to fully optimize the size and shape of our NMR coil, and estimate that the sample volume is as little as 10 % of the coil's total volume. The small change in frequency may also be attributed, however, to the sample itself, suggesting that K and/or Fe concentrations are not optimized for the largest superconducting volume fraction or T_c . When we apply $B_c = 8.3$ Tesla along the *c*-axis, we observe a small change beginning at $T_c \sim 31$ K, followed by a more substantial change



Figure 3.2: The change in tuning frequency, $-\Delta f_{tune}(T)$ of our NMR circuit with an external magnetic field of $B_{ab} = 8.3$ Tesla applied within the *ab*-plane.

near 28 K. This finding of the increase in breadth of the transition under an applied field along the *c*-axis may be connected to a report where the resistive superconducting transition also broadens under B_c due to strong two-dimensionality of the system [57]. This effect is related to the formation of flux vortices in type II superconductors, and the anisotropy of the upper critical field H_{c2} . When the external field is applied perpendicular to the superconducting layer, the orientation is more conducive to flux penetrating the superconducting layer than when an external field is applied parallel to the superconducting layer. With an applied field B_{ab} within the *ab*-plane, T_c decreases only slightly to ~ 32 K. The results for the change in tuning frequency with the field applied in the *ab*-plane are summarized in Fig. 3.2 for comparison.

3.2 ⁷⁷Se NMR Lineshapes

In Fig. 3.3 we present representative ⁷⁷Se NMR lineshapes observed at temperatures of 8, 40, 95, 205, and 290 K, under a magnetic field of $B_c = 8.3$ Tesla applied along the *c*-axis. Above T_c the integrated intensity of the lineshapes do not exhibit any noticeable temperature dependence. The full width at half maximum (FWHM) of the lineshape in the normal state just above T_c is as narrow as ~ 4.5 KHz. Compared with the ⁷⁵As NMR central line in optimally Co-doped superconducting Ba(Fe_{1.92}Co_{0.08})₂As₂, the ⁷⁷Se line is a factor of ~ 8 times narrower. This narrowness is largely due to the ⁷⁵As has nuclear spin 3/2, the second order nuclear quadrupole effects. Since ⁷⁵As has nuclear spin 3/2, the second order nuclear quadrupole effects contribute to the NMR line broadening.

Both the width and the position (peak frequency) of NMR lineshapes are rich with information. As



Figure 3.3: Representative ⁷⁷Se NMR lineshapes observed in an external magnetic field B_c Tesla applied along the crystal *c*-axis.



Figure 3.4: Temperature dependence of the full width at half maximum (FWHM), $\triangle f_{NMR}$, of the ⁷⁷Se NMR lineshapes in $B_c = 8.3$ Tesla. Note the enhancement below T_c , induced by the Abrikosov lattice of superconducting vortices and proportional to the in-plane penetration depth λ_{ab} .

mentioned in section 2.3, the peak position relative to the bare frequency determines the Knight shift, a reflection of local electron spin susceptibility, χ_{spin} . Evidently the size of the shift, and therefore spin susceptibility, increases with temperature, and will be discussed in detail in the next section. The temperature dependence of the FWHM of our lineshapes, Δf_{NMR} , is plotted in Fig. 3.4 for the *c*-axis measurements. The dramatic increase in Δf_{NMR} below T_c is a feature expected of type II superconductors and is a consequence of the Abrikosov lattice. When the external magnetic field penetrates our sample along the crystal *c*-axis, a lattice of superconducting vortices forms - the Abrikosov lattice. The *local magnetic field* will then have a position-dependent distribution, and near the superconducting flux $\phi_0 = hc/2e = 2.07 \times 10^{-7}$ Oe-cm² the local field will decay. The scale of the length of this decay is determined by the London penetration depth, λ_{ab} . If this position dependence yields a second moment, defined as a distribution in the local field, ΔB $\equiv \sqrt{\langle B_{loc}^2 \rangle - \langle B_{loc} \rangle^2}$ then so too will the NMR linewidth, with $\Delta f_{NMR}^{vortex} = \gamma_n \Delta B$. We can theoretically express the additional second moment as $\Delta B \sim 0.0609 \frac{\phi_0}{\lambda^2}$ [58,59], assuming a type II superconductor in the clean limit, and therefore relate the enhancement in lineshape width with λ_{ab} via

$$\Delta f_{NMR}^{vortex} \sim 0.0609 \frac{\gamma_n \phi_0}{\lambda_{ab}^2}.$$
(3.2)

Using this relation we estimate from the observed increase in Δf_{NMR} that the penetration depth at 8 K is $\lambda_{ab} \sim 290$ nm. This value is roughly comparable to the LaFeAsO_{0.91}F_{0.09} value of ~ 550 nm [60]. We can

also estimate the density of superconducting electrons, n_s , using the London relation,

$$n_s = \frac{m^* c^2}{4\pi e^2 \lambda_{ab}^2},\tag{3.3}$$

and by taking m^{*}, the effective mass enhancement, to be $2 \sim 4$ [61,62] we obtain $n_s \sim (0.7 \sim 1.2) \times 10^{21}$ cm⁻³. Fig. 3.4 also depicts the *gradual* increase in the FWHM with temperature in the normal state, readily observable from our lineshapes in Fig. 3.3 as well. This effect is caused by the increase in peak position or Knight shift, as a larger Knight shift implies a larger distribution in the effective field B_{eff} seen by the nuclear spins.

For comparison, we also show in Fig. 3.5 the NMR lineshape we observe at 50 K with the external field oriented arbitrarily within the *ab*-plane. While the overall temperature dependence of the *ab* lineshape is very similar to the *c*-axis lineshapes, it always splits into two separate peaks with identical integrated intensities. Analogous splitting with B \parallel ab was reported by Kotegawa *et al.* for their single crystal as well [45]. Furthermore, the separation of the peaks, which is ~ 12 kHz in B_{ab} = 8.3 Tesla, changes in proportion to the strength of the applied field B_{ab}, indicating that the splitting is caused by paramagnetic effects.

We therefore rule out the possibility that the line splitting is caused by magnetic long range order, because the splitting of the two peaks would not be proportional to B_{ab} in that case. We find absolutely no evidence for the coexistence of such order with superconductivity. Our results, however, do not rule out the possibility that there is a mixture of AF ordered domains, phase separated from the superconducting domains. In fact, Mossbauer measurements for another crystal from the same batch showed static AF order in approximately 50% of the sample volume [C. Petrovic, private communication].

We also rule out the possibility of our sample being of mixed paramagnetic phase for several reasons. Given that the two lineshapes maintain the same integrated intensity, it is very unlikely they are caused by different domains each with their own K or Fe compositions (deficiencies). Powder x-ray diffraction measurements also indicate the crystal is not of mixed-phase, and we do not see the c-axis NMR lineshapes split into two as we would expect for a sample with two different paramagnetic phases. This evidence suggests that there are, locally, two structurally inequivalent Se environments under the presence of the magnetic field in-plane. In fact, single crystal x-ray measurements reveal the formation of a superstructure in the K and Fe defects [63], which may lower the local four-fold symmetry to a two-fold symmetry without altering the overall symmetry of the *average* structure. The lineshape splits in two in this case, because the orientation of the two Se environments relative to B_{ext} results in two slightly different Knight shifts, and therefore resonance at slightly different frequencies. If B_{ext} is increased in strength then the discrepancy between the two different Knight shifts will increase, and the splitting of the peaks will increase accordingly.



Figure 3.5: A representative FFT lineshape observed at 50 K with the external magnetic field $B_{ab} = 8.3$ Tesla applied within the *ab*-plane. The *c*-axis lineshape at 50 K is plotted as well for comparison.

3.3 ⁷⁷K Knight Shift

By measuring the peak position of our ⁷⁷Se NMR lineshapes relative to the bare frequency f_0 , we determine the ⁷⁷K Knight shift and in Fig. 3.6 we summarize its temperature dependence. Recall that the Knight shift is proportional to the spin susceptibility of electrons near the selenium sites, with ⁷⁷K = $\frac{A_{hf}}{g\mu_B}\chi_{spin}$ + K_{chem} . The asymptotic behaviour of ⁷⁷K well below T_c permits us to estimate $K_{chem} \sim 0.11$ %, assuming $\chi_{spin} \rightarrow 0$ at $T \rightarrow 0$ (i.e. singlet pairing). Iron based superconductors are multi-orbital systems, meaning that - as described in the previous chapter - different orbitals may make separate contributions to both A_{hf} and χ_{spin} . In the interest of simplicity, we interpret the Knight shift data in terms of the *cumulative* behaviour of χ_{spin} ; one should bear in mind though, that ⁷⁷K may reflect a weighted average of the spin susceptibility of different orbitals.

In the normal state, above T_c , χ_{spin} decreases monotonically with temperature, qualitatively similar to the behaviour of other iron based systems, including LaFeAsO_{1-x}F_x [11,60], Ba(Fe_{1-x}Co_x)₂As₂ [10,12,13, 64], and FeSe [15]. Upon careful observation one can also see that near 200 K, the curvature of ⁷⁷K changes slightly from positive to negative. This may be a precursor of the saturation of χ_{spin} at greater temperatures. We also see an analogous saturation behaviour in the relaxation rate $1/T_1T$, as we will present in the next section. Qualitatively, χ_{spin} exhibits a temperature dependence most similar to that of LaFeAsO_{1-x}F_x (x $\gtrsim 0.1$) [11,60] among the iron based superconducting systems.



Figure 3.6: Temperature dependence of the ⁷⁷Se NMR Knight shift, reflecting the local spin susceptibility, χ_{spin} , near the Se sites. Results with the field applied both in the *c*-axis direction and within the *ab*-plane show the same qualitative behaviour. Notice the sharp drop below T_c, as well as a slight change in curvature in the normal state near 200 K.

Approaching T_c , χ_{spin} is gradually suppressed. The mechanism for this effect in iron based systems is not definitive and has stirred controversy within the field. In one view, the proximity of the superconducting state with the SDW ordered state suggests that an antiferromagnetic short range order may be developing toward T_c , reducing χ_{spin} . This scenario is certainly in congruence with earlier observations of the enhancement of short range antiferromagnetic spin correlations near T_c in the optimally doped superconducting phase of Ba(Fe_{1-x}Co_x)₂As₂ [12,13]. It has since been demonstrated, however, that heavily over-doped (Co concentration as much as 20 %), non-superconducting, non-magnetic Ba(Fe_{1-x}Co_x)₂As₂ exhibits analogous behaviour [10,65], suggesting that the presence of magnetic order may not be a requisite.

On the other hand, the temperature dependence and suppression of χ_{spin} may be dominated by frustration effects between nearest and next-nearest neighbour Fe-Fe exhange interactions. In this scenario it is possible that *pseudo-gap*-like behaviour emerges as the system cools and the available excited states of electron spins are no longer reachable or are suppressed with the decrease in thermal energy, as observed in related systems [11,60,66]. The dashed curve in Fig. 3.6 is a phenomenological fit for the normal state data, with

$$^{77}K \sim \alpha + \beta exp(-\Delta/k_BT),$$
(3.4)

where \triangle represents the pseudo-gap, α denotes the ⁷⁷K value near T_c, and β is a constant. Our fit from T_c to 290 K reproduces the saturating tendency fairly successfully, and yields a gap value of $\triangle/k_B = 435$ K. This gap estimate is greater than the value of 140 ~ 172 K found in LaFeAsO_{1-x}F_x [11,67], but comparable to the value of $\triangle/k_B = 450 \sim 711$ K found in Ba(Fe_{1-x}Co_x)₂As₂ [10,13].

Below T_c , ⁷⁷K_c suddenly dives from 0.25 % to $K_{chem} = 0.11 \pm 0.01$ %. We confirmed that ⁷⁷K_{ab} also dives below T_c . These findings are consistent with the singlet formation of Cooper pairs. Ignoring the potential complications of estimating diamagnetic effects and the fact that our application of an 8.3 Tesla magnetic field may skew the temperature dependence of ⁷⁷K in the superconducting state by destroying Cooper pairs, we attempt to fit its low temperature behaviour with an activation law ⁷⁷K_{spin} ~ exp(- Δ_{sc}/k_BT), shown as a solid curve in Fig. 3.6. Assuming isotropic energy gaps for all sections of the Fermi surface sheets, we obtain a lower bound estimate of $\Delta_{sc}/k_B \sim 92$ K. This yields a ratio of $\Delta_{sc}/k_BT_c \sim 2.8$ - considerably larger than the BCS value of 1.76. This means that Δ_{sc} is indeed larger than the prediction of the BCS weak coupling theory, and/or diamagnetic effects induce an additional decrease in ⁷⁷K below T_c .

The temperature dependences of Knight shift both with the external field applied in the crystal c direction and within the ab-plane are qualitatively similar throughout the entire temperature range. In Fig. 3.7 we plot ⁷⁷K_{ab} vs ⁷⁷K_c, using temperature as the implicit parameter. The slope of the fits to each peak in the abplane lineshape are identical within experimental uncertainties, taking a value of 1.21 ± 0.02 . The linearity in this plot implies that the spin susceptibility along the c-axis, χ^c_{spin} , and within the ab-plane, χ^{ab}_{spin} , indeed exhibit identical behaviour. If we assume that $A^c_{hf} \sim A^{ab}_{hf}$, *i.e.* the hyperfine coupling is isotropic, then we may estimate the anisotropy of the spin susceptibility to be $\chi^{ab}_{spin}/\chi^c_{spin} = 1.21 \pm 0.02$.



Figure 3.7: ⁷⁷K_{ab} with both *ab*-plane peak positions plotted as a function of ⁷⁷K_c with temperature as the implicit parameter. The linear fit is good, implying a nearly identical temperature dependence of χ^{ab}_{spin} and χ^{c}_{spin} , with a slope of 1.21 ± 0.02. The dashed vertical line denotes our estimate for K_{chem} ~ 0.11 %, and the arrow denotes T_c.

3.4 Nuclear Spin-lattice Relaxation Rate, $^{77}(1/T_1)$

Fig. 3.8 presents the temperature dependence of the ⁷⁷Se nuclear spin-lattice relaxation rate, $1/T_1$, in a field of $B_c = 8.3$ Tesla applied along the crystal *c*-axis. We plot the relaxation rate temperature dependence of FeSe and Ba(Fe_{0.92}Co_{0.08})₂As₂, earlier results obtained by our group, in Fig. 3.8 as well. Measurements in $B_{ab} =$ 8.3 Tesla applied within the *ab*-plane show nearly identical behaviour, at least up to 160 K. The relaxation rate ⁷⁷(1/T₁) dives below T_c and does not exhibit a Hebel-Slichter coherence peak expected for conventional isotropic BCS s-wave superconductors. Similar behaviour is seen in FeSe and Ba(Fe_{0.92}Co_{0.08})₂As₂, as well as other iron-based high T_c superconductors [11,12,15,68–71]. We did not, in this study, attempt to follow $1/T_1$ well below T_c predominantly due to a poor signal-to-noise-ratio induced by the line broadening caused by superconducting vortice effects, as evidenced in our 8 K lineshape, and the superconducting shielding effects of B₁. In addition, these vortex effects as well as relaxation processes at the vortex cores make interpretation of the relaxation rate rather complicated well below T_c . (Some authors derivatively ignore these complications).

In Fig. 3.9 we plot the relaxation rate divided by temperature, $1/T_1T$, as a function of temperature. We remind the reader that $1/T_1T$ probes the **q**-summation of the imaginary part of the dynamical electron spin susceptibility in the first Brillouin zone, weighted by the hyperfine form factor:

$$\frac{1}{T_1 T} \propto \sum_{\mathbf{q} \in B.Z.} |A(\mathbf{q})|^2 \frac{\chi''(\mathbf{q}, f_0)}{f_0}.$$
(3.5)



Figure 3.8: Temperature dependence of the nuclear spin-lattice relaxation rate $1/T_1$ for ⁷⁷Se sites in $K_x Fe_{2-y}Se_2$. We compare with the relaxation rate observed at ⁷⁷Se sites in FeSe ($T_c = 9$ K) [15] and at ⁷⁵As sites in Ba(Fe_{0.92}Co_{0.08})₂As₂ ($T_c = 25$ K) [12]. Arrows mark the superconducting transition temperature in each sample.



Figure 3.9: The temperature dependence of $^{77}(1/T_1T)$ observed in $K_x Fe_{2-y}Se_2$ with $B_c = 8.3$ T. Results for FeSe in ambient pressure ($T_c = 9$ K) as well as 0.7 GPa ($T_c = 14$ K) are presented as well for comparison [15].

This means we are probing the various **q**-modes of spin fluctuations in our system at the low energy scale (hf_0) set by the NMR frequency f_0 . Our results indicate that qualitatively, the temperature dependence of $^{77}(1/T_1T)$ is similar to that of ^{77}K , including the previously mentioned saturating tendency toward room temperature.

It was shown in FeSe that an increase in enhancement of the low frequency components of antiferromagnetic spin fluctuations (AFSF) measured by $1/T_1T$ correlated directly with an increase of T_c under applied pressure [15]. We present this data, at representative pressures of 0 and 0.7 GPa, alongside our results for comparison. The FeSe sample at 0 GPa exhibits a small but finite enhancement in $1/T_1T$ toward T_c , which is 9 K at ambient pressure. At 0.7 GPa, we see that the enhancement of $1/T_1T$ has increased, and T_c is pushed up to 14 K. Our results indicate that in $K_xFe_{2-y}Se_2$ there is no such enhancement present. Naturally, one may be inclined to interpret this result as a counterexample to the possible connection between the enhancement of low frequency AFSF and T_c , but there are other potential explanations as well.

If we examine the temperature dependence of $Ba(Fe_{1-x}Co_x)_2As_2$, depicted in Fig. 3.10 for two representative concentrations of x = 0.08 (optimally doped) and x = 0.14 (over-doped), we see that the concentration that optimizes T_c displays a large enhancement of AFSF, while the over-doped concentration exhibits no enhancement toward T_c whatsoever. Our results are qualitatively similar to the latter concentration, and suggest that our $K_xFe_{2-y}Se_2$ system may lie in the 'over-doped' region of the superconducting dome. In



Figure 3.10: The temperature dependence of ${}^{75}(1/T_1T)$ observed in Ba(Fe_{1-x}Co_x)₂As₂ at two representative concentrations. The optimally doped x = 0.08 concentration exhibits a large enhancement of low frequency antiferromagnetic spin fluctuations, while the over-doped x = 0.14 concentration shows no enhancement [10].

Ba(Fe_{1-x}Co_x)₂As₂ the absence of AFSF was interpreted as being a consequence of the lack of Fermi surface nesting between hole and electron bands, with over-doped electrons filling up the hole band at the Brillouin zone center [10]. ARPES data suggest that a holelike Fermi surface is absent in $K_xFe_{2-y}Se_2$ [29], which is consistent with such an interpretation. We also caution that $1/T_1T$ probes spin fluctuations at a low energy scale set by our NMR frequency f_0 , and that AFSF may be enhanced at energies greater than hf_0 . Additionally, since we are measuring the summation of various **q** modes, it is possible that an enhancement in AFSF for a particular **q** mode may be masked by the overwhelming tendency of all other modes to continue decreasing through T_c .

Finally, let us return to the qualitative similarity in the temperature dependences of ⁷⁷(1/T₁T) and Knight shift, ⁷⁷K. ⁷⁷(1/T₁T) probes all wavevector **q** modes of spin fluctuations, whereas ⁷⁷K picks up only the uniform **q** = 0 mode, so there is no reason to expect that they would exhibit qualitatively similar behaviour. One explanation may be that both behaviours are dominated by the effective density of states $N(E_F)$ at the chemical potential of a Fermi liquid. Recall from Ch.2 that in this picture, ⁷⁷(1/T₁T) \propto [N(E_F)]², and ⁷⁷K_{spin} \propto [N(E_F)]. One would expect, then, that a *Korringa relation*, ⁷⁷(1/T₁T)^{0.5} \propto ⁷⁷K_{spin} would indicate the applicability of Fermi liquid theory. In Fig. 3.11 we plot both ⁷⁷(1/T₁T) and its square root, ⁷⁷(1/T₁T)^{0.5} vs ⁷⁷K_c with temperature chosen as the implicit parameter. Though it is not impossible to draw a straight line through the data, the precision of our data points above T_c allows us to more accurately discern a fit with negative curvature. In the form of ⁷⁷(1/T₁T) = (⁷⁷K_{spin,c})ⁿ, we obtain a value of n ~ 1.6 instead of the Fermi liquid value of n = 2. In addition, extrapolation of a linear fit to the horizontal intercept, which represents K_{chem}, yields an estimate of 0.04 %, considerably smaller than the 0.11 % estimate directly obtained from the temperature dependence of the Knight shift (Fig. 3.6). This suggests that Fermi liquid theory is not applicable in this system as the Korringa relation is not quite held, although it may be moving closer toward a Fermi liquid picture.



Figure 3.11: The normal state data for $^{77}(1/T_1T)^{0.5}$ and $^{77}(1/T_1T)$ plotted vs $^{77}K_c$ with temperature as the implicit parameter. A linear relationship between $^{77}(1/T_1T)^{0.5}$ and $^{77}K_c$ would indicate a Korringa relation, represented by the dashed line. The solid lines are free parameter fits for $^{77}(1/T_1T) = (^{77}K_c - K_{chem})^n$, which gives a value of $n \sim 1.6$ instead of the Fermi liquid value of 2. The horizontal intercept in this plot represents K_{chem} , the temperature independent chemical shift. Extrapolating a linear fit yields a K_{chem} estimate of ~ 0.04 %, much smaller than the 0.11 % value obtained from the temperature dependence of ^{77}K in Fig. 3.6.

CHAPTER 4

SULPHUR SUBSTITUTED $K_x Fe_{2-y} Se_{2-z} S_z$

We shall now turn our attention to the effect of substituting sulphur (S) into the Se sites of $K_x Fe_{2-y}Se_{2-z}S_z$. As stated, sulphur substitution gradually supresses T_c , enabling us to perform a microscopic NMR investigation of the evolution of electronic properties in going from a high- T_c superconductor to a non-superonducting semiconductor. We will examine two concentrations, one with z = 0.8 (40 % substitution), and one with z = 1.6 (80 % substitution), and compare these results with our findings for $K_x Fe_{2-y}Se_2$ (z = 0).

As indicated in Fig. 1.8, the lattice constant along the crystal c-axis decreases from ~ 14.0 to 13.9 and then to 13.7 Å as S concentration goes from z = 0 to 0.8 and then to 1.6, respectively. Sulphur substitution tends to generate chemical pressure on the lattice because its ionic radius is smaller than that of Se, and its correlation with a supressed T_c in this system mimics the situation in FeSe, where over-pressurizing results in suppression of T_c [16]. Our NMR investigation of the electronic properties in the "over substituted" region of the superconducting dome in $K_x Fe_{2-y} Se_{2-z} S_z$ thus gives us an analog to investigate the possible correlations between T_c , structure, and pressure in these types of superconductors. In this chapter we will present our NMR lineshapes, spin susceptibility from Knight shift, and spin dynamics from $1/T_1$ for the sulphur substituted systems. Results will be presented alongside the non-substituted data, and in some cases with related iron-based systems, for the sake of comparison and the contextual placement of evolution in electronic properties.

4.1 NMR Lineshapes

Prior to obtaining NMR lineshapes, we again check the T_c of our samples by using our NMR tank circuit to measure the magnetic susceptibility *in-situ*. As depicted in Fig. 1.9, in zero external magnetic field, the z = 0.8 sample exhibits a T_c of 26 K, while the z = 1.6 sample - precisely the concentration where superconductivity is destroyed - does not exhibit any superconducing transition. This confirms that our



Figure 4.1: Representative ⁷⁷Se NMR FFT lineshapes for $K_x Fe_{2-y} Se_{2-z} S_z$ at 50 K with $B_c = 8.33$ Tesla applied along the *c*-axis. The non-substituted z = 0 lineshape is presented for comparison as well, with the lineshapes normalized for an equal integrated instensity. In addition to the broadening in the S substituted lineshapes, note the systematic lowering of the NMR peak frequency with increased S content.

oxygen-sensitive samples, transported in sealed quartz tubes and mounted in our NMR spectrometer in less than several minutes, did not degrade or suffer in integrity in moving from the source of crystal growth to our apparatus. We also find that in an external applied field of $B_c = 8.33$ Tesla along the crystal *c*-axis, the T_c of the z = 0.8 sample decreases to ~ 13 K.

In Fig. 4.1 we present our ⁷⁷Se NMR lineshapes for sulphur substituted z = 0.8 and z = 1.6 compositions in an applied field of $B_c = 8.33$ Tesla along the *c*-axis, compared with our lineshape for the z = 0 non-substituted sample, at the representative temperature of 50 K. After scaling the lineshapes according to selenium content in each crystal, integrated intensities for each system are equal within experimental uncertainties.

The narrowest lineshapes are observed for the z = 0 system; both S substituted samples exhibit line broadening, indicative of disorder effects in local electronic and structural properties at the Se sites. The Gaussian fits for each lineshape, depicted in Fig. 4.1, determine full widths at half maximum (FWHM) of ~ 4.5 kHz, 24 kHz, and 14 kHz for z = 0, 0.8, and 1.6, respectively. The mid range z = 0.8 composition is broadest because at 40 % substitution the Se nuclei are in a more non-uniform environment than the Se nuclei with 80 % substitution. In addition to the change in shape of the FFT lineshape, the NMR peak frequency is systematically lowered with increasing z (sulphur content) as well. Peaks for the z = 0, 0.8, and 1.6 samples are found at ~ 67.805 MHz, 67.780 MHz, and 67.760 MHz, respectively. With the expected Larmor frequency of $f_0 = \gamma_n B = 67.622$ MHz, this means that the *Knight shift* is also systematically lowered with increased S concentration.

4.2 ⁷⁷K Knight Shift

In Fig. 4.2 we summarize the temperature and S-content dependence of the Knight shift, ⁷⁷K. There are qualitative similarities in the behaviour of all three compositions, but at room temperature the magnitude of the spin contribution to the shift, ⁷⁷K_{spin} = $\frac{A_{hf}}{g\mu_B}\chi_{spin}$, is substantially reduced in the S substituted samples. In principle, the overall suppression of ⁷⁷K_{spin} may be caused by a reduction in the hyperfine coupling constant, A_{hf} , induced by evident structural changes. The Fe-Se bond length *shortens*, however, as one substitutes sulphur [18], which would cause greater overlap of the wavefunctions between Fe and the Se(S) layers. Naively, A_{hf} , would therefore increase in this scenario, and since we see an overall *decrease* in Knight shift, this implies χ_{spin} would have to drop even more substantially if A_{hf} indeed increases. That is, our results in Fig. 4.2 imply that S substitution supresses χ_{spin} .

Let us now shift our focus to the temperature dependence of ⁷⁷K. All three compositions evidently exhibit a monotonic decrease in Knight shift with temperature, behaviour which is consistent with that in related, previously reported iron based superconductors such as LaFeAsO_{1-x}F_x [11,60], Ba(Fe_{1-x}Co_x)₂As₂ [10,12, 13,64], FeSe [15], and Ba_xK_{1-x}Fe₂As₂ [68]. Our K_xFe_{2-y}Se_{2-z}S_z systems differ from Ba(Fe_{1-x}Co_x)₂As₂ in their substitution dependence. In Ba(Fe_{1-x}Co_x)₂As₂ the temperature dependence of the Knight shift remains qualitatively similar regardless of the Cobalt concentration, x [10,13]. In the present situation, however, the temperature dependence of the Knight shift becomes far less pronounced with S substitution.

The increase in the Knight shift at higher temperatures for the z = 0 non-substituted sample may be caused by the presence of excited states of electron spins, which may be reached at higher temperatures with sufficient thermal energy. In this pseudo-gap scenario [11,60,66], our observations then imply that in the S substituted systems either these excited states are diminished, or the energy threshold required to excite the spins up to these states is too great, and beyond our temperature range.

The dashed line through each of the samples in Fig. 4.2 is, again, a purely phenomenological fit to the normal state with a pseudo-gap. As was done for $K_x Fe_{2-y} Se_2$ in chapter 3, we again use

$$^{77}K \sim \alpha + \beta exp(-\Delta/k_BT), \tag{4.1}$$

where \triangle represents the pseudo-gap, α denotes the ⁷⁷K value near T_c, and β is a constant. We had hoped to investigate any systematic change (or lack thereof) in \triangle as a function of S substitution, but due to inherent



Figure 4.2: Temperature dependence of the ⁷⁷Se NMR Knight shift, ⁷⁷K, for $K_x Fe_{2-y}Se_{2-z}S_z$ with z = 0.8 and 1.6 and $B_c = 8.33$ Tesla along the *c*-axis. $K_x Fe_{2-y}Se_2$ is presented as well for comparison, and arrows mark T_c for the two superconducting compositions: z = 0 ($T_c = 25$ K) and z = 0.8 ($T_c = 13$ K). The dashed curve is a phenomenological fit with a pseudo-gap, ⁷⁷K ~ $\alpha + \beta \exp(-\Delta/k_B T)$, with $\Delta/k_B = 435$ K for all samples. Note the overall suppression of ⁷⁷K with S substitution.

uncertainty in its magnitude from our fits we were unable to do so. We found that the gap derived from our fit was extremely sensitive to the choices of α and β , and, in fact, all three samples could be fit with the same $\Delta/k_B = 435$ K as previously found for the non-substituted $K_x Fe_{2-y}Se_2$. We emphasize that the extracted estimate for Δ varies by as much as a factor of 2 while still maintaining a good fit to our data, indicating that we do not have sufficient resolution to discern the difference between the pseudo-gaps at each concentration. This situation was previously encountered by our group in Ba(Fe_{1-x}Co_x)₂As₂ [10].

Within a conventional Fermi liquid picture, the density of states at the Fermi energy may be responsible for the behaviour of ⁷⁷K. In a Fermi liquid, the Knight shift would be dominated by Pauli spin susceptibility, $\chi_{spin} = \mu_B^2 N(E_F)$. This implies that our observed decrease in ⁷⁷K suggests that the density of states at the Fermi energy decreases as S concentration is raised, and temperature is decreased. To check for Fermi liquid-like behaviour, we again will test the *Korringa relation*, which means that we will need to examine the nuclear spin-lattice relaxation rate, $1/T_1$, to go beyond the $\mathbf{q} = \mathbf{0}$ mode of spin susceptibility.

4.3 Nuclear Spin-Lattice Relaxation Rate $^{77}1/T_1$

In Fig. 4.3 we show representative signal recovery curves after saturation, recorded for T_1 measurements for all three samples. Single exponential fits are satisfactory for the data of all compositions, as expected in the case of nuclear spin I = 1/2 for ⁷⁷Se. One can see clearly the general trend that substituting sulphur slows the spin-lattice relaxation rate. Making this trend explicit, we plot in Fig. 4.4 the temperature dependence of $1/T_1T$, the relaxation rate divided by temperature, for $B_c = 8.33$ Tesla along the *c*-axis. Recall that $1/T_1T$ measures the wave-vector **q** integral of the imaginary part of the dynamical electron spin susceptibility in the first Brillouin zone, with

$$\frac{1}{T_1 T} \propto \sum_{\mathbf{q} \in B.Z.} |A(\mathbf{q})|^2 \frac{\chi''(\mathbf{q}, f_0)}{f_0}.$$
(4.2)

Here f_0 is the NMR frequency, and sets the energy scale at $\hbar f_0 \sim \mu eV$ for the spin dynamics we are probing.

As mentioned in the previous chapter, many iron-arsenide systems show an enhancement of low frequency AFSF in the optimally superconducting regime, reflected by $1/T_1T$ as one decreases temperature toward T_c [10–13,68]. For Ba(Fe_{1-x}Co_x)₂As₂, once the system enters the overdoped regime, the enhancement of the AFSF and T_c both begin to decrease [10]. Additionally, in FeSe an analogous enhancement in AFSF is seen, and a greater enhancement in the AFSF correlates with increased T_c and applied pressure [15]. It was also shown, however, that after reaching optimal T_c (~ 37 K), further applied pressure only suppressed T_c and the AFSF [16]. The over-pressured side of the T-pressure phase diagram is poorly explored due to practical constraints of such high pressures, which in part provided motivation for studying S substitution in this system. In K_xFe_{2-y}Se₂ we saw no enhancement of AFSF toward T_c , which seemed to imply that either this system provided a counterexample to the idea that AFSF and the high- T_c mechanism are connected, or that our K_xFe_{2-y}Se₂ was already pushed past optimal superconductivity and into the 'right hand side'



Figure 4.3: Representative T_1 recovery curves measured at the center of the FFT lineshapes presented in Fig. 4.1 at 50 K. Signal intensity is normalized for clarity, and solid lines represent single exponential fits through each data set, the argument of which gives our T_1 value. The strong tenedency of the relaxation rate to slow down with increased S substitution is evident.



Figure 4.4: $1/T_1T$ as a function of temperature for S substituted samples measured in $B_c = 8.33$ Tesla applied along the *c*-axis. The z = 0 composition is again presented alongside for comparison. Relaxation rate and therefore spin excitations systematically slow with S substitution. Neither of the two superconducting samples exhibits an enhancement toward T_c .

(overdoped, overpressured etc.) of the superconducting dome.

Our findings in the S substituted systems, then, provide stronger suggestion that the latter of the these two implications may be the more accurate. By adding chemical pressure via S substitution, the system is pushed further away from optimal superconductivity, which is reflected in our results through the suppression of spin excitations. In $K_x Fe_{2-y}Se_{1.2}S_{0.8}$ the temperature dependent behaviour is qualitatively similar to the non-substituted composition, but there is evident overall suppression of the magnitude of spin excitations. The non-superconducting $K_x Fe_{2-y}Se_{0.4}S_{1.6}$ data is nearly temperature independent, similar to overdoped, non-superconducting, metallic $Ba(Fe_{0.7}Co_{0.3})_2As_2$ [10]. We again caution the reader that our results in Fig. 4.4 do not rule out the possible enhancement of AFSF at energy scales much higher than $\hbar f_0$, and that it is the **q** summation over various modes which shows no net enhancement, meaning small AFSF may be present for some **q**-modes.

If either of the S substituted systems clearly satisfies the Korringa relation, it would indicate a dependence of both spin susceptibility and dynamics on the density of states at the Fermi energy, $N(E_F)$, perhaps giving information about the mechanism(s) behind their suppression. Though we reported that the non-substituted sample does not seem to fit the Korringa relation, we again check the S substituted samples for this benchmark test of the applicability of Fermi liquid theory by plotting $1/\sqrt{T_1T}$ vs ⁷⁷K(%) with temperature as the implicit parameter in Fig. 4.5. The slightly negatively curved z = 0 composition is again depicted for comparison. The $K_x Fe_{2-y}Se_{1.2}S_{0.8}$ system exhibits positive curvature, which suggests that it does not fit in a simple Fermi liquid picture either. The $K_x Fe_{2-y}Se_{0.4}S_{1.6}$ data may exhibit a relationship somewhat closer to being linear, but this could easily be a fictitious linearity in view of the very weak temperature dependences of ⁷⁷K and $1/T_1T$ in the temperature range we investigated. Additionally, extraplotation of the apparent linear fit to the intercept of the horizontal axis would imply that K_{chem} is as large as 0.22 % in this composition. If the Fermi liquid picture applies to the $K_x Fe_{2-y}Se_{0.4}S_{1.6}$ system, K_{chem} would have to double in magnitude compared with the superconducting $K_x Fe_{2-y}Se_2$.

4.4 Probing the Microscopic Inhomogeneity of the ⁷⁷Se Magnetic Environment

Our group earlier made note of the interesting variation of the relaxation rate in Ba(Fe_{1-x}Co_x)₂As₂ [13] within the single NMR peak. By measuring T₁ not just at the peak position, but also at the half-intensity position on the high frequency side and low frequency side of the ⁷⁵As lineshape, Ning *et al.* determined that T₁ exhibits a systematic variation. This systematic dependence was also consistent regardless of whether T₁ was measured along a single lineshape or across multiple lineshapes corresponding to different doping concentrations. That is, the T₁ values measured for two different doping concentrations were comparable when measured at a frequency where the lineshapes overlap, and values measured for lineshapes that did not overlap but were nearby in frequency exhibited consistent progression.

By examining the variation in the relaxation rate across a single NMR peak, we are checking its de-

53



Figure 4.5: $1/\sqrt{T_1T}$ vs ⁷⁷K(%) with temperature as the implicit parameter for all three compositions. A constant slope would indicate a Korringa relation, an indicator for Fermi liquid theory. The extrapolated horizontal intercept corresponds to K_{chem}.



Figure 4.6: Variation of the relaxation rate, $1/T_1$ as measured across the $K_x Fe_{2-y} Se_{1.2}S_{0.8}$ lineshape.

pendence on the local magnetism at the ⁷⁷Se site. Inhomogeneity in the ⁷⁷K Knight shift causes a slight local variation in the magnetic environment, and by measuring T_1 at different positions within the single peak lineshape we gain information on how this affects the relaxation rate. To check for this behaviour in our $K_x Fe_{2-y}Se_{2-z}S_z$ systems, we measured $1/T_1$ across the lineshape of our 'mid-range' concentration, z =0.8, at a representative temperature of 78 K. We plot these measurements in Fig. 4.6 along with the FFT lineshape itself. At this temperature, the non-substituted z = 0 lineshape is centered at a higher frequency than the z = 0.8 lineshape, and has a faster T_1 peak value, while the heavily substituted z = 1.6 lineshape is positioned at a lower frequency and has a slower T_1 value. Our results, which indicate a faster T_1 on the high frequency half-intensity position and a slower T_1 on the low frequency half-intensity position of the z = 0.8 composition, are consistent with the results observed in Ba(Fe_{1-x}Co_x)₂As₂ [13].

CHAPTER 5

SUMMARY AND CONCLUSIONS

In this thesis we have presented NMR studies on the recently discovered potassium iron-selenide superconductor, $K_x Fe_{2-y}Se_2$, and two variant systems in which sulphur is substituted for selenium, $K_x Fe_{2-y}Se_{1.2}S_{0.8}$ and $K_x Fe_{2-y}Se_{0.4}S_{1.6}$. In several FeAs high- T_c superconductors, T_c was shown to correlate with the largest AFSF enhancement as evidenced by $1/T_1T$, including both the 1111 LaFeAsO and 122 BaFeAs based systems [10–14]. Furthermore, our group earlier demonstrated that in the simple 11 FeSe superconductor, an increased T_c with applied pressure correlated to an enhancement in AFSF, and that the highest T_c corresponded to a pressure which produced the greatest enhancement in AFSF [15]. $K_x Fe_{2-y}Se_2$ ($T_c \sim 33$ K) therefore offered another system in which we could check if the enhancement of AFSF was related to the superconducting mechanism of iron based high- T_c materials. The $K_x Fe_{2-y}Se_{2-z}S_z$ systems meanwhile provided an alternate avenue to study the overpressured side of the superconducting dome in FeSe materials, since the mechanical pressure sequired for this region are experimentally difficult ($\gtrsim 9$ GPa), and sulphur can provide chemical pressure due to its ionic radius being smaller than that of selenium. This chapter briefly summarizes the results of our research, as well as any conclusions that can be drawn which might contribute to the understanding of the high- T_c mechanism in these materials.

In K_xFe_{2-y}Se₂, our ⁷⁷Se NMR lineshapes are very sharp and exhibit paramagnetic behaviour, and we find no evidence for the coexistence of a magnetically ordered phase with superconductivity in our sample. Our *ab*-plane lineshapes also show splitting caused by paramagnetic effects of two structurally inequivalent Se sites, suggesting that the tetragonal four-fold symmetry is broken down at least locally at the Se sites, and a two-fold symmetry in the local crystal structure may be induced by the formation of a defect superstructure. We also used the NMR line broadening below T_c induced by the Abrikosov lattice to estimate the London penetration depth, $\lambda_{ab} \sim 290$ nm, and the superconducting carrier concentration, $n_s \sim 1 \ge 10^{21}$ cm⁻³.

The static magnetic properties in $K_x Fe_{2-y} Se_2$ were found to share many common traits with the low- T_c superconductor FeSe as well as with iron-arsenide high- T_c superconductors. The uniform spin susceptibility,

for example, decreases with temperature toward T_c, as observed in FeSe and all other iron-arsenide high-T_c systems. Below T_c the Knight shift ⁷⁷K suddenly dives, and then levels off at K_{chem} ~ 0.11 %. This observation is consistent with the suppression of χ_{spin} , as expected for singlet pairing of Cooper pairs.

Turning to the dynamic magnetic information studied via the relaxation rate $1/T_1$, we observe no Hebel-Slichter coherence peak in its temperature dependence just below T_c . The spin dynamics in this material provided some interesting information regarding the superconducting mechanism. Despite the high T_c in this system, we observed no enhancment of the AFSF as one approaches T_c . This apparent counterexample to the connection between AFSF and the superconducting mechanism needs to be interpreted carefully, however. In the low- T_c FeSe, the presence of AFSF was difficult to detect because a small percent of defects could wipe out the AFSF signature as well as T_c [15,71,72], and in Ba(Fe_{1-x}Co_x)₂As₂, overdoping by only a few percent was enough to wipe out the signature of enhanced AFSF while suppressing T_c and the volume fraction [10]. It is thus possible that our sample represents the slightly overdoped or overpressured side of the superconducting dome, which accounts for the lack of the AFSF enhancement.

Extending our investigation to include $K_x Fe_{2-y} Se_{2-z} S_z$, we examined the evolution of the electronic properties as a function of sulphur (S) substitution to study the suppression and eventual destruction of superconductivity in a layered FeSe material. NMR lineshapes were found to broaden in comparison with the non-substituted $K_x Fe_{2-y} Se_2$ material, indicative of greater local disorder at the Se sites. We found that with increasing S substitution, both the overall magnitude as well as the strength of the temperature dependence of spin susceptibility χ_{spin} are suppressed. Spin excitations are also suppressed with increasing S substitution, as seen in our $1/T_1T$ data. In general, pseudo-gap-like behaviour is strongly suppressed with S substitution, and is nearly non-existent in the non-superconducting $K_x Fe_{2-y} Se_{0.4}S_{1.6}$ sample, as both Knight shift and $1/T_1T$ exhibit nearly flat temperature dependencies in the normal state above T_c .

None of the systems we studied *conclusively* satisfy the Korringa relation expected for canoncial Fermi liquids, but the z = 1.6 composition may in fact be close to qualifying for Fermi liquid-like behaviour. To reconcile the discrepancy between the observation of antiferromagnetic ordering by neutron scattering, and our ruling out its coexistence with superconductivity in our sample, we contend that measurements on samples with very precisely controlled stoichiometry, defect ordering, and aging effects are required.

Appendices
APPENDIX A

CRYOMECH PTS 410 HELIUM RELIQUIFIER

The PTS 410 Helium Reliquifier by Cryomech is a helium reliquification system meant to be used in conjunction with a cryostat or liquid helium dewar, and is capable of producing 12 litres of liquid helium per day. It consists of three main components: a compressor package (CP) to compress low pressure helium gas, a pulse tube cold head mounted on an aluminum beam in which liquifying takes place, and two stainless steel helium 'flex lines' to circulate helium gas between the cold head and CP. As a research group studying novel electronic and magnetic systems, helium temperature range (< 77 K) measurements are essential. For the purposes of both liquid helium cost reduction and time efficiency for the researcher, the capability for recycling boil off helium gas into liquid helium is a tremendous asset.

Cryomech provides an installation, operation, and routine maintenance manual that should serve as the *primary resource* for the user of the PTS 410. The purpose of this appendix is to supplement Cryomech's manual with some additional operation instructions that are specific to the configuration of the PTS 410 within the Imai group laboratory at McMaster University. The information contained herein is the result of months of testing and extensive discussion with Cryomech engineers.

Prior to operating the PTS 410, one should perform the following steps *in addition* to any preliminary checks and instructions listed in Cryomech's manual.

- 1. On the cooling water pipes located beside the CP, open both red quarter-turn values at the top of each pipe as well as the ball value at the base inlet pipe to provide cooling water flow. This needs to be done 10-15 minutes prior to starting the PTS 410 to allow the water to get cold. It is especially crucial that the water be cold (< 10° Celcius) during the first two hours of operation, as this is when the compressor is working hardest. For details on cooling water specifications see Appendix A of the Cryomech manual.</p>
- 2. On the compressor, flip the 'Main Breaker' switch, wait 5 seconds, then flip the 'Power' switch. The green light on the compressor should illuminate, the compressor will emit a series of beeps, and display

the number of hours used.

- 3. On the PC located above the compressor, open the Cryomech LabVIEW Virtual Instrument (VI) by clicking Start>All Programs>Cryomech>Virtual Panel. A LabVIEW front panel will appear which monitors cooling water in and out temperatures, helium gas temperature, oil temperature, and gas pressure at both the high and low sides. When the VI is first opened these readings tend to fluctuate wildly, settling down to accurate readings after several minutes. The measurements can always be checked locally by pushing the 'Service/Rtn' button on the compressor, and using the 'Select/Enter' button to cycle through the various sensors. The PTS 410 is designed to automatically shut down should any of these values fall outside its safe operating range, specified in Appendix A of the Cryomech manual.
- 4. Carefully check the liquid helium level in the cryostat to be used. For the Janis model SVT cryostats the level should be somewhere between 20 % and 80 % full. A lower helium level allows for deeper placement of the drain leg of the cold head, since it must always be positioned as close to the liquid as possible ($\sim 1/2$ " above) without submerging it. The deeper the drain leg, the less of it is exposed to room temperature, which means the PTS 410 operates slightly more efficiently. A higher helium level will of course last much longer, at the expense of some efficiency. We suggest beginning with a low helium level for shorter term use (days), and a high helium level for longer term use (weeks), continually lowering the drain leg as the helium level reduces.
- 5. Remove the shield on the drain leg. Prepare and connect all hoses and joints to feed boil off from the cryostat into the PTS 410. Both the sample and helium spaces of the Janis cryostat should be connected to the loop, even if the sample space is empty, as the slight pressure from the gas will prevent air from leaking in. This must be done prior to inserting the drain leg in order to purge the cold head of any air, and one should check that boil off gas is indeed exiting the drain leg. As an option, one can incorporate the use of our helium gas bag in the loop. This is useful for collecting the excess helium gas that is produced during the intial 2 hours of operation while the cold head cools down to liquifying temperature. The gas bag also collects any excess gas should the system become overpressured, rather than allowing the built-in valves to release the excess pressure to the room. The PTS 410's proper operation, however, is strongly dependent on a good *thermosiphon* in the gas loop. The boil off must be forced through the cold head; it will not 'pull' helium gas as needed. If one uses the gas bag it should be appropriately separated from the rest of the gas loop by a one way pressure release valve (1-2 PSI) so as to preserve the thermosiphon.
- 6. Prior to raising the cold head, connect the temperature sensor of the temperature controller (provided by Cryomech) to the cold head sensor port. **Caution:** the cable connecting the temperature controller and cold head is quite short; one must place the temperature controller at a height that does not result in tension in the cable when the cold head is raised.

- 7. Switch the temperature controller on, and ensure that it correctly reads room temperature. The temperature controller is used to add heat to the system so as to prevent it from becoming underpressurized. Press the 'Control' button, and then select the Normal program (program 1) by pushing '1' or by pushing 'Control' again. The mode of operation for the controller, displayed in the lower right corner, should now read "NPID" instead of "Stop". The setpoint should be set to ~ 3.8 K to begin. During testing the PTS 410 operated best with the setpoint between 3.6 and 3.8 K. If set to 4.2 K as Cryomech instructs, the efficiency becomes quite poor. The exact setpoint for optimal performance depends on several factors such as the quality of the vacuum within the cold head, the liquid helium level, etc. and may need to be tweaked during operation. The user should monitor helium level and pressure carefully during the initial stages of operation, and adjust it accordingly.
- 8. Raise the cold head by turning the crank on the aluminum cart. Ensure the cold head brackets are unlocked by turning the red handles at the top and bottom bracket. Position the tip of the drain leg directly above the helium port to be used, and slide a 'quick connect' onto the drain leg, letting it sit near the tip.
- 9. Remove the stopper from the helium port, and quickly lower the drain leg, partially sealing the quick connect as soon as possible. The goal in this step is to minimize the time during which the liquid helium is open to the room.
- 10. Lower the drain leg to the appropriate level. The ideal position must be such that the tip of the drain leg is within 1" of the liquid helium. The helium space of the Janis SVT cryostat is precisely 12.6" deep, the top of the helium space is located 10.5" below the top of the transfer port, and the drain leg is 26" long. With this information one can calculate how much of the drain leg needs to be exposed for ideal positioning. **Example:** The helium level is measured to be 42 %, corresponding to 58 % empty space, or $(0.58) \times (12.6) = 7.31$ " from the top of the helium space to the liquid. This means there are 7.31 + 10.5 = 17.81" of space between the top of the helium port and the liquid level, so there should be 26 16.81 = 9.19" of exposed drain leg if the tip is to be placed 1" above the liquid.

Note: Placement of the drain leg need not be precise for liquification to occur. During tests, placement of the tip 2" above liquid did not affect performance, while placing it 4" above the liquid resulted in helium loss of $\sim 1 \%$ per hour. Submerging the drain leg as much as 2" in the liquid also did not affect performance, though this should be avoided, especially during initial operation when warm gas will be leaving the drain leg.

11. Once lowered, fully seal the quick connect. Double check the system for any possible leaks or weak seals; not only might helium be lost, but impurities may enter the system which can collect on the inside of the cold head and significantly affect performance. Push the green 'compressor on' button on the compressor. The PTS 410 will turn on and begin cooling down immediately. During operation the compressor will emit a constant buzzing sound, and the cold head will emit rythmic chirping sounds.

The cold head should reach 4 K in 1.5-2 hours. The first 5 hours are most crucial, and the entire system should be monitored very carefully during this time.

When finished, the PTS 410 can be turned off by pushing the black 'off' button on the compressor. The 'Power' switch and the 'Main Breaker' switch should be flipped off as well, and the cooling water valves closed. It is best to let the cold head warm up to room temperature before removing it or altering the configuration in any way, but not absolutely necessary. Once warm, the drain leg shield should be replaced and the needle valve on the boil off intake line should be closed.

APPENDIX B_____

_NMR PROBE DESIGN FOR 16 TESLA MAGNET

The following are designs for an NMR cryogenic probe, drawn using CAD software for submission to the McMaster Engineering Machine Shop. The NMR probe must contain a space for mounting sample and pickup coils, variable tuning capacitors, a temperature sensor, and a heater wire as its principle components. The probe must also be sealed for high vacuum, capable of operating in cryogenic temperatures, and fit into our 16 Tesla magnet with a cross-sectional sample bore diameter of 30.5 mm. Our goal is to construct a probe that is as modular and compartmentalized as possible to facilitate future repairs. At the time of preparing this thesis, all components have been machined, and construction is in progress.

























After the machining of these components was complete, the following modifications were made.

- 1. Reduce 'center sections' of both canisters' wall thickness by ~ 25 % (from 0.08" = 2.05 mm to ~ 0.06 " = 1.5 mm) from the outside.
- 2. Etch groove for heater wire from the bottom of the sample canister to its central section.
- 3. Drill 2 small holes (2 mm in diameter) in the bottom of the sample canister, 3 holes in the wall of the sample canister, and 5 holes in the wall of the capacitor canister to allow for gas exchange.
- 4. Enlarge the inner diameter of the brass cylinder mounts to 0.136".
- 5. Machine 3 additional radiation shields, one of which will have all 6 holes with diameter 0.189" to be soldered nearest the flange for structural stability.

BIBLIOGRAPHY

- J. Bardeen, L. N. Cooper, and J. R. Schrieffer, "Theory of superconductivity," *Phys. Rev.*, vol. 108, pp. 1175–1204, 1957.
- [2] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, "Superconductivity at 39 K in magnesium diboride," *Nature*, vol. 410, p. 63, 2001.
- [3] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, "Iron-based layered superconductor $La[O_{1-x}F_x]FeAs$ (x = 0.05 0.12) with $T_c = 26$ K," J. Amer. Chem. Soc., vol. 130, p. 3296, 2008.
- [4] X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, "Superconductivity at 43 K in SmFeAsO_{1-x}F_x," *Nature*, vol. 453, p. 761, 2008.
- [5] Z. A. Ren, J. Yang, W. Lu, W. Yi, G. C. Che, X. L. Dong, L. L. Sun, and Z. X. Zhao, "Superconductivity at 52 K in iron based F doped layered quaternary compound Pr[O_{1-x}F_x]FeAs," *Materials Research Innovations*, vol. 12, p. 105, 2008.
- [6] M. Norman, "High-temperature superconductivity in the iron pnictides," *Physics*, vol. 1, p. 21, 2008.
- [7] A. S. Sefat, R. Jin, M. A. McGuire, B. C. Sales, D. J. Singh, and D. Mandrus, "Superconductivity at 22 K in Co-doped BaFe₂As₂ single crystals," *Phys. Rev. Lett.*, vol. 101, p. 117004, 2008.
- [8] Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi, and Y. Takano, "Superconductivity at 27 K in tetragonal FeSe under high pressure," *Appl. Phys. Lett.*, vol. 93, p. 152505, 2008.
- [9] T. Park, E. Park, H. Lee, T. Klimczuk, E. D. Bauer, F. Ronning, and J. D. Thompson, "Pressure induced superconductivity in CaFe₂As₂," J. Phys.: Condens. Matter, vol. 20, p. 322204, 2008.
- [10] F. L. Ning, K. Ahilan, T. Imai, A. S. Sefat, M. A. McGuire, B. C. Sales, D. Mandrus, P. Cheng, B. Shen, and H.-H. Wen, "Contrasting spin dynamics between underdoped and overdoped Ba(Fe_{1-x}Co_x)₂As₂," *Phys. Rev. Lett.*, vol. 104, p. 037001, 2010.

- [11] Y. Nakai, K. Ishida, Y. Kamihara, M. Hirano, and H. Hosono, "Evolution from itinerant antiferromagnet to unconventional superconductor in LaFeAs(OF)," J. Phys. Soc. Jpn., vol. 77, p. 073701, 2008.
- [12] F. Ning, K. Ahilan, T. Imai, A. S. Sefat, R. Jin, M. A. McGuire, B. C. Sales, and D. Mandrus, "Co and As NMR investigation of electron-doped high T_c superconductor BaFe_{1.8}Co_{0.2}As₂ (T_c = 22 K)," J. Phys. Soc. Jpn., vol. 77, p. 103705, 2008.
- [13] F. Ning, K. Ahilan, T. Imai, A. S. Sefat, R. Jin, M. A. McGuire, B. C. Sales, and D. Mandrus, "Spin susceptibility, phase diagram, and quantum criticality in the electron-doped high T_c superconductor Ba(Fe_{1-x}Co_x)₂As₂," J. Phys. Soc. Jpn., vol. 78, p. 013711, 2009.
- [14] T. Oka, Z. Li, S. Kawasaki, G. F. Chen, N. L. Wang, and G. qing Zhen, "Antiferromagnetic spin fluctuations above the dome-shaped and full-gap superconducting states of LaFeAsO_{1-x}F_x revealed by ⁷⁵As-nuclear quadrupole resonance," *Phys. Rev. Lett.*, vol. 108, p. 047001, 2012.
- [15] T. Imai, K. Ahilan, F. L. Ning, T. M. McQueen, and R. J. Cava, "Why does undoped FeSe become a high T_c superconductor under pressure," *Phys. Rev. Lett.*, vol. 102, p. 177005, 2009.
- [16] S. Medvedev, T. M. McQueen, I. Trojan, T. Palasyuk, M. I. Erements, R. J. Cava, S. Naghavi, F. Casper, V. Ksenofontov, G. Wortmann, and C. Felser, "Electronic and magnetic phase diagram of β-Fe_{1.01}Se with superconductivity at 36.7 K under pressure," *Nature Materials*, vol. 8, pp. 630–633, 2009.
- [17] J. Guo, S. Jin, G. W. S. Wang, K. Zhu, T. Zhou, M. He, and X. Chen, "Superconductivity in the iron selenide $K_x Fe_2 Se_2$ ($0 \le x \le 1.0$)," *Phys. Rev. B.*, vol. 82, p. 180520, 2010.
- [18] H. Lei, M. Abeykoon, E. S. Bozin, K. Wang, J. B. Warren, and C. Petrovic, "Phase diagram of K_xFe_{2-y}Se_{2-z}S_z and the suppression of its superconducting state by an Fe₂-Se/S tetrahedron distortion," *Phys. Rev. Lett.*, vol. 107, p. 137002, 2011.
- [19] H. Lei and C. Petrovic, "Upper critical fields and superconducting anisotropy of $K_{0.70}Fe_{1.55}Se_{1.01}S_{0.99}$ and $K_{0.76}Fe_{1.61}Se_{0.96}S_{1.04}$ single crystals," *EPL*, vol. 95, p. 57006, 2011.
- [20] H. Lei, M. Abeykoon, E. S. Bozin, and C. Petrovic, "Spin-glass behavior of semiconducting K_xFe_{2-y}S₂," *Phys. Rev. B.*, vol. 83, p. 180503, 2011.
- [21] M. Rotter, M. Tegel, and D. Johrendt, "Spin-density-wave anomaly at 140 K in the ternary iron arsenide BaFe₂As₂," *Phys. Rev. B.*, vol. 78, p. 020503, 2008.
- [22] F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schafer, "Superconductivity in the presence of strong Pauli paramagnetism: CeCu₂Si₂," *Phys. Rev. Lett.*, vol. 43, pp. 1892–1896, 1979.
- [23] Y. Kasahara, T. Iwasawa, H. Shishido, T. Shibauchi, K. Behnia, T. D. Matsuda, Y. Haga, Y. Onuki, M. Sigrist, and Y. Matsuda, "Gap structure and exotic superconducting state of URu₂Si₂," J. Phys.: Conf. Ser., vol. 150, p. 052098, 2009.

- [24] Z. Wang, Y. J. Song, H. L. Shi, Z. W. Wang, Z. Chen, H. F. Tian, G. F. Chen, J. G. Guo, H. X. Yang, and J. Q. Li, "Microstructure and ordering if iron vacancies in the superconductor system K_xFe₂Se₂ as seen via transmission electron microscopy," *Phys. Rev. B.*, vol. 83, p. 140505(R), 2011.
- [25] H. Lei and C. Petrovic, "Anisotropy in transport and magnetic properties of K_{0.64}Fe_{1.44}Se₂," Phys. Rev. B., vol. 83, p. 184504, 2011.
- [26] Y. Sekiba, T. Sato, K. Nakayama, K. Terashima, P. Richard, J. H. Bowen, H. Ding, Y.-M. Xu, L. J. Li, G. H. Cao, Z.-A. Xu, and T. Takahashi, "Electronic structure of heavily electron-doped BaFe_{1.7}Co_{0.3}As₂ studied by angle-resolved photemission," *New J. Phys.*, vol. 11, p. 025020, 2009.
- [27] M. Yi, D. H. Lu, J. G. Analytis, J.-H. Chu, S.-K. Mo, R.-H. He, R. G. Moore, X. J. Zhou, G. F. Chen, J. L. Luo, N. L. Wang, Z. Hussain, D. J. Singh, I. R. Fisher, and Z.-X. Shen, "Electronic structure of of the BaFe₂As₂ family of iron-pnictide superconductors," *Phys. Rev. B.*, vol. 80, p. 024515, 2009.
- [28] W. Malaeb, T. Yoshida, A. Fujimori, M. Kubota, K. Ono, K. Kihou, P. M. Shirage, H. Kito, A. Iyo, H. Eisaki, Y. Nakajima, T. Tamegai, and R. Arita, "Three-dimensional electronic structure of superconducting iron pnictides observed by angle-resolved photemission," J. Phys. Soc. Jpn., vol. 78, p. 123706, 2009.
- [29] T. Qian, X.-P. Wang, W.-C. Jin, P. Zhang, P. Richard, G. Xu, X. Dai, Z. Fang, J.-G. Guo, X.-L. Chen, and H. Ding, "Absence of a holelike fermi surface for the iron-based K_{0.8}Fe_{1.7}Se₂ superconductor revealed by angle-resolved photoemission spectroscopy," *Phys. Rev. Lett.*, vol. 106, p. 187001, 2011.
- [30] T. Berlijn, P. J. Hirschfeld, and W. Ku arXiv:1204.2849, 2012.
- [31] C. de la Cruz, Q. Huang, J. W. Lynn, J. Li, W. R. II, J. L. Zarestky, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang, and P. Dai, "Magnetic order close to superconductivity in the iron-based layered LaO_{1-x}F_xFeAs systems," *Nature*, vol. 453, p. 899, 2008.
- [32] A. Jesche, N. Caroca-Canales, H. Rosner, H. Borrmann, A. Ormeci, H. H. Klauss, H. Luetkens, R. Khasanov, A. Amato, A. Hoser, K. Kaneko, C. Krellner, and C. Geibel, "Strong coupling between magnetic and structural order parameters in SrFe₂As₂," *Phys. Rev. B.*, vol. 78, p. 180504(R), 2008.
- [33] K. Kitagawa, N. Katayama, K. Ohgushi, M. Yoshida, and M. Takigawa, "Commensurate itinerant antiferromagnetism in BaFe₂As₂: ⁷⁵As-NMR studies on a self-flux grown single crystal," J. Phys. Soc. Jpn., vol. 77, p. 114709, 2008.
- [34] F. Chen, M. Xu, Q. Q. Ge, Y. Zhang, Z. R. Ye, L. X. Yang, J. Jiang, B. P. Xie, R. C. Che, N. Zhang, A. F. Wang, X. H. Chen, D. W. Shen, J. P. Hu, and D. L. Feng, "Electronic identification of the parental phases and mesoscopic phase separation of K_xFe_{2-y}Se₂ superconductors," *Phys. Rev. X.*, vol. 1, p. 021020, 2011.

- [35] Y. J. Yan, M. Zhang, A. F. Wang, J. J. Ying, Z. Y. Li, W. Qin, X. G. Luo, J. Q. Li, J. Hu, and X. H. Chen, "Electronic and magnetic phase diagram in K_xFe_{2-y}Se₂ superconductors," *Scientific Reports*, vol. 2, p. 212, 2012.
- [36] M.-H. Fang, H.-D. Wang, C.-H. Dong, Z.-J. Li, C.-M. Feng, J. Chen, and H. Q. Yuan, "Fe-based superconductivity with T_c = 31 K bordering an antiferromagnetic insulator in (TI,K)Fe_xSe₂," *EPL*, vol. 94, p. 27009, 2011.
- [37] W. Bao, Q.-Z. Huang, G.-F. Chen, M. A. Green, D.-M. Wang, J.-B. He, and Y.-M. Qiu, "A novel large moment antiferromagnetic order in K_{0.8}Fe_{1.6}Se₂ superconductor," *Chin. Phys. Lett.*, vol. 28, p. 086104, 2011.
- [38] F. Han, H. Yang, B. Shen, Z.-Y. Wang, C.-H. Li, and H.-H. Wen, "Metastable superconducting state in quenched K_xFe_{2-y}Se₂," *Philosophical Magazine*, vol. 92, pp. 2553–2562, 2012.
- [39] D. A. Torchetti, M. Fu, D. C. Christensen, K. J. Nelson, T. Imai, H. Lei, and C. Petrovic, "⁷⁷Se NMR investigation of the K_xFe_{2-y}Se₂ high T_c superconductor (T_c = 33 k)," *Phys. Rev. B.*, vol. 83, p. 104508, 2011.
- [40] H. Lei and C. Petrovic, "Critical current density and vortex pinning and mechanism in $K_x Fe_{2-y} Se_2$ doped with S," *Phys. Rev. B.*, vol. 84, 2011.
- [41] B. Hunter, "Rietica a visual rietveld program," International Union of Crystallography Commission on Powder Diffraction Newsletter, p. 20, 1998.
- [42] A. C. Larson and R. B. V. Dreele, "General structure analysis system (GSAS)," Los Alamos National Laboratory Report LAUR, pp. 86–748, 1994.
- [43] B. H. Toby, "EXPGUI, a graphical user interface for GSAS," J. Appl. Crystallogr., vol. 34, p. 210, 2001.
- [44] W. Yu, L. Ma, J. B. He, D. M. Wang, T.-L. Xia, G. F. Chen, and W. Bao, "⁷⁷se nmr study of the pairing symmetry and the spin dynamics in K_yFe_{2-x}Se₂," *Phys. Rev. Lett.*, vol. 106, p. 197001, 2011.
- [45] H. Kotegawa, Y. Hara, H. Nohara, H. Tou, Y. Mizuguchi, H. Takeya, and Y. Takano, "Possible superconducting symmetry and magnetic correlations in K_{0.8}Fe₂Se₂: A ⁷⁷Se-NMR study," J. Phys. Soc. Jpn., vol. 80, p. 043708, 2011.
- [46] D. A. Torchetti, T. Imai, H. Lei, and C. Petrovic, "NMR characterization of sulphur substitution effects in the $K_x Fe_{2-y} Se_{2-z} S_z$ high- T_c superconductor," *Phys. Rev. B.*, vol. 85, p. 144516, 2012.
- [47] R. H. Hammond and G. M. Kelly, "Vanishing Knight shift in superconducting aluminum," *Phys. Rev. Lett.*, vol. 18, pp. 156–158, 1967.
- [48] L. C. Hebel and C. P. Slichter, "Nuclear spin relaxation in normal and superconducting Aluminum," *Phys. Rev.*, vol. 113, pp. 1504–1519, 1959.

- [49] Y. Masuda and A. G. Redfield, "Nuclear spin-lattice relaxation in superconducting Aluminum," Phys. Rev., vol. 125, pp. 159–163, 1962.
- [50] M. Mali, D. Brinkmann, L. Pauli, J. Roos, and H. Zimmermann, "Cu and Y NQR and NMR in the superconductor YBa₂Cu₃O_{7-δ}," *Physics Letters A*, vol. 124, p. 112, 1987.
- [51] R. E. Walstedt, W. W. Warren, R. F. B. Jr., G. F. Brennert, G. P. Espinosa, J. P. Remeika, R. J. Cava, and E. A. Rietman, "Nuclear magnetic resonanc and nuclear quadrupole resonance study of copper in Ba₂YCu₃O_{7-δ}," *Phys. Rev. B.*, vol. 36, p. 5727, 1987.
- [52] C. P. Slichter, Principles of Magnetic Resonance. Springer, 1996.
- [53] V. Jaccarino, "Studies of the hyperfine interaction in transition metals," Enrico Fermi Physics School, vol. 37, pp. 335–385, 1967.
- [54] N. W. Ashcroft and N. D. Mermin, Solid State Physics. Brooks/Cole, 1976.
- [55] R. M. White, Quantum Theory of Magnetism. Springer, 1970.
- [56] T. Moriya, "The effect of electron-electron interaction on the nuclear spin relaxation in metals," J. Phys. Soc. Jpn., vol. 18, p. 516, 1963.
- [57] Y. Mizuguchi, H. Takeya, Y. Kawasaki, T. Ozaki, and S. Tsuda, "Transport properties of the new Fe-based superconductor $K_x Fe_2 Se_2$ ($T_c = 33$ K)," Appl. Phys. Lett., vol. 98, p. 042511, 2011.
- [58] P. Pincus, A. C. Gossard, V. Jaccarino, and J. J. Wernick, "Nmr measurements of the flux distribution in type II superconductors," *Phys. Lett.*, vol. 13, p. 21, 1964.
- [59] E. H. Brandt, "Flux distribution and penetration depth measured by muon spin rotation in high-T_c superconductors," *Phys. Rev. B.*, vol. 37, p. 2349, 1988.
- [60] K. Ahilan, F. L. Ning, T. Imai, A. S. Sefat, R. Jin, M. A. McGuire, B. C. Sales, and D. Mandrus, "¹⁹F NMR investigation of LaFeAs(O_{0.89}F_{0.11})," *Phys. Rev. B.*, vol. 78, p. 100501, 2008.
- [61] S. E. Sebastian, J. Gillet, N. Harrison, P. H. C. Lau, D. J. Singh, C. H. Mielke, and G. G. Lonzarich, "Quantum oscillations in the parent magnetic phase of an iron arsenide high temperature superconductor," J. Phys. Cond. Matt., vol. 20, p. 422203, 2008.
- [62] H. Ding, K. Nakayama, P. Richard, S. Souma, T. Sato, T. Takahashi, M. Neupane, Y.-M. Xu, Z.-H. Pan, A. V. Fedorov, Z. Wang, X. Dai, Z. F. adn G. F. Chen, J. L. Luo, and N. L. Wang, "Electronic structure of optimally doped pnictide Ba_{0.6}K_{0.4}Fe₂As₂: a comprehensive angle-resolved photoemission spectroscopy investigation," J. Phys. Cond. Matt., vol. 13, p. 135701, 2011.
- [63] P. Zavalij, W. Bao, X. F. Wang, J. J. Ying, X. H. Chen, D. M. Wang, J. B. He, X. Q. Wang, G. F. Chen, P.-Y. Hsieh, Q. Huang, and M. A. Green, "Structure of vacancy-ordered single-crystalline super-conducting potassium iron selenide," *Phys. Rev. B.*, vol. 83, p. 132509, 2011.

- [64] X. F. Wang, T. Wu, G. Wu, H. Chen, Y. L. Xie, J. J. Ying, Y. J. Yan, R. H. Liu, and X. H. Chen, "Anisotropy in the electrical resistivity and susceptibility of superconducting BaFe₂As₂," *Phys. Rev. Lett.*, vol. 102, p. 117005, 2010.
- [65] N. Ni, M. E. Tillman, J.-Q. Yan, A. Kracher, S. T. Hannahs, S. L. Bud'ko, and P. C. Canfield, "Effects of co substitution on thermodynamic and transport properties and anisotropic H_{c2} in Ba(Fe_{1-x}Co_x)₂As₂ single crystals," *Phys. Rev. B.*, vol. 78, p. 214515, 2008.
- [66] M. Liu, L. W. Harriger, H. Luo, M. Wang, R. A. Ewings, T. Guidi, H. Park, K. Haule, G. Kotliar, S. M. Hayden, and P. Dai, "Nature of magnetic excitations in superconducting BaFe_{1.9}Ni_{0.1}As₂," *Nature Physics*, vol. 8, p. 376, 2012.
- [67] T. Imai, K. Ahilan, F. L. Ning, M. A. McGuire, A. S. Sefat, R. Jin, B. C. Sales, and D. Mandrus, "Nmr measurements of intrinsic spin susceptibility in LaFeAsO_{0.9}F_{0.1}," *J. Phys. Soc. Jpn. Suppl. C.*, vol. 77, p. 47, 2008.
- [68] K. Matano, Z. A. Ren, X. L. Dong, L. L. Sun, Z. X. Zhao, and G. qing Zheng, "Spin-singlet superconductivity with multiple gaps in PrFeAsO_{0.89}F_{0.11}," *Europhysics Letters*, vol. 83, p. 57001, 2008.
- [69] H.-J. Grafe, D. Paar, G. Lang, N. J. Curro, G. Behr, J. Werner, J. Hamann-Borrero, C. Hess, N. Leps, R. Klingeler, and B. Buchner, "⁷⁵As NMR studies of superconducting LaFeAsO_{0.9}F_{0.1}," *Phys. Rev. Lett.*, vol. 101, p. 047003, 2008.
- [70] M. Yashima, H. Nishimura, H. Mukuda, Y. Kitaoka, K. Miyazawa, P. M. Shirage, K. Kihou, H. Kito, H. Eisaki, and A. Iyo, "Strong-coupling spin-singlet superconductivity with multiple full gaps in holedoped Ba_{0.6}K_{0.4}Fe₂As₂," J. Phys. Soc. Jpn., vol. 78, p. 103702, 2009.
- [71] H. Kotegawa, S. Masaki, Y. Awai, H. Tou, Y. Mizuguchi, and Y. Takano, "Evidence for unconventional superconductivity in arsenic-free iron-based superconductor FeSe: A ⁷⁷Se-NMR study," J. Phys. Soc. Jpn., vol. 77, p. 113703, 2008.
- [72] T. M. McQueen, Q. Huang, V. Ksenofontov, C. Felser, Q. Xu, H. Zandbergen, Y. S. Hor, J. Allred, A. J. Williams, D. Qu, J. Checkelsky, N. P. Ong, and R. Cava, "Extreme sensitivity of superconductivity to stoichiometry in Fe_{1+δ}Se," *Phys. Rev. B.*, vol. 79, p. 014522, 2009.