Nuclear magnetic resonance studies of magnetic fluctuations and nematic order in iron-based superconductors

Paul Waymouth Wiecki
Iowa State University

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Nuclear magnetic resonance studies of magnetic fluctuations and nematic order in iron-based superconductors

by

Paul Waymouth Wiecki

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

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Program of Study Committee:
Yuji Furukawa, Major Professor
   David Johnston
   Sergey Bud’ko
   James Vary
   Vincenzo Venditti

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
2018

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DEDICATION

This thesis is dedicated to my father, Dr. Ron V. Wiecki (PhD in Musicology, University of Wisconsin-Madison, 1992), and to my grandfather, Dr. John F. Waymouth II (PhD in Physics, Massachusetts Institute of Technology, 1950).
TABLE OF CONTENTS

LIST OF FIGURES ........................................................... vii

ACKNOWLEDGEMENTS ..................................................... xxiii

ABSTRACT ................................................................. xxiv

CHAPTER 1. INTRODUCTION TO IRON-BASED SUPERCONDUCTORS .......... 1
  1.1 Introduction .......................................................... 1
  1.2 Structure and Phase Diagram ....................................... 4
  1.3 Electronic Structure and Fermi Surface ......................... 5
  1.4 Magnetic Order ....................................................... 7
    1.4.1 Structure ........................................................ 7
    1.4.2 Weak-coupling itinerant vs. strong-coupling local moment pictures . 10
  1.5 Nematic Order ....................................................... 12
  1.6 Superconducting Properties ....................................... 16
  1.7 Motivation ............................................................ 18
    1.7.1 FM correlations in iron-based superconductors ............. 20
    1.7.2 KFe$_2$As$_2$ ..................................................... 21
    1.7.3 FeSe$_{1-x}$S$_x$ .................................................. 22

CHAPTER 2. NUCLEAR MAGNETIC RESONANCE ............................... 24
  2.1 Basics ............................................................... 24
  2.2 Motion of nuclear moments and free induction decay signal ........ 25
  2.3 Spin Echo and Pulse NMR measurements .......................... 28
    2.3.1 Spin echo measurement of $T_2$ .............................. 30
    2.3.2 Spin echo measurement of $T_1$ .............................. 30
2.4 Hyperfine field in materials ................................................. 31
2.5 NMR Shift ........................................................................ 32
2.6 Spin-Lattice Relaxation Rate, $1/T_1$ .................................... 34
2.7 Spin-Spin Relaxation Rate, $1/T_2$ ....................................... 37
2.8 Korringa relation .............................................................. 38
2.9 Electric Quadrupole Interaction ............................................. 39
  2.9.1 Nuclear Quadrupole Resonance (NQR) ............................ 39
  2.9.2 NMR spectrum in the presence of Quadrupole Effects ........ 40
2.10 Powder Lineshape ............................................................ 42
  2.10.1 Quadrupole Satellite Powder Pattern ............................ 43
  2.10.2 Quadrupole Split Central Transition Line Powder Pattern .... 44

CHAPTER 3. EXPERIMENTAL DETAILS ........................................... 48
  3.1 NMR coil configurations .................................................... 48
  3.2 Superconducting Magnets .................................................. 49
  3.3 The NMR Spectrometer ..................................................... 50
    3.3.1 What happens inside the receiver .................................. 53
  3.4 $T_1$ fitting functions ....................................................... 56
  3.5 NMR under hydrostatic pressure ....................................... 57

CHAPTER 4. COEXISTENCE OF ANTFERROMAGNETIC AND FERROMAGNETIC
SPIN CORRELATIONS IN SrCo$_2$As$_2$ REVEALED BY $^{59}$Co AND $^{75}$As NMR ....... 60
  4.1 Abstract ........................................................................ 60
  4.2 Introduction ..................................................................... 61
  4.3 Results ........................................................................... 62
  4.4 Conclusions ..................................................................... 70
  4.5 Acknowledgments ............................................................ 70
CHAPTER 5. COMPETING MAGNETIC FLUCTUATIONS IN IRON PNICTIDE SUPERCONDUCTORS ................................................................. 72
  5.1 Abstract .............................................................................................................. 72
  5.2 Introduction ......................................................................................................... 72
  5.3 Results ............................................................................................................... 74
  5.4 Conclusions ....................................................................................................... 81
  5.5 Acknowledgments ............................................................................................. 81

CHAPTER 6. KFe$_2$As$_2$: PRESSURE DEPENDENCE OF COHERENCE—INCOHERENCE CROSSOVER BEHAVIOR OBSERVED BY RESISTIVITY AND $^{75}$As-NMR/NQR . . 82
  6.1 Abstract .............................................................................................................. 82
  6.2 Introduction ......................................................................................................... 83
  6.3 Experimental Details .......................................................................................... 85
  6.4 Results and Discussion ....................................................................................... 87
    6.4.1 $T_c$ and critical pressure ............................................................................... 87
    6.4.2 NMR spectrum ............................................................................................ 87
    6.4.3 Crossover temperature $T^*$ ......................................................................... 91
    6.4.4 NQR Spin-Lattice Relaxation Rate ............................................................... 96
  6.5 Conclusions ....................................................................................................... 103
  6.6 Acknowledgments ............................................................................................. 104

CHAPTER 7. NMR EVIDENCE FOR STATIC LOCAL NEMATICITY AND ITS COOPERATIVE INTERPLAY WITH LOW-ENERGY MAGNETIC FLUCTUATIONS IN FeSe UNDER PRESSURE ................................................................. 106
  7.1 Abstract .............................................................................................................. 106
  7.2 Introduction ......................................................................................................... 106
  7.3 Results ............................................................................................................... 108
  7.4 Conclusions ....................................................................................................... 116
  7.5 Acknowledgements .......................................................................................... 116
# 7.6 Supplemental Information

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.6.1 Experimental Details</td>
<td>116</td>
</tr>
<tr>
<td>7.6.2 Ambient Pressure Results</td>
<td>118</td>
</tr>
<tr>
<td>7.6.3 Single Lorentzian fit results</td>
<td>120</td>
</tr>
<tr>
<td>7.6.4 In-plane anisotropy of spectrum splitting</td>
<td>120</td>
</tr>
<tr>
<td>7.6.5 Additional Data</td>
<td>121</td>
</tr>
</tbody>
</table>

## CHAPTER 8. CORRELATION BETWEEN SUPERCONDUCTIVITY AND MAGNETIC FLUCTUATIONS IN FeSe$_{1-x}$S$_x$ REVEALED BY $^{77}$Se NMR

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1 Abstract</td>
<td>124</td>
</tr>
<tr>
<td>8.2 Introduction</td>
<td>124</td>
</tr>
<tr>
<td>8.3 Results</td>
<td>126</td>
</tr>
<tr>
<td>8.4 Conclusions</td>
<td>133</td>
</tr>
<tr>
<td>8.5 Acknowledgements</td>
<td>134</td>
</tr>
<tr>
<td>8.6 Supplementary Information</td>
<td>134</td>
</tr>
<tr>
<td>8.6.1 Sample growth and characterization</td>
<td>134</td>
</tr>
<tr>
<td>8.6.2 Methods</td>
<td>136</td>
</tr>
<tr>
<td>8.6.3 Additional data</td>
<td>139</td>
</tr>
</tbody>
</table>

## CHAPTER 9. CONCLUSIONS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
</table>

## BIBLIOGRAPHY

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
</table>

## APPENDIX A. FORM FACTOR CALCULATION FOR KORRINGA RATIO ANALYSIS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.1 Introduction</td>
<td>169</td>
</tr>
<tr>
<td>B.2 Application to Aluminum</td>
<td>173</td>
</tr>
<tr>
<td>B.3 Application to KFe$_2$As$_2$</td>
<td>174</td>
</tr>
</tbody>
</table>

## APPENDIX B. CALCULATION OF $1/T_1$ IN THE SUPERCONDUCTING STATE

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
</table>

## APPENDIX C. FeSe ADDITIONAL RESULTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1</td>
<td>Unit cells for prototypical parent compounds. Red: Fe atoms. Gold: As/Se atoms. Blue: Sr atoms. Green: La atoms. Gray: O atoms. Credit: [17]...4</td>
</tr>
<tr>
<td>Figure 1.2</td>
<td>Phase diagram of hole- and electron-doped BaFe$_2$As$<em>2$. (a) The hole-doped series Ba$</em>{1-x}$K$_x$Fe$_2$As$_2$. Superconductivity persists all the way to $x = 1$ (KFe$_2$As$<em>2$). (b) The electron-doped series Ba(Fe$</em>{1-x}$Co$_x$)$_2$As$_2$. For $x &gt; 0.12$, superconductivity is gone. “AF”/“AFM”: Antiferromagnetic order. “O/Ort”: Orthorhombic. “Tet”: Tetragonal. Credit: [22]...6</td>
</tr>
<tr>
<td>Figure 1.3</td>
<td>(a) Schematic electronic band structure showing hole-like bands at $\Gamma$ and electron-like bands at $M$. (b) Fermi surface of BaFe$<em>2$(As$</em>{0.7}$P$<em>{0.3}$)$<em>2$. The Brillouin zone shown is correct for the body-centered tetragonal 122 structure. However, the letters $\Gamma$, $M$, $Z$ and $A$ (denoting particular wavevectors) refer to the Brillouin zone of a primitive tetragonal lattice. The inconsistency (and confusion) of notation in the literature has been pointed out by Johnston [16]. The M point should be understood as corresponding to the wavevector $\mathbf{q} = (\pi/a_T, \pi/a_T, 0)$, where $a_T$ is the lattice constant of the BCT 122 structure. The notation used in the figure $\mathbf{q} = (\pi/a</em>{Fe}, 0, 0)$ refers to the 2D Fe square lattice of side $a</em>{Fe} = a_T/\sqrt{2}$, oriented at a 45° angle relative to the tetragonal $a$ axis. Credit: [21]...6</td>
</tr>
<tr>
<td>Figure 1.4</td>
<td>The stripe-type AFM phase of prototypical FeAs parent compounds. The magnetic moments on the Fe sites form a pattern of FM stripes (shading), which are AFM aligned along the perpendicular direction. Red: Fe atoms. Gold: As/Se atoms. Credit: [17]...8</td>
</tr>
</tbody>
</table>
Figure 1.5 Depiction of the orthorhombic distortion and structural twin domains in the magnetic ordered phase. The structure shown is schematic and does not exactly represent the true crystal structure, but is simplified to emphasize the orthorhombic distortion. (a) The high-temperature tetragonal phase. (b) The twinned orthorhombic state. Different colors represent the different domains. Note that the orthorhombic unit cell is rotated by 45° relative to the tetragonal unit cell. (c) De-twinning by external force (purple arrows) along the tetragonal [110] direction. Favorably aligned domains (those with shorter $b_O$ axis along the direction of the applied force) expand and unfavorably aligned domains contract. In contrast, force applied along the tetragonal [100] direction does not de-twin the sample, as depicted in (b).

Credit: [26]

Figure 1.6 Magnetic susceptibility in paramagnetic and nematic phases. The magnetic susceptibility $\chi$ measures the amplitude of the fluctuations of the magnetic order parameter, i.e. $\chi(Q_X) \sim \langle M_X^2 \rangle / k_B T$. In the tetragonal paramagnetic phase $\langle M_X^2 \rangle = \langle M_Y^2 \rangle$ thus $\chi(Q_X) = \chi(Q_Y)$. In the nematic phase, however, $\chi(Q_X) \neq \chi(Q_Y)$. The magnetic fluctuations break the tetragonal symmetry.

Credit: [32]

Figure 1.7 The stripe-type magnetic structure can be viewed as two interpenetrating Néel-type sublattices with order parameters $M_1$ and $M_2$ (green and yellow). The nematic order parameter can be expressed as $\phi = \langle M_1 \cdot M_2 \rangle$, the correlation function of the two sublattices.

Credit: [32]
Figure 1.8  (a) 2D depiction of an isotropic $s$-wave gap as in BCS superconductors. (b) Nodal $d$-wave gap as in high-$T_c$ cuprate superconductors. In the $d$-wave case, the gap phase changes sign on different regions of the Fermi surface. These regions are separated by nodes where the gap is zero. (c) The $s_{\pm}$ gap proposed for Fe-based SCs. The gap has a different sign on different Fermi surface branches, but no nodes. Credit: [29] .......................... 17

Figure 1.9  Comparison of the electronic density of states $N(E)$ as function of energy for a full gap (left) and a nodal gap (right). Here, the Fermi energy is defined as zero ($E_F = 0$). .......................... 18

Figure 1.10  The superconducting gap magnitude (color scale) on the Fermi surfaces of BaFe$_2$(As$_{1-x}$P$_x$)$_2$ and Ba$_{1-x}$K$_x$Fe$_2$As$_2$, as determined by ARPES experiments. The gap magnitude is generally different on each Fermi surface sheet. While Ba$_{1-x}$K$_x$Fe$_2$As$_2$ has isotropic, nodeless gaps (apart from a small $k_z$ dependence), BaFe$_2$(As$_{1-x}$P$_x$)$_2$ features a unique circular line node on the $\alpha$ band. Credit: [44] .......................... 19

Figure 2.1  Energy levels for a nucleus with spin $I = 1/2$ in a magnetic field. The spacing between energy levels is $\Delta E = \gamma \hbar H_{\text{mic}} = \hbar \omega_L = hf_L$. Credit: [45] ... 25

Figure 2.2  The RF field $H_1$ perpendicular to the static external field is applied by wrapping the sample in a coil whose axis is perpendicular to the external field and passing an RF current through the coil. Credit: [46] ............... 26

Figure 2.3  The effect of the field $H_1$ is to rotate the magnetization away from the $z$ axis, by precessing about the $x$ axis. A precession by $\pi/2$ radians is called a “$\pi/2$ pulse”. Credit: [46] .......................... 26
Figure 2.4  Formation of the spin echo. (a) Initial $\pi/2$ pulse puts spins in phase along $y$ axis. (b) De-phasing of nuclear Larmor precessions. (c) A $\pi$ pulse causes a rotation of spins about $x$ axis by $\pi$ radians. (d) Nuclear spins now re-phase. (e) The spin echo, where spins are again completely in phase. (f) Another de-phasing after the spin echo. At time $\tau_2$ passes between the $\pi/2$ (a) and $\pi$ (c) pulses. A time $2\tau_2$ passes between the initial $\pi/2$ pulse and the spin echo formation. Credit: [46] .

Figure 2.5  FID and spin echo signals due to the $\pi/2$–$\pi$ pulse sequence. The high frequency sine wave represents the Larmor (carrier) frequency. The FID decays with time constant $T_2^*$. The spin echo consists of back-to-back copies of the FID (growing and then decaying), both with time constant $T_2^*$. The maximum intensity of the spin echo decays according to time constant $T_2 \gg T_2^*$. Credit: [48] .

Figure 2.6  Imaginary part $\chi''(E)$ of the dynamical magnetic susceptibility in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ with $x = 0.075$ (near optimal doping). NMR $1/T_1 T$ measures $\frac{d\chi''(E)}{dE}|_{E=0}$, the slope at low temperature, which is clearly greatest at $T = 60$ K. The data for $T = 4$ K (below $T_c = 25$ K for this sample) show the neutron spin resonance mode and corresponding low-energy gap below 2.5 meV. Credit: [40] .

Figure 2.7  NQR energy levels and NQR spectrum for a nucleus with $I = 5/2$ ($h = 1$). Credit: [46] .

Figure 2.8  NMR spectrum with quadrupole perturbation for $I = 3/2$ nucleus, showing a central transition and two quadrupole satellites. In this example, the $m = \pm 1/2$ energy levels are lowered, while the $m = \pm 3/2$ energy levels are raised. Credit: [46] .
Figure 2.9  $|u|$ as a function of $\nu$ for the quadrupole split central transition line in a powder sample. Here, for illustration, $\nu_L = 10$ and $\nu_Q = 3$. The lower blue branch takes the minus sign in Eq. 2.52. The upper orange branch takes the plus sign in Eq. 2.52. The frequency range is between $\nu_L - \frac{\nu_Q^2}{3\nu_L}$ and $\nu_L + \frac{3\nu_Q^2}{16\nu_L}$.

Figure 2.10  NMR spectrum in a powder sample with quadrupole effects ($I = 3/2$). Here, for illustration, $\nu_L = 10$ and $\nu_Q = 3$. Top: Zoom of the central transition line. The high frequency peak corresponds to $\theta = 90^\circ$, while the low frequency peak corresponds to $\theta = 41.8^\circ$. The frequency range is again between $\nu_L - \frac{\nu_Q^2}{3\nu_L}$ and $\nu_L + \frac{3\nu_Q^2}{16\nu_L}$. Bottom: Full NMR spectrum including satellite lines. The two peaks in the satellite spectrum both correspond to $\theta = 90^\circ$.

Figure 3.1  NMR coil tank circuits. (a) Parallel tuned series matched. (b) Series tuned parallel matched. (c) Pickup coil.

Figure 3.2  Block diagram of the NMR spectrometer. See §3.3.1 for an explanation of $f_{\text{ref}}$ and the 750 MHz intermediate frequency.

Figure 3.3  The basic principle of quadrature ("phase-sensitive") detection using RF mixers (circle with cross). Low pass filters remove the $f_{\text{ref}} + f_L$ Fourier component emerging from the mixer.

Figure 3.4  Practical implementation of a homodyne quadrature NMR receiver. A frequency band selection switch is needed. BPF: Band-pass filter.

Figure 3.5  Heterodyne quadrature NMR receiver. All signals are mixed into the intermediate frequency (IF = 750 MHz) band. No band selection switch is needed. BPF: Band-pass filter.
Figure 3.6  Left panel: Schematic of the hybrid CuBe-NiCrAl piston-cylinder clamp cell used for high pressure NMR measurements. (WC: Tungsten Carbide.) Right panel: Phase diagram of the pressure medium Daphne 7373. Credit: [55; 56] ................................. 59

Figure 4.1 (Color online) (a) Field-swept $^{59}$Co-NMR spectra at frequency $f = 66.3$ MHz for magnetic fields $H \parallel c$ axis (black) and $H \parallel ab$ plane (red) to at various values of $T$. The vertical dashed line represents the zero-shift position ($K = 0$). (b) $T$ dependence of the $^{59}$Co-NMR shifts $K_c$ and $K_{ab}$. The black and red dashed lines are corresponding to $K_0$ for $K_c$ and $K_{ab}$, respectively. Inset: $K$ vs $\chi$ plots for each field direction where we used $\chi$ data reported in Ref. [66]. The thick solid lines are fitting results and two thin lines above and below the thick line give an error for our estimate of $K_0$ for each $H$ direction. (c) $T$ dependence of the full width at half maximum (FWHM) of the spectra for each field direction. ...................... 63

Figure 4.2 (Color online) $T$ dependence of $1/T_1$ for both magnetic field directions, $H \parallel c$ axis [$1/(T_1 T)_{H\parallel c}$] and $H \parallel ab$ plane [$1/(T_1 T)_{H\parallel ab}$]. Inset: Recovery curves at $T = 2.4$ K for both $H$ directions. The solid lines are fits by the relaxation function described in the text. ......................... 64

Figure 4.3 (Color online) Top panel: $T$ dependence of the Korringa ratios $1/T_{1,\perp}TK_{spin,ab}^2$ (red) and $1/T_{1,\parallel}TK_{spin,c}^2$ (black) for spin correlations in the $ab$ plane and along the $c$ axis, respectively. The solid lines are guides to the eye. Lower panel: $T$ dependence of the parameter $\alpha_{\perp}$ for spin correlations in the $ab$ plane (red) and $\alpha_{\parallel}$ along the $c$ axis (black). ......................... 66

Figure 4.4 (Color online) (a) $T$ dependence of the $^{75}$As NMR shift for both field directions in SrCo$_2$As$_2$ (black) and BaCo$_2$As$_2$ (red) [83]. (b) $T$ dependence of $1/T_1 T$ at the $^{75}$As sites for both field directions in SrCo$_2$As$_2$ (black) and BaCo$_2$As$_2$ (red). ......................... 67
Figure 4.5 (Color online) Top panel: $T$ dependence of the Korringa ratios $1/T_{1,\perp}TK_{\text{spin,ab}}^2$ (open symbols) and $1/T_{1,\parallel}TK_{\text{spin,c}}^2$ (closed symbols) for spin correlations in the $ab$ plane and along the $c$ axis, respectively, for SrCo$_2$As$_2$ (black) and BaCo$_2$As$_2$ (red). Lower panel: $T$ dependence of $\alpha_{\perp}$ and $\alpha_{\parallel}$ for SrCo$_2$As$_2$ and BaCo$_2$As$_2$. .................................................. 69

Figure 5.1 (Color online) (a) $T$ dependence of the NMR shift $K$ for a variety of indicated samples. (b) $T$ dependence of NMR spin-lattice relaxation rate $1/T_1T$ for the same samples. Here, and throughout, filled (open) symbols are used for $H_{\parallel\text{ab}}$ ($H_{\parallel\text{c}}$). (c) $K_i(T)$ vs. $\chi_i(T)$ ($i = ab, c$) for a variety of samples. Data are from Refs. [51; 103; 38; 104; 69; 61; 60; 105]. For KFe$_2$As$_2$, $K_c$ is nearly $T$ independent making a $K$ vs. $\chi$ analysis impossible. From the relative values of $K_{ab}$ and $K_c$, we estimate $K_{0,c} \sim 0.21\%$. For BaFe$_2$As$_2$, $K_{0,ab} = 0.14\%$ and $K_{0,c} = 0.21\%$ are from Ref. [38]. For the 8% Co doped sample, $K_{0,c} = 0.22\%$ from Ref. [51]. .................................................. 75

Figure 5.2 (Color online) (a) Korringa ratios $\alpha_{\perp}$ (filled symbols) and $\alpha_{\parallel}$ (open symbols) as a function of $T$ in a variety of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ and Ba$_{1-x}$K$_x$Fe$_2$As$_2$ samples. (b) Same for intraband Korringa ratios $\alpha_{\text{intra,\parallel}}$ and $\alpha_{\text{intra,\perp}}$, obtained by subtracting the interband (Curie-Weiss) contributions. .................................................. 77

Figure 5.3 (Color online) (a),(b): Competing sources of hyperfine field fluctuations along the $c$ axis. (c),(d): Competing sources of hyperfine field fluctuations in the $ab$ plane. Competition between (a) and (b) [(c) and (d)] determines the value of $\alpha_{\parallel}$ ($\alpha_{\perp}$). .................................................. 78
Figure 5.4 (Color online) Potential relevance of FM spin fluctuations to iron pnictide phase diagram: (a) Doping dependence of the nearly $T$-independent values of $\alpha^{\text{intra}}_{\parallel}$ and $\alpha^{\text{intra}}_{\perp}$, which parameterize the strength of FM fluctuations [106]. We also show the doping dependence of the Curie-Weiss parameters $C_{\perp}$ and $C_{\parallel}$, which parameterize the strength of 2D AFM fluctuations. (b) The doping dependence of the Curie-Weiss temperature $\Theta_{\text{CW}}$. Solid lines are guides to the eye. 

Figure 6.1 Superconducting transition temperature $T_c$ as a function of pressure determined by onset of Meissner effect measured by in situ ac-susceptibility. $p_c \sim 1.8$ GPa marks the critical pressure where $T_c$ changes slope. Previously reported data are shown for comparison: Terashima et al. Ref. [118]; Wang et al. Ref. [108]; Tafti et al. Ref. [117]; Taufour et al. Ref. [119]; Grinenko et al. Ref. [139]. Inset shows the typical temperature dependence of the change in the NMR coil tank circuit resonance frequency, $\Delta f$, under different pressures.

Figure 6.2 Representative field-swept $^{75}$As NMR spectrum of KFe$_2$As$_2$ powder measured at $T = 10$ K and $p = 1.9$ GPa. The central transition line is split into two lines by the second order quadrupole effect. $\theta$ is the angle between the external field and the principal axis of the electric field gradient (see text). The red curve is a simulated powder spectrum with $\nu_Q = 12.66$ MHz.

Figure 6.3 Nuclear quadrupole resonance (NQR) frequency as a function of temperature for indicated pressures. Upper inset: Representative NQR spectrum at $p = 2.1$ GPa and $T = 4.2$ K, shown with a Lorentzian fit. Lower inset: NQR frequency as a function of pressure at $T = 4.2$ K. Lines are guides to the eye.
Figure 6.4  NMR shift with external field aligned in the \(ab\) plane (\(K_{ab}\)) for indicated pressures. The dashed lines are guides to the eye. The arrows represent the crossover temperature \(T_{\text{NMR}}^*\) as determined by NMR \(1/T_1\) measurements (see text and Fig. 6.5). The horizontal bars denote the uncertainty in estimation of \(T_{\text{NMR}}^*\) (±20 K). 92

Figure 6.5  NMR spin-lattice relaxation rate \(1/T_1\) as a function of temperature. The coherence/incoherence crossover temperature \(T_{\text{NMR}}^*\) is found by the change of slope of \(1/T_1\). The uncertainty in estimation of \(T_{\text{NMR}}^*\) is ±20 K (see text). 93

Figure 6.6  (a) Resistivity of KFe\(_2\)As\(_2\) single crystals [119] for selected pressures. (b) Resistivity plotted as a function of \(T/t^*\) where the scaling coefficient \(t^*\) is chosen so as to merge each curve with the ambient pressure curve. For ambient pressure, \(t^* \equiv 1\). Upper inset: pressure dependence of the unitless scaling factor \(t^*\). Lower inset: Comparison of pressure dependence of \(T^*\) as measured by resistivity (\(T_R^*\); filled symbols) and NMR (\(T_{\text{NMR}}^*\); open symbols). For resistivity \(T_R^* = (157 \text{ K})t^*\), where \(T_R^*\) at 0 GPa is determined by the crossing of two tangent lines, as proposed in Ref. [127] (see text). 94

Figure 6.7  Plot of \(T_c\) vs \(T^*\) for AFe\(_2\)As\(_2\) (\(A = \text{K, Rb, Cs}\)) family at ambient pressure [127] (black). The orange arrow illustrates the increase of chemical pressure from CsFe\(_2\)As\(_2\) to KFe\(_2\)As\(_2\). The green data plots \(T_c\) vs \(T^*\) for KFe\(_2\)As\(_2\) with indicated pressure as an implicit parameter, using \(T_{\text{NMR}}^*\) extracted from NMR measurements (see Fig. 6.5). Similarly, the red data shows \(T_c\) vs \(T^*\) for KFe\(_2\)As\(_2\) using \(T_R^*\) extracted from resistivity measurements (see Fig. 6.6). 97

Figure 6.8  NQR \(1/T_1T\) above \(T_c\) for various pressures. The solid red curve for ambient pressure is a power law fit (see text). Inset: The value of NQR \(1/T_1T\) at 4.2 K as a function of pressure. 98
Figure 6.9  $T$ dependence of the ratio $R \equiv T_{1,c}/T_{1,ab}$ for different pressures where NQR-$T_1$ data are used for $T_{1,c}$, in addition to $R$ obtained from $T_{1,c}/T_{1,ab}$ at ambient pressure from Ref. [69]. NQR $1/T_1$ above $T_c$ for various pressures. The inset shows the $T$ dependence of $1/T_1$ for $H||c$ and $H||ab$ from Ref. [69], together with NQR $1/T_1$ data.

Figure 6.10 NQR $1/T_1$ for indicated pressures. The arrows denote $T_c$ at each pressure. The dashed lines are power law fits to the PM state data for each pressure. The red solid line below $T_c$ shows the power law with $1/T_{1S} \propto T^{1.3}$ at ambient pressure. Below $T \sim 1$ K, a component with long $T_1$ appears. The solid pink line represents $1/T_{1L} \propto T^2$ behavior. Upper inset: The typical two exponential behavior (black squares) of the nuclear magnetization recovery curve observed at low temperature ($T = 0.4$ K; $p = 1.5$ GPa), together with a single exponential behavior (red circles) at $T = 3.73$ K and $p = 1.5$ GPa. Lower Inset: Fraction $A$ of nuclei relaxing with the short $T_1$ (see text).

Figure 7.1  Representative NMR spectra at indicated $T$ for all measured pressures. The two peaks arise from inequivalent nematic domains with $H||a$ and $H||b$. The solid red line is the bulk $T_s$, as determined by a kink in the NMR shift (see Fig. 7.2). The dashed blue line is $T_N$ and the dot-dash dark yellow line is $T_c$. $T_N$ and $T_c$ were determined from data shown in in [171]. The colors of the spectra correspond to different phases: black for the paramagnetic state, dark yellow for below $T_c$, blue for below $T_N$, and red for the bulk nematic ordered state.
Figure 7.2  Upper panels: NMR shift $K$ as a function of $T$ as obtained from a two-Lorentzian fit for indicated pressures. Orange triangles and teal circles represent $K_a$ and $K_b$, while the black squares are the average of the two, $K_{\text{avg}}$. The black vertical lines indicate the corresponding bulk $T_s$ for each pressure. $T_c$ and $T_N$ for different pressures are also shown by the vertical broken lines. Lower panels: Full-width-at-half-maximum (FWHM) of NMR spectral peaks for two $ab$ plane orientations: $\theta = 0^\circ$ (filled symbols) and $\theta \sim 25^\circ$ (open symbols). Below $T_s$, the FWHM of each of the two peaks is shown separately. The low-frequency peak (teal) has consistently greater FWHM than the high-frequency peak (orange). Above $T_s$ the FWHM of a single-peak model is shown (black). Arrows denote $T_{\text{FWHM}}^*$.  

Figure 7.3  $T$ dependence of $\Delta K$ for the indicated pressures. $\Delta K$ is a measure of the local nematic order parameter. The dashed vertical lines indicate the bulk $T_s$.  

Figure 7.4  $\sqrt{1/T_1 T}$ versus $K(T)$ plot with $T$ as an implicit parameter for indicated pressures. $T_{\text{spin}}^*$, the onset of low-energy spin fluctuations, is determined by the deviation of the data from high-$T$-linear behavior shown by solid lines (see text). Bulk $T_s$ is indicated for comparison.  

Figure 7.5  Phase diagram of pressurized FeSe incorporating microscopic details of the paramagnetic phase as revealed by NMR.  

Figure 7.6  (Color online) Representative recovery curves at $p = 0.5$ GPa. Single component behavior is observed even at 25 K, deep in the nematic ordered state.  

Figure 7.7  (Color online) Upper panel: NMR shift at ambient pressure. Lower panel: FWHM at ambient pressure. Orange: high frequency peak. Teal: low-frequency peak. Black: Average of two peaks, below $T_s$; single peak, above $T_s$.  

References: 

111

112

114

115

117

118
Figure 7.8 (Color online) Upper panel: Coefficient of determination $R^2$ for a single-peak-model fit of the NMR spectrum as a function of temperature. At high temperature, we find that $R^2$ is nearly independent of temperature (dotted horizontal line). Deviation from this temperature-independent behavior is observed at low $T$ due to the appearance of two resolvable peaks in the spectrum (see text). Vertical dashed lines indicate the bulk $T_s$. Lower panels: Detail of the $R^2$ results above $T_s$ (indicated by vertical lines). Dotted horizontal lines denote an average of the $R^2$ values between 100 K and 200 K.

Figure 7.9 NMR spectral splitting $\Delta K$ as a function of $T$ with the external magnetic field applied in the $ab$ plane at an angle $\theta \sim 25^\circ$ from the $[110]$ direction of the tetragonal phase, with the 0.5 GPa data at $\theta \sim 0^\circ$ for comparison.

Figure 7.10 (Color online) NMR shift showing the full range of $K$ values up to room temperature. $K$ decreases monotonically in contrast to the increase of FWHM.

Figure 7.11 $^{77}$Se spin-lattice relaxation rate divided by temperature, $1/T_1 T$, for indicated pressures.

Figure 7.12 NMR coil tank circuit resonance frequency $f$ as a function of $T$ for all pressures (see text). Data are offset vertically for clarity.

Figure 8.1 Representative NMR spectra with $H||ab$ (upper panels) and $H||c$ (lower panels) at $T = 20$ K (unless otherwise specified) for indicated S concentrations $x$.

Figure 8.2 $T$ dependence of the NMR shift $K$ for indicated S concentrations $x$ for external fields $H||ab$ (filled symbols) and $H||c$ (open symbols). Inset: Splitting $\Delta K$ of the $H||ab$ NMR spectrum due to twinned nematic domains. Vertical lines represent $T_s$ determined by resistivity measurements [198]. Arrows in inset represent $T_c(H)$ determined by in situ ac-susceptibility [198].
Figure 8.3  

$T$ dependence of NMR spin-lattice relaxation rate $1/T_1 T$ for $H || ab$ (upper panel) and $H || c$ (lower panel) for indicated $S$ concentrations $x$. Arrows denote observed $T_c(H)$ as determined from $in situ$ ac-susceptibility [198] (not shown for $x = 0\% H || ab$). For $S$-doped samples, missing arrows indicate $T_c(H) < 4.0 \, K$. Inset: The $T$ dependence of the anisotropy ratio $R = T_{1,c}/T_{1,ab}$ above $T_c$ (see text). Data for $x = 0\%$ ($ab$ plane average $1/T_1 T$ and ratio $R$ at $H = 9 \, T$) are from Ref. [164]. Data for $x = 0\%$ ($H || c$ at $H = 7 \, T$) are from Ref. [209].

Figure 8.4  

Comparison of $1/T_1 T$ (left axes, filled symbols) with $CK^2_{spin}$ (right axes, open symbols) for indicated doping levels. The upper panels compare $1/T_{1,||} T$ to $CK^2_{spin,c}$, while the lower panels compare $1/T_{1,+} T$ to $CK^2_{spin,ab}$ (see text). The empirical value of $C$ (in units of $10^4 \, s^{-1} K^{-1}$) for each panel is indicated (see [198]).

Figure 8.5  

(a) Band dispersion of pure FeSe in the tetragonal phase, with bands of $d_{xy}$ orbital character indicated. (b) Cross-sections of the Fermi surface in the tetragonal phase at $k_z = 0$ for $x = 0\%$ (red) and $x = 9\%$ (blue). (c) Comparison of AFM fluctuations in pure FeSe under pressure [199] (left panel) and the FeSe$_{1-x}S_x$ system (right panel). Here, the AFM contribution to $1/T_1 T$ is defined by $(1/T_1 T)_AFM \equiv (1/T_1 T) - (1/T_1 T)_{q=0}$ using $H || ab$ data [198]. Solid lines show $T_s$ (orange), $T_N$ (green) and $T_c$ (red) determined from resistivity [161; 157; 204; 194]. Data points show $T_s$, $T_N$ and $T_c(H)$ from NMR (this work and [199]).

Figure 8.6  

Change of $a$- and $c$-axis lattice parameters of FeSe$_{1-x}S_x$ with sulfur content $x$ from room-temperature powder diffraction data. For each batch shown as a full symbol, $x$ was determined by energy-dispersive x-ray spectroscopy (EDS). Open symbols have been placed by interpolating both $a$ and $c$ lattice parameters. Literature data from Ref. [195] has been added for comparison.
Figure 8.7  Phase diagram of FeSe$_{1-x}$S$_x$. The samples investigated by NMR in the main paper are highlighted by full symbols.

Figure 8.8  Electrical resistance of the investigated FeSe$_{1-x}$S$_x$ samples normalized at room temperature. A single sample with $x = 0.09$, 4 samples with $x = 0.15$ and a collection of $\sim 30$ samples with $x = 0.29$ were studied by NMR. For this highest sulfur content, the resistance of two representative samples is shown. For comparison, the resistance of an undoped FeSe single crystal [173] is added. The upper inset shows the temperature derivative which is used to define $T_s$, the lower inset shows the low-temperature resistance on a magnified scale. $T_c$ is defined as the zero-resistance temperature.

Figure 8.9  In situ ac-susceptibility $\chi_{ac}$ measurement of $T_c$. The NMR coil tank circuit resonance frequency $f$ is a measure of $\chi_{ac}$ since $f = 1/\sqrt{L_0(1+\chi_{ac})C}$. Small arrows denote $T_c$ as determined by the intersection of two linear trends (black lines). For $x = 15\%$ $H||c$, $T_c$ is not observed above $T = 4.0$ K. Data have been shifted vertically for clarity. Data for different samples have been obtained using different NMR coils, therefore the magnitude of the jump below $T_c$ cannot be directly compared.

Figure 8.10  Contour plot of AFM fluctuations in FeSe$_{1-x}$S$_x$. Here we define $(1/T_1T)_\text{AFM} \equiv (1/T_1T)_\parallel - CK_{\text{spin.c}}^2$ in contrast to the main paper.

Figure 8.11  NMR shift with $H||ab$ in pure FeSe under pressure.

Figure 8.12  $K$ vs $\chi$ plot analysis for $x = 0$, $x = 15\%$ and $x = 29\%$.

Figure B.1  Superconducting density of states functions $N_s(E)$ (left) and $M_s(E)$ (right). Here, the Fermi energy is defined as zero ($E_F \equiv 0$). The integrals in Eqs. B.4 and B.5 have been integrated numerically using $\Delta = 2$ and $\sigma_a = \sqrt{\langle a^2 \rangle} = 0.05$ for a Gaussian distribution $P(a)$ (illustrated in Fig. B.2).

Figure B.2  Gaussian and simplified (Eq. B.6) broadening functions. For the Gaussian, $\sigma_a = 0.05$ and we plot $P_{10}(a)$ for the simplified form.
Figure B.3  Superconducting density of states functions $N_s(E)$ (left) and $M_s(E)$ (right). Here, the Fermi energy is defined as zero ($E_F \equiv 0$). The integrals in Eqs. B.4 and B.5 have been integrated analytically using $\Delta = 2$ and $n = 10$ for $P(a)$ given by Eq. B.6.

Figure B.4  Superconducting gap as a function of temperature for Aluminum ($T_c = 1.2$ K). The value of the maximum gap shown is the best fit value of $\Delta_0 = 0.165$ meV, for which $2\Delta_0 = 3.2k_BT_c$, which differs slightly from the BCS prediction [50; 212].

Figure B.5  Temperature dependence of $1/T_1$ in the superconducting state of Aluminum. The experimental data points are from [212]. The parameters in Eq. B.14 are $A = 35$, $n = 10$, $T_c = 1.2$ K and $\Delta_0 = 0.165$ meV. The integral is evaluated numerically from analytical expressions for $N_s$ and $M_s$ (Eqs. B.7, B.8).

Figure B.6  Density of states $N_s(E)$ for a nodal superconducting gap with $\Delta_k = \Delta \cos(2\phi)$. Here, the Fermi energy is defined as zero ($E_F \equiv 0$). Shown for $\Delta = 2$.

Figure B.7  Left: Total two-nodal gap density of states in a model for KFe$_2$As$_2$. Right: Temperature dependence of $1/T_1$ assuming the density of states on the left. Data from Ref. [110]. The parameters in Eq. B.18 are $A = 140$, $\Delta_1 = 0.602$ meV, $\Delta_2 = 0.07$ meV, $f_1 = 0.45$, $f_2 = 0.55$ and $T_c = 3.5$ K.

Figure B.8  Left: Total two-full gap (broadening parameter $n = 5$ in Eq. B.7) density of states in a model for KFe$_2$As$_2$. Right: Temperature dependence of $1/T_1$ assuming the density of states on the left. The other parameters are the same as in Fig. B.7.

Figure B.9  Left: A single nodal gap with $\Delta_1 = 0.602$ meV ($f_1 = 1$, $f_2 = 0$, $A = 70$). Right: A single nodal gap with $\Delta_2 = 0.07$ meV ($f_1 = 0$, $f_2 = 1$, $A = 70$).
Figure C.1  The FWHM of a single-Lorentzian fit to the NMR spectrum with $H_{\parallel [110]}$ tetragonal (filled symbols) and with the crystal rotated by $\theta = 25^\circ$ away from $H_{\parallel [110]}$ tetragonal within the $ab$ plane. The arrow denotes $T_{\text{FWHM}}^*$, which is essentially pressure independent. .................................................. 179

Figure C.2  Same as Fig. C.1, but with the vertical axes for $\theta = 0^\circ$ and $\theta = 25^\circ$ scaled by a constant factor (1.78). .................................................. 179
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ABSTRACT

This thesis illustrates the use of the nuclear magnetic resonance (NMR) technique as a local probe for the study of static and dynamic magnetism in the iron-based superconductors.

First, a Korringa ratio analysis of $^{59}$Co and $^{75}$As NMR data reveals the existence of ferromagnetic (FM) spin fluctuations in SrCo$_2$As$_2$ and the hole- and electron-doped BaFe$_2$As$_2$ families of iron-pnictide superconductors. The analysis further shows that the FM fluctuations compete with AFM fluctuations to suppress superconductivity in these materials. The FM fluctuations are thus a crucial ingredient to understanding the variability of the superconducting transition temperature ($T_c$) and the shape of the superconducting dome in these and other iron-pnictide families.

Secondly, a study of KFe$_2$As$_2$ under pressures up to 2.1 GPa reveals a crossover between a high-temperature incoherent, local-moment behavior and a low-temperature coherent behavior at a crossover temperature, $T^*$. The $T^*$ is found to increase monotonically with pressure, consistent with increasing hybridization between localized 3$d$ orbital-derived bands with the itinerant electron bands. No anomaly in $T^*$ is seen at the critical pressure where a change of slope of $T_c(p)$ has been observed. In the superconducting state, two-component nuclear spin-lattice relaxation is observed at low temperatures, suggesting the existence of two distinct local electronic environments.

Finally, $^{77}$Se-NMR studies of FeSe subjected to external pressure and sulfur doping are presented. In pure FeSe under pressure, the NMR spectra reveal the existence of a short-range, local nematic ordered state above the bulk nematic ordering temperature. Furthermore, this local nematic order does not compete with low-energy AFM spin fluctuations. In sulfur-doped FeSe$_{1-x}$S$_x$, the observed behavior of the magnetic fluctuations parallels the $T_c$, providing strong evidence for the primary importance of magnetic fluctuations for superconductivity, despite the presence of nematic quantum criticality in this system.
CHAPTER 1. INTRODUCTION TO IRON-BASED SUPERCONDUCTORS

1.1 Introduction

On 10 July 1908, the Dutch physicist H. Kamerlingh Onnes first succeeded in liquifying Helium. He was subsequently the first to use liquid Helium as a cryogenic refrigerant. Then, on 8 April 1911, while measuring the electrical resistance of pure mercury metal at low temperature, he made an unexpected discovery. He found that the resistivity dropped to an immeasurably small value suddenly when cooled below a temperature of $T_c = 4.1 \text{ K}$ [1]. He recognized that he had observed a phase transition to a new state of matter, which he termed the “superconducting” state.

However, a superconductor is not a mere perfect electrical conductor. The most precise definition the superconducting state is the presence of the Meissner effect [2], the active expulsion of magnetic flux from the interior of the superconductor. If the superconducting state were simply a state of infinite conductivity, one could apply a magnetic field before cooling the material below its $T_c$ and the magnetic flux inside the sample would remain even below $T_c$. In contrast, a superconductor will actively expel the magnetic flux completely in such a case [3]. However, while electromagnetic fields are expelled from the bulk of the superconductor, they can exist a short distance below the surface, known as the penetration depth. It is important to note that the true Meissner state exists only in so-called “Type I” superconductors. In “Type II” superconductors, the Meissner state is observed only for magnetic fields less than $H_{c1}$, while the superconductivity is not destroyed until a field $H_{c2} > H_{c1}$ is applied. Between $H_{c1}$ and $H_{c2}$ (known as the mixed state), magnetic flux penetrates the sample in flux tubes, surrounded by vortices of supercurrent.

With the advent of the famous Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity in 1957 [4], the following physical understanding emerged. The superconducting ground state is a phase-coherent condensate of electron pairs, known as Cooper pairs. The attractive interaction necessary to create the electron-electron bound state is provided by the exchange of lattice phonons.
The superconducting state results in the formation of an energy gap at the Fermi surface, where the gap corresponds to the binding energy of a Cooper pair. As a result of the phonon-based pairing mechanism, the two electrons in each pair have opposite momenta and are in a spin singlet configuration. The Meissner effect is the result of the normally massless photon acquiring a mass inside the superconductor [5; 6; 7]. When the Cooper-pair condensate selects a particular value for its quantum phase, it breaks the local U(1) gauge symmetry of the vacuum, thereby causing the photon (the gauge boson) to acquire a mass via an abelian version of the famous Higgs mechanism. When the photon is massive, the electromagnetic field is no longer a long-range force, but instead operates only on length scales associated with the Compton wavelength of the massive photon. This explains the expulsion of magnetic flux as well as the observed non-zero penetration depth of electromagnetic radiation into the superconductor. The zero resistance property of superconductors is a result of the coherence of the Cooper pair condensate [7; 8; 9]. The movements of the electrons forming the condensate are highly correlated, such that the entire condensate moves as a whole, and it is this object which carries the supercurrent. This collective behavior of the condensate is crucial.

Superconductivity is a common phenomenon. Many metallic elements are superconducting at ambient pressure. The highest ambient pressure $T_c$ for a pure element is 9.3 K in niobium (Nb). Even more elements are superconducting under external pressure. In 1973, superconductivity was discovered in the metallic alloy Nb$_3$Ge with $T_c = 23$ K. This was the highest known $T_c$ at the time, but was well understood in terms of the BCS theory.

The field of superconductivity was revolutionized in 1986 by the discovery of $T_c \approx 38$ K in the ceramic material La$_{2-x}$Ba$_x$CuO$_4$ [10; 11]. Soon after, $T_c \approx 92$ K was observed in YBa$_2$Cu$_3$O$_7$ [12], the first material to show superconductivity above the boiling temperature of liquid nitrogen (77 K). This is significant since the much more expensive liquid helium is not required to produce the superconducting state. The highest $T_c$ at ambient pressure ever observed in these “high-$T_c$ cuprate” materials is 135 K. An important common feature of these materials is the highly two-dimensional character of the well-separated CuO layers. While superconductivity in the cuprates
is also due to the formation of a Cooper-pair condensate, the mechanism for the formation of the Cooper pairs is believed to be different from the BCS superconductors. The parent compounds, for example La$_2$CuO$_4$, are antiferromagnetic Mott insulators, and the high-$T_c$ superconductivity arises when this ordered state is suppressed. This suggests that the Cooper pair formation is mediated by the exchange of antiferromagnetic spin fluctuations, as opposed to lattice phonons [13; 14]. Due to the different pairing mechanism, the Cooper pair wavefunction is also different. In BCS superconductors, the pairs are spin singlets ($S = 0$) with no orbital angular momentum ($L = 0$), termed “$s$-wave” superconductivity. There is strong experimental evidence that the Cooper pairs in the high-$T_c$ cuprates have both $S = 0$ and $L = 2$, termed “$d$-wave” superconductivity [15].

As a consequence of the $d$-wave symmetry of the Cooper-pair wavefunction, the superconducting energy gap at the Fermi surface is forced to be zero at particular wavevectors. These locations in reciprocal space are known as gap “nodes.” In contrast, in BCS superconductors the gap magnitude is constant over the entire Fermi surface.\footnote{Superconductors with $s$-wave symmetry may have gaps which are anisotropic (or even nodal) in reciprocal space. See, for example, Ref. [114].} Despite these advances in the qualitative understanding of the high-$T_c$ cuprate materials, no microscopic theory has emerged which can coherently explain all observations, as the BCS theory has done for conventional superconductors.

The field of high-$T_c$ superconductivity was given new life in 2008 by the discovery of a new class of materials based on iron, showing $T_c$ values up to 56 K [16; 17; 18; 19; 20; 21; 22; 23]. The hope is that by considering the similarities between the two distinct classes of high-$T_c$ superconductors, one may be able to extract the common ingredients which are the most important keys for superconductivity. This new understanding may lead to a coherent theory of high-$T_c$ superconductivity, as well as to the discovery of long-sought room-temperature superconductors. In this context, this introductory chapter gives a basic introduction to the phenomenology of the iron-based superconductors.
1.2 Structure and Phase Diagram

The prototypical parent compounds of the iron-based superconductors are displayed in Fig. 1.1. These include LaFeAsO ("1111"), SrFe$_2$As$_2$ ("122") and FeSe ("11"). These are the structures at room temperature, which all have tetragonal symmetry (a 4-fold rotation axis), with in-plane lattice parameters $a_T = b_T$. The common structural motif of the iron-based superconductors is the quasi-2D Fe-As(Se) layer in the $ab$ plane of the crystal, as emphasized by the shading in the figure. The planes are stacked along the crystal $c$ axis. Since arsenic is a member of the pnictogen family (Group 15 of the periodic table), these compounds are commonly referred to as “iron pnictides.” The 11 compounds are likewise known as iron chalcogenides (Group 16). Within the Fe-As(Se) layer, the Fe atoms are (approximately) tetrahedrally coordinated with four As(Se) atoms. The Fe atoms themselves form a true 2D square lattice of side $a_{Fe} = a_T/\sqrt{2}$, oriented at a 45° angle relative to the tetragonal $a$ axis.

Superconductivity in the 122 and 1111 families is induced by chemical doping or applied pressure. For example, the initial discovery of superconductivity in iron compounds was in the F-doped 1111 compound LaFeAsO$_{1-x}$F$_x$ ($x \sim 0.11$), for which $T_c \approx 26$ K [24]. The typical phase diagram
for the 122 iron-pnictide superconductors is shown in Fig. 1.2. The substitution of Co for Fe adds electrons the Fe-As layer. Similarly substitution of K for Ba creates holes in the Fe-As layer. The parent compound BaFe$_2$As$_2$ is not superconducting but has an antiferromagnetic (AFM) ordered ground state with a transition temperature of $T_N \sim 135$ K. Both hole- and electron-doping gradually decrease $T_N$ and superconductivity arises when magnetic order is almost completely suppressed, but strong fluctuations of the magnetic order parameter (“AFM spin fluctuations”) are still present. These AFM spin fluctuations are believed to give rise to the Cooper pairing in the SC state.

Note also that the AFM phase is also associated with a tetragonal-to-orthorhombic structural distortion below $T_s$. In the hole-doped series, the AFM and structural transitions coincide, as they do in the parent compound. In the electron-doped series, however, the structural transition occurs before the AFM transition, that is $T_s > T_N$. The phase between $T_s$ and $T_N$ is known as the “nematic” phase, and will be discussed later.

As indicated in the phase diagram, there is a region of overlap between the magnetic and superconducting regions. In these regions of the phase diagram, both magnetic and superconducting orders coexist microscopically. However, the two orders compete with one another. Thus, for example, the static ordered moment and accompanying orthorhombic distortion both decrease below $T_c$ [25]. It is important to note that, while the coexistence of SC and AFM is observed in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ and Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ as shown here, such coexistence is not always observed, as in Ca(Fe$_{1-x}$Co$_x$)$_2$As$_2$, for example [211].

### 1.3 Electronic Structure and Fermi Surface

The iron-based superconductors and parent compounds are semi-metals, meaning that the conduction and valence bands overlap one another in energy near the Fermi level, thus leading to free holes in the conduction band (a “hole pocket”) and free electrons in the valence band (an “electron pocket”) even at absolute zero temperature. A schematic band structure of the iron-based superconductors is shown in Fig. 1.3(a). The bands near the Fermi level originate from the hy-
Figure 1.2 Phase diagram of hole- and electron-doped BaFe$_2$As$_2$. (a) The hole-doped series Ba$_{1-x}$K$_x$Fe$_2$As$_2$. Superconductivity persists all the way to $x = 1$ (KFe$_2$As$_2$). (b) The electron-doped series Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$. For $x > 0.12$, superconductivity is gone. “AF”/“AFM”: Antiferromagnetic order. “O/Ort”: Orthorhombic. “Tet”: Tetragonal. Credit: [22]

Figure 1.3 (a) Schematic electronic band structure showing hole-like bands at $\Gamma$ and electron-like bands at M. (b) Fermi surface of BaFe$_2$(As$_{0.7}$P$_{0.3}$)$_2$. The Brillouin zone shown is correct for the body-centered tetragonal 122 structure. However, the letters $\Gamma$, M, Z and A (denoting particular wavevectors) refer to the Brillouin zone of a primitive tetragonal lattice. The inconsistency (and confusion) of notation in the literature has been pointed out by Johnston [16]. The M point should be understood as corresponding to the wavevector $\mathbf{q} = (\pi/a_T, \pi/a_T, 0)$, where $a_T$ is the lattice constant of the BCT 122 structure. The notation used in the figure $\mathbf{q} = (\pi/a_{Fe}, 0, 0)$ refers to the 2D Fe square lattice of side $a_{Fe} = a_T/\sqrt{2}$, oriented at a 45° angle relative to the tetragonal $a$ axis. Credit: [21]
bridization and overlap of the Fe d-orbitals on each Fe site. Conventionally, the bands are labeled with lower-case Greek letters. Hole-like bands are found centered on the wavevectors $\Gamma = (0,0,0)$ while electron-like bands are centered on $M = (\pi/a_T, \pi/a_T, 0)$.

The first Brillouin zone for a 122 compound, which has a body-centered tetragonal (BCT) crystal structure (Fig. 1.1), is shown in Fig. 1.3(b). In contrast, the 11 and 1111 compounds have a primitive tetragonal (PT) crystal structure and the first Brillouin zone therefore has a simpler geometry. The Fermi surface is shown inscribed within the Brillouin zone. The Fermi surface consists of roughly cylindrical hole and electron pockets at $\Gamma$ at M, respectively. The roughly cylindrical nature of the pockets indicates that the $c$-axis overlap between electron orbitals from adjacent quasi-2D FeAs layers is relatively small. Thus, often the Fermi surface is drawn in 2D cross sections for simplicity. Note here, however, that the $\alpha$ band shows significant $c$-axis dispersion due to interlayer electron motion.

1.4 Magnetic Order

1.4.1 Structure

The specific pattern of the magnetic moments on the Fe sites often found in the parent compounds of Fe-based SCs is shown in Fig. 1.4. This pattern consists of stripes of ferromagnetically aligned moments (shading in the figure). These stripes are then antiferromagnetically aligned perpendicular to the stripes. The magnetic state is referred to as “stripe-type” order. The magnetic order can be described by the in-plane wavevector $Q_{AFM} = (\pi/a_T, \pi/a_T)$, where $a_T$ is the in-plane lattice parameter of the tetragonal unit cell introduced above (dashed line in Fig. 1.4). In terms of the iron square lattice of side $a_{Fe} = a_T/\sqrt{2}$, it is clear that $Q_{AFM} = (\pi/a_{Fe}, 0)$.

As discussed above, the tetragonal symmetry of the high-temperature phase is actually not preserved in the stripe-AFM phase. Instead the structure undergoes an orthorhombic distortion (the 4-fold rotational symmetry about the tetragonal $c$ axis is lowered to 2-fold). This is illustrated in Fig. 1.5. Note that the orthorhombic unit cell is rotated by $45^\circ$ relative to the tetragonal unit cell. We refer to the longer (shorter) orthorhombic lattice parameter as $a_O$ ($b_O$). The amount of
lattice distortion is quantified by $\delta = (a_O - b_O)/(a_O + b_O)$. Experiments show that this distortion is small, a typical value being $\delta = 0.5\%$ [18]. In the stripe-AFM state, the Fe spins point along $a_O$. The ordered moment in $\text{BaFe}_2\text{As}_2$ is $\sim 0.9 \ \mu_B$/Fe.

Below $T_N$, the tetragonal symmetry is not broken in the same way throughout the entire crystal. In fact two types of domains form in which the $a_O$ axes point in different directions. These are referred to as “twinned” structural domains. The existence of multiple domains means that bulk measurements cannot resolve the in-plane anisotropy of the magnetic state, as bulk measurements average over the microscopic domain structure. Crystals can be “de-twinned” by applying external stress to the crystal along the tetragonal [110] (orthorhombic [100]) direction. The external stress serves as an external field for the orthorhombic distortion and results in the expansion of favorably oriented orthorhombic domains, as illustrated in Fig. 1.5(c). This allows for bulk measurements of in-plane anisotropic properties.

The physics here is very similar to the more familiar case of magnetic domains in a ferromagnet. In a typical ferromagnet, spins are aligned within individual domains, but the bulk magnetization of
Figure 1.5 Depiction of the orthorhombic distortion and structural twin domains in the magnetic ordered phase. The structure shown is schematic and does not exactly represent the true crystal structure, but is simplified to emphasize the orthorhombic distortion. (a) The high-temperature tetragonal phase. (b) The twinned orthorhombic state. Different colors represent the different domains. Note that the orthorhombic unit cell is rotated by 45° relative to the tetragonal unit cell. (c) De-twinning by external force (purple arrows) along the tetragonal [110] direction. Favorably aligned domains (those with shorter bO axis along the direction of the applied force) expand and unfavorably aligned domains contract. In contrast, force applied along the tetragonal [100] direction does not de-twin the sample, as depicted in (b). Credit: [26]
the material is zero because the magnetizations of the domains are not all aligned with each other. Applying an external field will cause the favorably oriented domains to expand at the expense of other domains.²

So far we have focussed on the in plane ordering wavevector \( Q_{\text{AFM}} = (\pi/a_T, \pi/a_T) \). However, there is also a coupling between FeAs layers. The full 3D wavevector for 122 compounds is given by \( Q_{\text{AFM}} = (\pi/a_T, \pi/a_T, 2\pi/c) \). Since the unit cell for 122 compounds contains two FeAs layers, this implies that the coupling between layers is AFM. The magnetism is therefore three dimensional (albeit anisotropic), unlike the cuprate superconductors, which can be considered pure 2D systems due to negligible coupling between CuO layers [27].

### 1.4.2 Weak-coupling itinerant vs. strong-coupling local moment pictures

A central question in the field of iron-based superconductivity is the extent of the localization of the Fe 3d electrons. At one extreme, the electrons are stuck at particular Fe sites due to strong on-site electron repulsion (a “Mott insulator”), as is the case in the compound FeO. At the other extreme, the electrons are conducting and weakly correlated, obeying conventional band theory. Static magnetic order can still arise in such cases as an itinerant Spin Density Wave (SDW), as in pure Cr metal [28]. The situation in iron pnictides is believed to be intermediate between the two limits [20].

The strength of electron correlations is often discussed in terms of the Hubbard model. In the most basic Hubbard model, electron double-occupancy of a single lattice site incurs an energy cost \( U \) due to electronic repulsion. The strength of electron correlations is then determined by the ratio \( U/W \), where \( W \) is the electronic bandwidth (kinetic energy). The strong and weak coupling limits correspond to \( U/W \gg 1 \) and \( U/W \ll 1 \), respectively [20].

An itinerant nature of the magnetic state in iron pnictides is suggested by the small ordered moment on each Fe site (\( \sim 0.9\mu_B \) in BaFe\(_2\)As\(_2\)). Since a single unpaired electron has a moment

²If a ferromagnet spontaneously breaks a continuous O(3) symmetry, the magnetization of each domain can, in principle, point in any direction. Note that an O(3) symmetry ignores the (very real) possibility of single-ion anisotropy and other types of magneto-crystalline anisotropy. The point, however, is simply that in the twinned magnetic state of the iron pnictides, it is a \( Z_2 \) (Ising-type) symmetry between the tetragonal \( a \) and \( b \) axes which is broken, and there are therefore only two types of domain.
of 1 $\mu_B$, the ordered moment cannot be less than 1 $\mu_B$ within a local moment picture (although frustration and fluctuation effects can complicate this simple picture). For example, the ordered moment of the Fe$^{2+}$ ion in the Mott insulator FeO is 3.22 $\mu_B$/Fe [16].

It is important to point out that the AFM ordering wavevector $Q_{AFM} = (\pi/a_T, \pi/a_T)$ is exactly the wavevector that connects the hole (at the $\Gamma$ point) and electron pockets (at the $M$ point) on the Fermi surface (see Fig. 1.3). From this observation, it was suggested very early on in the field that the magnetic order is itinerant in origin [29]. Due to the cylindrical nature of the electron and hole pockets, as seen in Fig. 1.3(b), the wavevector $Q_{AFM}$ connects large parallel portions of the Fermi surface, leading to enhanced magnetic susceptibility at this wavevector, a phenomenon called Fermi surface “nesting” [20; 30].

Within the itinerant picture, the SDW state is a coherent condensate of electron-hole pairs [31]. The idea is similar to the condensate of electron pairs (Cooper pairs) in the superconducting state. From a theoretical perspective, the superconducting state is described by the order parameter $\Delta = \sum_k \langle c_{k\uparrow} e^{-ik\cdot r} c_{-k\downarrow} \rangle$, where $c$ is the electron creation operator [3]. That is, the superconducting state is a condensate of electron pairs of opposite momentum in the spin singlet $S = 0$ state. Similarly, the SDW state is described by the order parameter $M_Q = \sum_k \langle c_{k+Q,\sigma} \sigma_{\alpha\beta} c_{k,\beta} \rangle$ [32], which describes a condensate of electron-hole pairs with momenta differing by the AFM ordering wavevector $Q$ in the spin triplet $S = 1$ state ($\sigma$ are the Pauli matrices).

However, several results suggest that the weak-coupling, itinerant, Fermi surface nesting picture is insufficient in the iron pnictides [20; 23]. For example, correlation effects can be quantified by the ratio $R$ between the experimental electronic kinetic energy (measured by optical conductivity) and that of band-theory calculations [33]. For a good metal like Cu, $R \sim 1$. In contrast, for a Mott insulator like La$_2$CuO$_4$, $R \sim 0$. For Cr, the archetype of weak-coupling itinerant SDW materials, $R \sim 0.8$. Therefore, the value of $R \sim 0.3$ observed for BaFe$_2$As$_2$ suggests that this parent compound is a correlated metal. Another example comes from Fe x-ray emission spectroscopy experiments [34], which found fluctuating local moments on the Fe sites at room temperature in BaFe$_2$As$_2$. This is inconsistent with the pure itinerant SDW scenario [20].
Since the iron-pnictides have several orbitals active at the Fermi surface, the simple Hubbard model has to be extended to include the multiple orbitals (see, for example, Eq. 3 of Ref. [35]). These models then distinguish between the same-site, same orbital Coulomb repulsion $U$ and the same-site, different-orbital repulsion $U'$. Furthermore, the models include the Hund coupling $J_H$, which reflects the energetic preference for electrons in different orbitals on the same site to have parallel spins. The importance of the Hund coupling for electronic correlations in iron-pnictides is well documented [36; 37].

1.5 Nematic Order

As we have seen, the parent compounds of iron-pnictide superconductors have a magnetic ordered ground state of orthorhombic symmetry, where the spins on the Fe sites are ordered at the wavevector\(^3\) $Q_{\text{AFM}} = (\pi, 0)$ with the spins oriented along the $a_O$ axis. This magnetically ordered state breaks two distinct symmetries of the high-temperature paramagnetic tetragonal phase. First, the selection of a particular direction for the spins to point (here $\hat{a}_O$) breaks an $O(3)$ spin rotational symmetry. The breaking of spin rotational symmetry also breaks time-reversal symmetry\(^4\). Here, the $O(3)$ spin rotation symmetry is an idealization. Real crystals will generally have magneto-crystalline anisotropy and therefore do not have full $O(3)$ spin rotation symmetry. However, this distinction will not be important in the arguments of this section. Secondly, the magnetic ordered state breaks the equivalence between the tetragonal $a$ and $b$ directions (a $Z_2$ non-continuous “Ising-type” symmetry), by selecting the ordering wavevector to be either $Q_X = (\pi, 0)$ or $Q_Y = (0, \pi)$ (in the tetragonal notation). In sum, the magnetic state breaks an $O(3) \times Z_2$ symmetry of the paramagnetic tetragonal phase [32].

In electron-doped $\text{BaFe}_2\text{As}_2$ the breaking of the $Z_2$ symmetry (at $T_s$) precedes the breaking of the $O(3)$ symmetry ($T_N$) as the temperature is decreased. This state below $T_s$ but above $T_N$ is

\(^3\)We write the wavevector with respect to the 2D lattice of Fe atoms: $Q_{\text{AFM}} = (\pi/a_{\text{Fe}}, 0)$. For simplicity, the lattice constant is often omitted when writing the wavevector.

\(^4\)Magnetic moments can always be considered to arise from microscopic currents. Time reversal symmetry reverses the direction of the currents, reversing the direction of the moment. Thus time reversal symmetry can be preserved then only when $\langle M \rangle = 0$. 
known as the “nematic” state. This terminology is a reference to the nematic phase of liquid crystals. At the temperature $T_s$, the symmetry of the lattice is lowered from tetragonal to orthorhombic. However, this is not a “typical” lattice-driven structural transition. In-plane anisotropies of the electronic properties are found to exceed the anisotropy of the lattice parameters. For example, early NMR measurements [38] on BaFe$_2$As$_2$ found that the orthorhombicity of the electronic charge distribution below $T_s = T_N$ (as measured by the quadrupole asymmetry parameter) exceeded that of the lattice itself. This result, among many others, suggests that the electron system breaks the tetragonal symmetry, and “pulls” the lattice along for the ride. Later elasto-resistivity measurements [39] provided strong evidence that $T_s$ is indeed electronically driven. The nematic ordered state then is an instability of the collective electron system, much like the spin-density wave or superconducting orders.

The non-magnetic nematic ordered phase also possesses a static domain structure similar to the stripe-type magnetic ordered state. Two types of domain form in which the $a_O$ axes differ by $90^\circ$. Bulk measurements of the in-plane anisotropy of the nematic state require external stress to de-twin the crystal.

The electron system can break the $Z_2$ symmetry (without breaking the $O(3)$ symmetry) in two main ways. In the “charge” scenario, the occupations of the Fe $d_{xz}$ and $d_{yz}$ orbitals become unequal. In the “spin” scenario, spin fluctuations become anisotropic in the $ab$ plane. Due to the bi-linear coupling of these order parameters in the Landau free energy expansion, the unequal occupation of $d_{xz}$ and $d_{yz}$ orbitals will cause anisotropic spin fluctuations and vice versa. Thus both orders are present in the nematic state. The question of which of the two mechanisms drives the nematic order (and which is the result of nematic order) is still an open question in the field [32]. Below, we focus on a description of spin nematicity.

Since there are two possible magnetic wavevectors, we need two magnetic order parameters to describe the physics, $M_X$ and $M_Y$, where $M_i$ is the Fourier component of the magnetization at wavevector $Q_i$. The real-space magnetization is

$$M(r) = \text{Re}[M_X \exp(iQ_X \cdot r) + M_Y \exp(iQ_Y \cdot r)].$$ (1.1)
Figure 1.6 Magnetic susceptibility in paramagnetic and nematic phases. The magnetic susceptibility $\chi$ measures the amplitude of the fluctuations of the magnetic order parameter, i.e. $\chi(Q_X) \sim \langle M_X^2 \rangle/k_BT$. In the tetragonal paramagnetic phase $\langle M_X^2 \rangle = \langle M_Y^2 \rangle$ thus $\chi(Q_X) = \chi(Q_Y)$. In the nematic phase, however, $\chi(Q_X) \neq \chi(Q_Y)$. The magnetic fluctuations break the tetragonal symmetry. Credit: [32]

That is, $M_i$ gives the amplitude and polarization of the magnetization with wavevector $Q_i$. For example, in the magnetically ordered state described above we have $\langle M_X \rangle = \mu \hat{a}_O$ and $\langle M_Y \rangle = 0$, where $\mu$ is simply the magnitude of the ordered moment.

In the paramagnetic phase, the $O(3)$ spin rotational symmetry requires that thermal fluctuations sample all spin directions equally, resulting in $\langle M_X \rangle = \langle M_Y \rangle = 0$. Furthermore, the $Z_2$ symmetry between the tetragonal $a$ and $b$ directions requires that the fluctuation amplitudes at $Q_X$ and $Q_Y$ are equal. That is $\langle M_X^2 \rangle = \langle M_Y^2 \rangle$. Nematic order is a state which preserves the $O(3)$ symmetry, while breaking the $Z_2$ symmetry. Therefore, in the nematic state we still have $\langle M_X \rangle = \langle M_Y \rangle = 0$, but now $\langle M_X^2 \rangle \neq \langle M_Y^2 \rangle$. The nematic order parameter can then be expressed as $\phi = \langle M_X^2 - M_Y^2 \rangle = \langle M_X^2 \rangle - \langle M_Y^2 \rangle$. This is illustrated in Fig. 1.6. If $\phi > 0$, fluctuations at $Q_X$ are stronger. Conversely if $\phi < 0$, fluctuations at $Q_Y$ are stronger. In the twinned state, some domains have $\phi = +\epsilon$ and the other domains have $\phi = -\epsilon$. 
Figure 1.7 The stripe-type magnetic structure can be viewed as two interpenetrating Néel-type sublattices with order parameters $M_1$ and $M_2$ (green and yellow). The nematic order parameter can be expressed as $\phi = \langle M_1 \cdot M_2 \rangle$, the correlation function of the two sublattices. Credit: [32]

What does nematic order look like in real space? The stripe-type magnetic order can be interpreted as two inter-penetrating Néel-type sublattices (Fig. 1.7). In terms of the two sublattices, the magnetization can be written as\(^5\)

$$M(r) = \text{Re}[M_1 \frac{\exp(iQ_X \cdot r) + \exp(iQ_Y \cdot r)}{2} + M_2 \frac{\exp(iQ_X \cdot r) - \exp(iQ_Y \cdot r)}{2}]. \tag{1.2}$$

Here, $M_i$ are the magnetic order parameters of each sublattice. By comparison with Eq. 1.1, we find that $M_1 = M_X + M_Y$ and $M_2 = M_X - M_Y$. Clearly then $M_1 \cdot M_2 = M_X^2 - M_Y^2$. In the stripe-type AFM state, $\langle M_1 \rangle = \pm \langle M_2 \rangle = \mu \hat{a}_O$, where the sign determines the ordering wavevector $Q_X$ or $Q_Y$. It is also clear that $\langle M_1 \cdot M_2 \rangle = \pm \mu^2$.

In the nematic state $\langle M_1 \rangle = \langle M_2 \rangle = 0$, while $\langle M_1 \cdot M_2 \rangle \neq 0$. The nematic order parameter can then be expressed as $\phi = \langle M_1 \cdot M_2 \rangle$. Physically, $\phi$ is the correlation function of the two sublattices. In the tetragonal phase $\phi = 0$ and the two sub-lattices are completely uncorrelated, fluctuating independently of each other. In the nematic phase the sublattices become increasingly correlated.

\(^5\)Consider the two oscillatory functions $\text{Re} \left[ \exp(iQ_X \cdot r) \pm \exp(iQ_Y \cdot r) \right]$. If we take the plus (minus) sign, the function has maxima and minima at the positions of sublattice 1 (2) and is zero at the positions of sublattice 2 (1).
1.6 Superconducting Properties

In the phase diagram of the iron pnictides, superconductivity arises near the point where the parent stripe-type, long-range AFM ordered state is strongly suppressed by doping. This suggests that the superconducting Cooper pairing may be provided by the exchange of the stripe-type AFM spin fluctuations between electrons. Superconductivity in the high-$T_c$ cuprates and heavy fermion superconductors is also found in the vicinity of AFM ordered phases.

Evidence for the intimate relationship between stripe-type spin fluctuations and the superconductivity is found in the existence of the so-called neutron spin resonance mode. In the superconducting state, the magnetic neutron scattering at the stripe-type AFM wavevector $Q_{\text{AFM}}$ is strongly enhanced at a particular resonance energy. For example, in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ with $x = 0.075$ (for which $T_c = 25$ K), $\chi''(Q_{\text{AFM}}, E)$ has a peak at $E = 9.5$ meV for temperatures below $T_c$ but not above [40]. The increased scattering intensity at the resonance energy comes at the expense of lower-energy scattering. Such a neutron spin resonance is also observed in the high-$T_c$ cuprates [41; 42].

To further understand the superconducting state, it is crucial to determine the total spin $S$ of the Cooper pairs. Two electrons can have either a spin singlet ($S = 0$) or spin triplet ($S = 1$) configuration. The strong decrease of the NMR Knight shift below $T_c$ conclusively shows that the Cooper pairs in iron pnictides are in the spin singlet state (see [43], for example). Since the spin singlet state is anti-symmetric, the spatial part of the Cooper pair wavefunction must be symmetric in order to maintain the anti-symmetry of the total wavefunction. Therefore the spatial part of the Cooper pair wavefunction can be either $s$-wave (angular momentum $L = 0$) or $d$-wave ($L = 2$).

One of the key features of the superconducting state is the existence of an energy gap about the Fermi surface. The SC gap is the real part of the SC order parameter, which is a complex quantity with both magnitude and phase. This energy gap depletes the density of states at the Fermi energy, leading to the “freeze out” of thermodynamic quantities such as specific heat for $T < T_c$. The spatial part of the Cooper pair wavefunction determines the symmetry of the superconducting gap in $k$ space. In the BCS theory of phonon-mediated superconductivity, the superconducting gap
1.2.4 Superconducting properties

Similar as the cuprates, the Cooper-pairing mechanism that causes the high temperature superconductivity in FeSCs is one of the most challenging problems in condensed matter physics field. Although the exact nature of the pairing is not known in FeSCs, many experiments have been performed to determine the pairing symmetry of the superconducting order parameter. For the FeSCs, the symmetry was predicted theoretically to have s-wave symmetry, but with a sign reversing that occurs between different bands in the complex multi-band electronic structure, the so called “s±” symmetry. The s±-wave symmetry, together with another possible scenario, d-wave symmetry for the superconducting order parameter symmetry in FeSCs, is shown in Fig. 1.7. In the s± model, the superconducting gaps which open at each Fermi surface upon entering the superconducting state are isotropic and similar in magnitude, but different in their sign (+ and −) on the hole and the electron pocket, respectively. Modulation of the gap amplitude in s±-wave symmetry may be present allowing plentiful low-energy excitations even at temperatures much below the energy of the gap, explaining the node observed in LaFePO [59], BaFe$_2$(As$_{1-x}$P$_x$)$_2$ [41] and KFe$_2$As$_2$ [62].

![Figure 1.7](image)

Figure 1.7 Schematic representation of the superconducting order parameter. (a) a uniform s-wave. (b) d-wave, with nodes in the order parameter. (c) s±-wave symmetry. [63]

The NMR technique is powerful to determine symmetry of superconducting order parameter. In the case of conventional superconductors, nuclear spin-lattice relaxation rate ($1/T_1$) is known to show the Hebel-Slichter peak just below $T_c$. [64] The singlet pairing can also be indicated by the sharp drop of Knight shift below $T_c$. The temperature dependence of the $1/T_1$ below $T_c$ are frequently used to discriminate conventional from unconventional pairings with absence of the Hebel-Slichter peak. For a single Fermi surface, nuclear spin-lattice relaxation rate of

has s-wave symmetry and is isotropic in $k$ space (Fig. 1.8(a)). In contrast, the superconducting gap of high-$T_c$ cuprates is anisotropic in $k$ space and has d-wave symmetry. Since the d-wave Cooper pair wavefunction has positive and negative lobes separated by nodes, the superconducting gap in $k$-space also inherits these features. That is, there are specific wavevectors at the Fermi surface which have zero gap. This is illustrated in Fig. 1.8(b).

The existence of nodes in the superconducting gap means that the density of states near the Fermi energy is not zero, in contrast to the s-wave case where the density of states is zero all the way out to the maximum gap value, as shown in Fig. 1.9. Due to this property of the density of states, more low-energy quasiparticles (roughly, broken Cooper pairs) can be present at non-zero temperatures. Therefore nodal superconductors have very different signatures in probes such as specific heat, magnetic penetration depth, thermal conductivity and NMR. For example, the NMR spin-lattice relaxation rate shows a power law decrease with decreasing temperature as opposed to the exponential decrease of the full gap case.

In iron pnictides, some materials show nodal signatures and others don’t. While optimally-doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ and Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ have been shown to have full (nodeless) gaps, BaFe$_2$(As$_{1-x}$P$_x$)$_2$ and KFe$_2$As$_2$ show signatures of nodal gaps (see Fig. 1.10). Any nodes which do exist are believed to be “accidental” and not imposed by a d-wave symmetry.
Figure 1.9 Comparison of the electronic density of states $N(E)$ as function of energy for a full gap (left) and a nodal gap (right). Here, the Fermi energy is defined as zero ($E_F = 0$).

Theoretical considerations suggest that the phase of the gap is opposite on the hole and electron pockets. This superconducting state is referred to as the $s_\pm$ or “extended $s$” state, and is illustrated in Fig. 1.8(c). While experimental results are consistent with this idea, direct proof has been elusive.

1.7 Motivation

Despite the rapid progress in the understanding of iron-based superconductors, several important general questions still remain, motivating the further study of these materials. First, although the Cooper pairing is widely believed to originate from the residual stripe-type AFM spin fluctuations, there is, as of yet, no accepted theory for $T_c$ in these materials with which to explain the large variability in maximum $T_c$ between different iron-based families and the different shapes of the SC dome with electron and hole doping. Is there a missing piece to the understanding of $T_c$ in these materials? In particular, what role do ferromagnetic and/or nematic fluctuations play in the superconductivity? Secondly, what is the symmetry of the superconducting gap? Does the gap symmetry vary from material to material? Furthermore, what is the strength of the electronic correlations? Are these materials in the vicinity of a Mott insulating state? Can these materials be understood as $d$-band heavy-fermion superconductors? Finally, what is the origin of the nematic
Figure 1.10 The superconducting gap magnitude (color scale) on the Fermi surfaces of BaFe$_2$(As$_{0.7}$P$_{0.3}$)$_2$ and Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$, as determined by ARPES experiments. The gap magnitude is generally different on each Fermi surface sheet. While Ba$_{1-x}$K$_x$Fe$_2$As$_2$ has isotropic, nodeless gaps (apart from a small $k_z$ dependence), BaFe$_2$(As$_{1-x}$P$_x$)$_2$ features a unique circular line node on the $\alpha$ band. Credit: [44]
order? Is it a magnetic or orbital instability? Does the origin of nematicity differ from material to material? The answers to these questions could provide the framework for a microscopic theory of high-$T_c$ superconductivity and the discovery of new superconductors. In this thesis, I examine these questions from a microscopic point of view using the nuclear magnetic resonance technique.

Here, I briefly describe our motivation and findings, which are elaborated in Chs. 4–8. The relevant citations to the literature for the factual claims made in this section can also be found in Chs. 4–8.

1.7.1 FM correlations in iron-based superconductors

In the standard paradigm of the iron-based superconductors, superconductivity is expected if strong stripe-type AFM fluctuations are present in the absence of long-range AFM order. This paradigm is put to the test in two curious materials of the 122 family. SrCo$_2$As$_2$ is the end member of the electron-doped series Sr(Fe$_{1-x}$Co$_x$)$_2$As$_2$. This compound displays no static magnetic order or superconductivity. However, AFM correlations were suggested by magnetic susceptibility measurements and confirmed to be stripe-type AFM correlations by inelastic neutron scattering measurements. The $x = 1$ member of the hole-doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ series, KFe$_2$As$_2$, has no long-range magnetic order and a similar temperature dependence of magnetic susceptibility. Likewise, AFM correlations were observed by inelastic neutron scattering. However, in contrast to SrCo$_2$As$_2$, KFe$_2$As$_2$ is a superconductor with $T_c \sim 3.4$ K. This raises the question of why KFe$_2$As$_2$ is a superconductor, while SrCo$_2$As$_2$ is not. According to the standard paradigm, both should be superconducting because both have strong AFM correlations in the absence of long-range AFM order.

To shed light on this question, we applied a modified Korringa ratio analysis to our $^{75}$As and $^{59}$Co NMR data on SrCo$_2$As$_2$ and found that strong low-energy ferromagnetic (FM) fluctuations are also present in this material and, in fact, dominate the low-energy AFM spin-correlations. In contrast, while FM correlations are also present in superconducting KFe$_2$As$_2$, the AFM correlations are stronger relative to the FM correlations in KFe$_2$As$_2$. This suggests that SrCo$_2$As$_2$ is not a
superconductor because the FM correlations compete with the AFM fluctuations and interfere with the AFM-based Cooper pairing.

While our initial analysis focussed on the samples on the far hole- and electron-doped edges of the iron-pnictide phase diagram, the discovery of FM correlations motivated a deeper look at the parent and high-\(T_c\) compounds as well. Therefore, we subsequently applied the same analysis to a variety of hole- and electron-doped compounds derived from the BaFe\(_2\)As\(_2\) and CaFe\(_2\)As\(_2\) parents. We found that a coexistence of AFM and FM correlations is a general feature of these Fe-based 122 compounds. Furthermore, we found that superconductivity is suppressed when FM correlations are strong relative to AFM correlations, suggesting that FM correlations play a role in determining \(T_c\) in these materials.

### 1.7.2 KFe\(_2\)As\(_2\)

Regardless of the FM fluctuations, KFe\(_2\)As\(_2\) is a fascinating material for several additional reasons. While \(T_c \sim 3.5\) K is low, the superconductivity is unconventional and the structure and symmetry of the superconducting gap are still very much in question. Specific heat capacity measurements conclusively show multi-gap (multi-band) superconductivity and that very small gap values exist. Several techniques have claimed nodes in the gap, and a possible \(d\)-wave symmetry has been suggested. In contrast, ARPES indicates an \(s\)-wave gap with accidental nodes. However, the observation of a hexagonal vortex lattice for \(H\parallel c\) argues against such a nodal structure. Furthermore, the ARPES gap magnitudes are inconsistent with thermodynamic measurements, so controversy still remains. An additional fascinating feature of the SC state in KFe\(_2\)As\(_2\) is that the \(H_{c2}\) for magnetic fields applied in the \(ab\) plane is limited by the Pauli pair-breaking effect instead of the usual orbital pair-breaking effect. Finally, under applied hydrostatic pressure \(p\), \(T_c\) decreases up to a critical pressure \(p^* \sim 1.8\) GPa, and increases thereafter. The reversal of \(T_c(p)\) has been suggested to be due to a change of superconducting gap structure at \(p^*\), possibly to a state with gap modulation along the \(k_z\) axis.
The non-superconducting state of KFe$_2$As$_2$ is also unusual. First, while AFM spin correlations are present at low-$T$, they are incommensurate with the lattice, in contrast to the parent and high-$T_c$ compounds. The normal state also has several properties reminiscent of $f$-electron heavy-fermion materials. The low-$T$ linear term of the specific heat ($\gamma \sim 100$ mJ/mol K$^2$) is enhanced, indicating a large electron effective mass. Furthermore, as the temperature is increased, several experiments show a crossover to high-$T$ local-moment behavior above a coherence temperature known as $T^*$, apparently due to a selective localization of electrons in the bands derived from the $d_{xy}$ orbitals (an orbital-selective Mott transition). These results suggest that KFe$_2$As$_2$ can be thought of as a $d$-band heavy fermion superconductor.

These unique properties of KFe$_2$As$_2$ motivate a microscopic study of this material, particularly under applied hydrostatic pressure. We carried out both high-$T$ NMR and low-$T$ NQR measurements to investigate the microscopic properties of the superconducting and normal state under applied pressures up to 2.1 GPa. We found that the coherence temperature $T^*$, increases with increasing pressure. This is consistent with an increasing hybridization between localized and itinerant orbitals. In addition, $T^*(p)$ shows no anomaly at the critical pressure $p^*$. Instead magnetic fluctuations appear to correlate with $T_c$ in KFe$_2$As$_2$ under pressure. Zero-field NQR measurements in the SC state could not confirm a change of gap symmetry at $p^*$. However, the NQR measurements revealed a two-component behavior of the nuclear spin-lattice relaxation rate, suggesting a real-space modulation of the SC gap magnitude.

1.7.3 FeSe$_{1-x}$S$_x$

In contrast to the 122 family, the iron-chalcogenide material FeSe is a unique case in which the stoichiometric parent compound is superconducting without doping at $T_c = 8$ K. While FeSe shows no AFM order, it does have a nematic ordered phase below $T_s = 90$ K. In 122 materials, the nematic phase transition is either coincident with (i.e. Ba$_{1-x}$K$_x$Fe$_2$As$_2$ and Ca(Fe$_{1-x}$Co$_x$)$_2$As$_2$) or just above (i.e. Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$) the magnetic transition to the stipe-ordered phase, suggesting a close relationship between magnetism and nematicity. Therefore, the presence of a nematic ordered
phase in the complete absence of a magnetic ordered phase in pure FeSe has posed a challenge to the field of iron-based superconductivity. The origin of the nematic state in FeSe and its relation to magnetism is still hotly debated, and a possible orbital ordering has been suggested.

However, while no magnetic order occurs in pure FeSe, the nematic state does nevertheless coexist with strong AFM fluctuations. Hydrostatic pressure enhances magnetic fluctuations and induces a magnetic ordered state above $\sim 0.8$ GPa. The superconducting $T_c$ is also enhanced. In addition, the nematic state is strongly suppressed by pressure application suggesting a competition between the nematic state and magnetism, in strong contrast to the 122 materials.

To shed light on these intriguing properties, we have conducted high-pressure NMR measurements on pure FeSe single crystals. Our measurements revealed a short-range local nematic order far above the bulk nematic transition temperature. Furthermore, this high-$T$ local nematicity appears to correlate with magnetic fluctuations, in contrast to the bulk nematic transition.

The nematic state of pure FeSe can also be suppressed by isoelectronic doping of S onto the Se site. In contrast to pressure application, no magnetic ordered state accompanies the suppression of the nematic state in the S-doped series FeSe$_{1-x}$S$_x$, leading to purely nematic quantum critical point near $x = 0.17$. In the 122 materials, nematic quantum criticality has been observed near optimal doping, suggesting that critical nematic fluctuations may play a role in enhancing $T_c$. However, the role of nematic fluctuations is unclear due to the simultaneous presence of critical magnetic fluctuations. The purely nematic QCP in FeSe$_{1-x}$S$_x$ is believed to offer a chance to distinguish the effects of critical nematic and magnetic fluctuations.

From NMR measurements on FeSe$_{1-x}$S$_x$ single crystals, we found that $T_c$ closely parallels the behavior of magnetic fluctuations with S doping and not nematic fluctuations. Thus our NMR results suggest that the critical nematic fluctuations do not enhance $T_c$ in the FeSe$_{1-x}$S$_x$ family.
CHAPTER 2. NUCLEAR MAGNETIC RESONANCE

2.1 Basics

The nucleus is a self-bound, many-body system of protons and neutrons. The ground state of this many-body system has a total angular momentum $\mathbf{J}$ and a magnetic dipole moment $\mu$ related by

$$ \mu = \gamma \mathbf{J}, $$

where $\gamma$ is known as the nuclear gyromagnetic ratio. It is conventional to define a unitless angular momentum $\mathbf{I}$ by $\mathbf{J} = \hbar \mathbf{I}$, such that $\mu = \gamma \hbar \mathbf{I}$. The Hamiltonian for this nuclear magnetic moment in a total magnetic field $\mathbf{H}_{\text{nuc}}$ is then

$$ \mathcal{H} = -\mu \cdot \mathbf{H}_{\text{nuc}} = -\gamma \hbar \mathbf{I} \cdot \mathbf{H}_{\text{nuc}}. $$

The terminology $\mathbf{H}_{\text{nuc}}$ is used to emphasize that the relevant magnetic field in NMR is the total magnetic field at the nuclear site, which may differ from the laboratory field $\mathbf{H}_0$. With the assumption that $\mathbf{H}_{\text{nuc}} = H_{\text{nuc}} \hat{z}$, the Hamiltonian is

$$ \mathcal{H} = -\gamma \hbar H_{\text{nuc}} I_z $$

which has energy eigenvalues given by

$$ E = -\gamma \hbar H_{\text{nuc}} m $$

where $m = -I, \ldots, I$ is the angular momentum projection quantum number. As illustrated in Fig. 2.1, the spacing between energy levels is

$$ \Delta E = \gamma \hbar H_{\text{nuc}} = \hbar \omega_L = \hbar f_L, $$

which defines a resonance frequency

$$ f_L = \frac{\gamma}{2\pi} H_{\text{nuc}} $$
known as the Larmor frequency. The frequency corresponds to the classical precession frequency of the moment about the field. For nuclei in typical laboratory fields, $f_L$ is in the radio-frequency (MHz) band of electromagnetic radiation. For example, $^{75}$As has $\gamma/2\pi = 7.2919$ MHz/T and resonance would be observed at $f_L \sim 51$ MHz in a 7 T magnetic field. For electron spins, $f_L$ is in the microwave (GHz) range.

Transitions between the nuclear energy levels can be induced by applying a time-varying perturbation consisting of a magnetic field (of frequency $f_L$) perpendicular to $H_{\text{nuc}}$. This time varying field is conventionally referred to as $H_1$. To see why $H_1$ must be perpendicular to $H_{\text{nuc}}$, we take $H_{\text{nuc}}$ to be along the $z$ direction (this is the quantization axis) and write the Hamiltonian as

$$\mathcal{H} = -\gamma h \mathbf{I} \cdot \mathbf{H}_1 \sim I^z H_1^z + \frac{1}{2} \left[ I^+ H^-_1 + I^- H^+_1 \right], \quad (2.7)$$

where $I^\pm = I^x \pm iI^y$ and $H^\pm_1 = H^x_1 \pm iH^y_1$ are raising and lowering operators. Only the components of $H_1$ perpendicular to $H_{\text{nuc}}$ couple to the nuclear spin raising and lowering operators $I^\pm$.

### 2.2 Motion of nuclear moments and free induction decay signal

We now discuss how such a resonance can be observed in the laboratory. In a typical case, the field at the nuclear site is dominated by the external field $H_0$. Let us therefore assume $H_{\text{nuc}} \simeq H_0$.
In this formula, it is important to remember that the magnetic moment of a nucleus is parallel to the external field and passing an RF current through the coil. Credit: [46]

Figure 2.2 The RF field $\mathbf{H}_1$ perpendicular to the static external field is applied by wrapping the sample in a coil whose axis is perpendicular to the external field and passing an RF current through the coil. Credit: [46]

Figure 2.3 The effect of the field $\mathbf{H}_1$ is to rotate the magnetization away from the $z$ axis, by precessing about the $x$ axis. A precession by $\pi/2$ radians is called a “$\pi/2$ pulse”. Credit: [46]

for this discussion. The field $\mathbf{H}_1 = H_1 \cos(\omega_L t)\hat{x}$ can be applied by wrapping the sample in a coil whose axis is perpendicular to $\mathbf{H}_0$ and passing an RF current ($f_L$) through the coil (Fig. 2.2).

NMR detects the motion of the macroscopic nuclear magnetization arising from the polarization of the moments of individual nuclei. The motion of the nuclear magnetization can be described using a classical picture, with the understanding that all statements apply to the quantum expectation values. In the absence of $\mathbf{H}_1$, the magnetization vector simply precesses about $\mathbf{H}_0 = H_0 \hat{z}$ at the Larmor frequency $\omega_L = \gamma H_0$. The analysis is simplified by considering the motion of the nuclear magnetization in a rotating coordinate system, which rotates at $\omega_L$. The details are given in several standard texts (e.g. [47]) and will not be repeated here. In this rotating reference frame, the magnetization is stationary in the absence of $\mathbf{H}_1$. It can be shown that the effect of the field $\mathbf{H}_1 = H_1 \cos(\omega_L t)\hat{x}$ is to cause the magnetization to precess about the $x$ axis in the rotating frame at a frequency $\omega = \gamma H_1$. This serves to rotate the magnetization away from the $z$ axis. In a time
the magnetization precesses through an angle \( \theta = \omega t = \gamma H_1 t \). Therefore, by applying a “\( \pi/2 \)” pulse of length \( t_{\pi/2} = \pi/(2\gamma H_1) \) the magnetization will be rotated into the \( xy \) plane (Fig. 2.3). After the completion of the \( \pi/2 \) pulse, the magnetization precesses in the \( xy \) plane about the \( z \) axis at frequency \( \omega_L \). The precession of the nuclear magnetization in the \( xy \) plane then induces a measurable voltage in the coil known as the “free induction decay” (FID) signal. In general, the intensity of the NMR signal is proportional to the \( xy \) component of the nuclear magnetization, since only this component produces a time varying flux through the coil cross section.

The precession of the nuclear magnetization in the \( xy \) plane after a \( \pi/2 \) pulse does not last forever. Two conceptually different processes are involved in the decay of the FID signal.

The absorption of RF energy by the spin system in the process of a \( \pi/2 \) pulse creates a non-equilibrium state. Of course, in the thermal equilibrium state the nuclear magnetization points along the \( z \) axis. In order to relax back to this state, the nuclear spin system must dissipate its extra energy into its surroundings (commonly referred to as the “lattice”). The transfer of energy to the lattice allows the magnetization to rotate back towards the \( z \) axis. In the process, the \( xy \) component of the magnetization vanishes, causing the NMR signal to vanish. This “longitudinal” or “spin-lattice” relaxation takes place over a time scale known as \( T_1 \).

However, there is a second process known as “transverse” or “spin-spin” relaxation, which takes place with a time constant \( T_2^* \). (The asterisk is used to distinguish \( T_2^* \) from another quantity \( T_2 \) to be defined later.) In solids, typically \( T_2^* \ll T_1 \), so that in practice the decay of the FID is due primarily to this transverse relaxation. How does it come about? In any real spin system, there is some distribution of the local magnetic field of the individual nuclei. This could arise, for example, from spatial non-uniformities of the external field throughout the sample volume or from dipole-dipole coupling among the nuclear moments. The distribution of local magnetic fields produces a distribution of precession frequencies \( f_L \) of width \( \sigma_{f_L} \). The precessions of individual nuclear moments are put in phase by the \( \pi/2 \) pulse. However, once the pulse is over, the distribution of precession frequencies causes the precessions of individual nuclear moments to go out of phase with each other, resulting in the decay of the measurable macroscopic nuclear magnetization over
a time scale $T_2^*$. Thus, the transverse relaxation time $T_2^*$ is also referred to as the “de-phasing” or “decoherence” time. It is clear from this physical description that the width of the NMR absorption spectrum ($\sigma_{fL}$) is proportional to the de-phasing rate, $1/T_2^*$. That is, $1/T_2^* \propto \sigma_{fL}$. For example, if the NMR spectrum is very sharp, the nuclei will stay in phase longer, leading to a longer decay time of the FID. In general, the FID signal (time domain) is the Fourier transform of the NMR absorption spectrum (frequency domain).

As alluded to above, in condensed matter systems, typically the transverse relaxation time $T_2^*$ of the FID (and the spin echo $T_2$ discussed below) are much shorter than the longitudinal, spin-lattice relaxation time $T_1$. In this situation, the relaxation of the nuclear spin system after a $\pi/2$ pulse can be thought of as a two-step process. First, the spins precess entirely in the $xy$ plane but the measurable nuclear magnetization decays to zero due spin-spin decoherence processes over a time scale $T_2$. Only later, on the time scale of $T_1$, do the nuclear spins rotate back towards the $z$-axis. In the presence of spin-spin decoherence effects, how can one measure the nuclear magnetization on the time scale of $T_1$? The answer involves additional pulses and spin-echo techniques, which are the focus of the next section.

### 2.3 Spin Echo and Pulse NMR measurements

Essentially all modern NMR is performed using pulsed RF fields, as opposed to the older continuous wave (CW) methods.

In the case of condensed matter NMR, the spectrum is often broad enough that the FID signal cannot be observed because $T_2^*$ is less than the “dead time” of the spectrometer, which typically lasts $\sim 8 \mu$s after the pulse. In this case, the NMR signal can nonetheless be observed by using the famous “spin echo” method (Fig. 2.4). In this method, the initial $\pi/2$ pulse is followed by an additional $\pi$ pulse after a time $\tau_2$. In the time between the $\pi/2$ pulse and the $\pi$ pulse, the nuclear spins de-phase as described above. The effect of the $\pi$ pulse is to cause the nuclear spins to come back into phase at a time $2\tau_2$ after the initial $\pi/2$ pulse, producing the spin echo signal. The spin echo signal consists of two back-to-back copies of the FID signal, the induced voltage rises as the
Due to distribution of Larmor frequencies, spins "dephase" and macroscopic nuclear magnetization decays to zero over time scale $T_2$. A $\pi$ pulse after time $\tau$ will bring spins back into phase at time $2\tau$. "Spin echo"

Figure 2.4 Formation of the spin echo. (a) Initial $\pi/2$ pulse puts spins in phase along $y$ axis. (b) De-phasing of nuclear Larmor precessions. (c) A $\pi$ pulse causes a rotation of spins about $x$ axis by $\pi$ radians. (d) Nuclear spins now re-phase. (e) The spin echo, where spins are again completely in phase. (f) Another de-phasing after the spin echo. At time $\tau_2$ passes between the $\pi/2$ (a) and $\pi$ (c) pulses. A time $2\tau_2$ passes between the initial $\pi/2$ pulse and the spin echo formation. Credit: [46]

Figure 2.5 FID and spin echo signals due to the $\pi/2–\pi$ pulse sequence. The high frequency sine wave represents the Larmor (carrier) frequency. The FID decays with time constant $T_2^*$. The spin echo consists of back-to-back copies of the FID (growing and then decaying), both with time constant $T_2^*$. The maximum intensity of the spin echo decays according to time constant $T_2 \gg T_2^*$. Credit: [48]
spins come back into phase approaching $2\tau_2$, and then falls after $2\tau_2$ as the spins de-phase again, with decay time $T_2^*$ (Fig. 2.5). The usefulness of the spin echo, then, is that it allows the tiny ($\sim \mu$V) NMR signal to be moved away (by an amount $\tau_2$) from the high power RF pulses which are required to excite the nuclei.

### 2.3.1 Spin echo measurement of $T_2$

When performing the $\pi/2-\pi$ spin-echo pulse sequence described above, one finds that the intensity of the spin echo signal (the time integral of the induced voltage) decreases as the pulse separation $\tau_2$ increases. The time $T_2$ is the decay constant of the echo intensity with respect to $\tau_2$, representing the time scale of the decoherence of the nuclear spins. To measure it, one varies $\tau_2$ in discrete steps, measuring the corresponding echo intensity for each $\tau_2$. One can then fit the curve to extract the time constant. Often the decay is Gaussian, but can be exponential in the presence of electronic spin fluctuations.

The spin-spin relaxation time measured in this way is referred to as the “spin echo” $T_2$ in order to distinguish it from the “FID” $T_2^*$ discussed above. Typically, $T_2 > T_2^*$, so that the spin echo $T_2$ is measurable even if the FID is too short to be observed (Fig. 2.5).

### 2.3.2 Spin echo measurement of $T_1$

The spin lattice relaxation rate $1/T_1$ is also conveniently measured using spin echo techniques. In this case, a three-pulse sequence is required. The pulse sequence begins with a $\pi/2$ pulse. A time $\tau_1$ then passes before a second $\pi/2$ pulse is given. A $\pi$ pulse is then given a time $\tau_2$ after the second $\pi/2$ pulse. A spin echo signal is observed at a time $2\tau_2$ after the second $\pi/2$ pulse. The initial $\pi/2$ pulse is referred to as the “saturation” pulse, and the final two pulses the “detection” pulses. To measure $T_1$, one fixes $\tau_2$ and varies $\tau_1$ in discrete steps, recording the spin echo intensity corresponding to each value of $\tau_1$.

To see how this pulse sequence measures $T_1$ recall that the NMR signal intensity is proportional to the $xy$ component of the nuclear magnetization, as this is the component which induces a voltage
in the NMR coil. The effect of the pulse sequence is easily understood by considering the limiting cases of short and long $\tau_1$. After the saturation pulse, the nuclear spins precess in the $xy$ plane. If the time $\tau_1$ is very small compared to the characteristic relaxation time $T_1$, the spins will not have had time to relax back towards the $z$ axis, and are therefore still precessing in the $xy$ plane. The second $\pi/2$ pulse will then rotate the spins towards the negative $z$ axis. Now, the $xy$ component of the nuclear magnetization is zero and therefore the spin echo signal intensity is zero. If, in contrast, $\tau_1$ is much larger than $T_1$ the nuclear spins have had time to fully relax back towards the $z$ axis after the initial saturation pulse. In this case, the second $\pi/2$ pulse will then rotate the spins into the $xy$ plane and a spin echo of maximum intensity will be observed. In this way, one can trace out the “recovery” curve showing how the spin echo intensity varies with $\tau_1$.\footnote{If the FID signal is measurable, the final $\pi$ pulse is unnecessary, and one can simply measure the intensity of the FID following the second pulse as a function of $\tau_1$.}

In the simplest case of an $I = 1/2$ nucleus, the recovery curve can be fit to

$$m(\tau_1) = m_0[1 - \exp(-\tau_1/T_1)], \quad (2.8)$$

where $m(\tau_1)$ is the spin echo intensity corresponding to time $\tau_1$ and $m_0$ is the maximum spin echo intensity at long $\tau_1$.

### 2.4 Hyperfine field in materials

Our main interest in condensed matter NMR is to use the nucleus as a microscopic probe of the electrons in the material. The Hamiltonian for the interaction between a nucleus and a single electron is

$$\mathcal{H}_{en} = -\gamma \hbar \mathbf{I} \cdot \mathbf{H}_{hf} = \gamma \hbar \mathbf{I} \cdot g\mu_B \left[ \frac{\mathbf{L}}{r^3} - \left( \frac{\mathbf{S}}{r^3} - \frac{3\mathbf{r}(\mathbf{S} \cdot \mathbf{r})}{r^5} \right) + \frac{8\pi}{3} \delta^{(3)}(r) \mathbf{S} \right]. \quad (2.9)$$

In this equation $r$ is the position vector of the electron relative to the nucleus and $\mathbf{L}$, $\mathbf{S}$ are the (unitless) orbital angular momentum and spin of the electron in units of $\hbar$. That is, $\mu_S = -g\mu_B S$, for example. Eq. 2.9 describes the interaction of the nuclear moment with a hyperfine magnetic field given by

$$\mathbf{H}_{hf} = -g\mu_B \left[ \frac{\mathbf{L}}{r^3} - \left( \frac{\mathbf{S}}{r^3} - \frac{3\mathbf{r}(\mathbf{S} \cdot \mathbf{r})}{r^5} \right) + \frac{8\pi}{3} \delta^{(3)}(r) \mathbf{S} \right], \quad (2.10)$$
where \( \delta^{(3)}(r) \) is the Dirac delta function. The first term is the magnetic field created by the orbital motion of the charged electron, the second term is the field created by the magnetic dipole moment of the electron and the third term is the “Fermi contact” term. The Fermi contact term is non-zero only when the electron is an atomic s orbital.

### 2.5 NMR Shift

As we have said above, nuclear magnetic resonance will be observed when

\[
f = f_L = \frac{\gamma}{2\pi} H_{\text{nuc}}. \tag{2.11}
\]

In this formula, it is important to remember that \( H_{\text{nuc}} \) is the magnitude of the magnetic field at the nuclear site, which may differ from that of the applied laboratory field \( H_0 \). There may be an additional hyperfine magnetic field \( (H_{\text{hf}}) \) at the nuclear site due to the electron bath. In a paramagnetic material the average value of \( H_{\text{hf}} \) is zero in the absence of an external field \( H_0 \). In the presence of \( H_0 \), \( H_{\text{hf}} \) will be parallel to \( H_0 \). The field magnitude at the nuclear site is now \( H_{\text{nuc}} = H_0 + H_{\text{hf}} \). For an NMR experiment at a fixed external field \( H_0 \), resonance will now be observed when

\[
f = f_L = \frac{\gamma}{2\pi}(H_0 + H_{\text{hf}}). \tag{2.12}
\]

Based on the expectation of Eq. 2.11, the resonance frequency is shifted by an amount \( \Delta f = \frac{\gamma}{2\pi} H_{\text{hf}} \). Similarly, if we consider a field-swept NMR experiment at a fixed frequency \( f \), resonance will be observed when the external field magnitude is \( H_0 = \frac{2\pi f}{\gamma} - H_{\text{hf}} \). That is, resonance is shifted by an amount \( \Delta H = H_{\text{hf}} \). The NMR shift, \( K \), is defined as

\[
K = \Delta H/H_0 = \frac{\Delta f}{f_0}, \tag{2.13}
\]

where \( f_0 = \frac{\gamma}{2\pi} H_0 \) is the Larmor frequency corresponding to the external field. This fractional shift is independent of \( H_0 \) and can be either positive or negative depending on the sign of \( \Delta H \).

As we have seen, internal magnetic fields at the nuclear site can be caused by both the orbital and spin degrees of freedom of the electrons. Internal fields generated by the orbital motion of
the electrons (partially unquenched by $\mathbf{H}_0$) give rise to the “chemical shift” $K_{\text{chem}}$, sometimes also called the “orbital shift”. The shift due to the spin paramagnetism of the electrons, $K_{\text{spin}}$, is historically referred to as the “Knight shift”. The total NMR shift, then, is expressed as a sum of two terms

$$K(T) = K_{\text{chem}} + K_{\text{spin}}(T).$$

As indicated, $K_{\text{chem}}$ is independent of temperature and the temperature dependence of the NMR shift comes from $K_{\text{spin}}(T)$.

The chemical shift is of primary importance to chemists, who use it to decode the structure of molecules. However, in condensed-matter NMR our interest is in using $K_{\text{spin}}$ to extract the spin susceptibility of the electrons. The spin-polarized electrons (with net thermal-average spin moment $\mu_S$) will create an internal field at the nuclear site. This is conventionally expressed as

$$H_{\text{hf}} = A_{\text{hf}} \mu_S.$$

$A_{\text{hf}}$ is known as the hyperfine coupling constant and is usually expressed units of Oe/$\mu_B$, implying that $\mu_S$ is measured in Bohr magneton units. It is important to remember here that $\mu_S$ is the (microscopic) spin moment at a particular magnetic site, not a bulk quantity. The bulk magnetization per mole of formula units can be expressed as $M = N_A \mu_S$, where $N_A$ is Avogadro’s number. Note that the previous expression gives $M$ in units of $\mu_B$/mol. Bulk measurements, however, are reported in emu/mol, where emu = Gcm$^3$ = erg/G is the CGS unit of magnetic moment. To convert the units, we use the conversion $1 \mu_B = 9.274 \times 10^{-21}$ emu. Therefore, we can express $M$ in emu/mol units as $M = (9.274 \times 10^{-21})N_A \mu_S$. As a shorthand, this can be written $M = N_A \mu'_B \mu_S$, with the understanding that in this expression $\mu'_B$ is a dimensionless number, simply the number of “emu” units in one “$\mu_B$” unit. Combining this with the bulk expression $M = \chi H_0$ and using Eq. 2.15, we find that

$$K_{\text{spin}} = \frac{H_{\text{hf}}}{H_0} = \frac{A_{\text{hf}}}{N_A \mu'_B \chi} = \frac{A_{\text{hf}}}{N_A \mu'_B \chi}.$$ 

Note that here we have assumed that the internal field is parallel to the spin moment. In a more general case (such as the Fe-based superconductors), $\mathbf{H}_{\text{hf}}$ is not parallel to $\mu_S$ and $A_{\text{hf}}$ becomes a tensor.

The bulk $\chi$ is typically expressed in units of cm$^3$ per mole of formula units. If there are $n$ magnetic ions per formula unit, we have instead $K = \frac{A_{\text{hf}}}{nN_A \mu'_B \chi}$. 

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2 Note that here we have assumed that the internal field is parallel to the spin moment. In a more general case (such as the Fe-based superconductors), $\mathbf{H}_{\text{hf}}$ is not parallel to $\mu_S$ and $A_{\text{hf}}$ becomes a tensor.

3 The bulk $\chi$ is typically expressed in units of cm$^3$ per mole of formula units. If there are $n$ magnetic ions per formula unit, we have instead $K = \frac{A_{\text{hf}}}{nN_A \mu'_B \chi}$. 

In this expression, $A_{hf}$ has units of Oe/$\mu_B$, $N_A$ has units of mol$^{-1}$, $\chi$ has units of cm$^3$/mol and $\mu'_{B} = 9.274 \times 10^{-21}$ emu/$\mu_B$ (a dimensionless number). An alternative way of interpreting this equation is to let $\mu'_{B}$ have its usual units (emu), but in this case $A_{hf}$ has units of Oe (not Oe/$\mu_B$). The apparent dimensional inconsistency of the standard NMR equation (Eq. 2.16) was pointed out by Johnston [16].

As shown in Eq. 2.16, the NMR shift is proportional to the bulk magnetic susceptibility $\chi$ of the electrons. Combining Eqs. 2.14 and 2.16, we find

$$K(T) = K_{chem} + \frac{A_{hf}}{N_A\mu'_{B}} \chi(T).$$

As a result, a plot of $K(T)$ vs $\chi(T)$ will be a straight line. Such a “$K$ vs $\chi$” plot is generally linear and can be used to extract the hyperfine coupling $A_{hf}$ (from the slope) or $K_{chem}$ (from the $K$ intercept at $\chi = 0$).

### 2.6 Spin-Lattice Relaxation Rate, $1/T_1$

We have seen that the nuclear energy levels in a magnetic field $H_{nuc}$ are

$$E = -\gamma \hbar H_{nuc} m$$

where $m = -I, \ldots, I$ is the angular momentum projection quantum number. In thermal equilibrium, the relative populations of the energy levels are given by the Boltzmann factor $e^{-\Delta E/k_B T}$. For example, consider nuclei with $I = 1/2$. There are two energy levels. The lower energy state has a greater population, while the population of the upper energy state is lower by a factor of $1 - e^{\gamma \hbar H_{nuc} / k_B T}$. During a $\pi/2$ pulse, nuclei from the lower state are excited into the upper state until the populations are equal, a condition known as “saturation.” Over a time scale $T_1$, the nuclei in the upper state will relax back to the lower state until the thermal equilibrium populations are re-established. To make the transition from the upper state back to the lower state, nuclei must be

---

4Eq. 2.16 is dimensionally consistent. $K_{spin}$ is unitless by definition. The units of $\frac{A_{hf} \chi}{N_A\mu'_{B}}$ are (Oe/$\mu_B$)(cm$^3$/mol)/(1/mol)(emu/$\mu_B$), which is unitless since G = Oe and emu = Gcm$^3$ in CGS units.
"stimulated" by fluctuating fields of the correct frequency [49]. Spin-lattice relaxation is therefore induced by fluctuations of the hyperfine field at the NMR frequency.

In the most general density-matrix treatment of nuclear spin-lattice relaxation (see Ref. [47] §5.12 and/or Ref. [50] §3.5), $1/T_1$ (measured with the external field in the $i$ direction) can be expressed in terms of hyperfine field fluctuations at wavevector $q$ and frequency $\omega$ as

$$
\left( \frac{1}{T_1} \right)_i = \frac{\gamma^2}{2} \sum_q \left[ |H_{\text{hf}}^i(q,\omega_N)|^2 + |H_{\text{hf}}^k(q,\omega_N)|^2 \right]
$$

(2.19)

where $(i, j, k)$ are mutually perpendicular axes and

$$
|H_{\text{hf}}^j(q,\omega_N)|^2 = \int \langle H_{\text{hf}}^j(q,t)H_{\text{hf}}^j(q,0) \rangle e^{i\omega_N t} dt
$$

(2.20)

is the Fourier transform of the time-autocorrelation function of the randomly fluctuating hyperfine field, evaluated at the NMR frequency. $|H_{\text{hf}}^j(q,\omega_N)|^2$ is referred to as the "power spectral density" and has units of Oe$^2$/Hz. Similar to Eq. 2.15, the hyperfine field is determined by the electron spin moment according to

$$
H_{\text{hf}}^i(q,t) = A_{\text{hf}}^i(q)\mu_S^i(q,t),
$$

(2.21)

where $A_{\text{hf}}^i(q)$ is called the hyperfine form factor. Conventionally, $A_{\text{hf}}^i(q)$ has units of Oe/$\mu_B$, implying that $\mu_S^i$ is measured in $\mu_B$ units. $1/T_1$ can then be expressed as

$$
\left( \frac{1}{T_1} \right)_i = \frac{\gamma^2}{2} \sum_q \left[ A_{\text{hf}}^i(q)^2|\mu_S^i(q,\omega_N)|^2 + A_{\text{hf}}^k(q)^2|\mu_S^k(q,\omega_N)|^2 \right]
$$

(2.22)

Another useful expression for $1/T_1$ can be obtained by invoking the fluctuation-dissipation theorem:

$$
|\mu_S^j(q,\omega)|^2 = \frac{k_B T}{N A_B \mu_B^2} \chi''_j(q,\omega) \frac{\omega}{\omega}.
$$

(2.23)

In this expression, $\chi''_j(q,\omega)$ is the imaginary part of the dynamical magnetic susceptibility, and is measured in cm$^3$/mol units. As in Eq. 2.16, in this equation $\mu_B^2$ is a dimensionless number

---

5 Again, here we have assumed that the hyperfine field is parallel to the spin moment. In the general case $A_{\text{hf}}(q)$ is a tensor.

6 The dynamical magnetic susceptibility is defined by $M(q,\omega) = \chi(q,\omega)H(q,\omega)$, where $\chi$ is a tensor. If the tensor $\chi$ is diagonal, the induced magnetization $M$ is parallel to the applied field $H$. Here we use a simplified notation for the diagonal elements $\chi_j \equiv \chi_{jj}$. 
needed convert between “μB” units and “emu” units. The fluctuation-dissipation theorem relates the spontaneous spin fluctuations \(|\mu_S|^2\) to the dissipative part of the susceptibility \(\chi''\). Note that Eq. 2.23 is an approximation valid only when \(\hbar\omega \ll k_B T\), which is true for NMR.

Using Eq. 2.23, \(1/T_1\) is given by

\[
\left(\frac{1}{T_1}\right)_i = \frac{\gamma^2 N}{2} \frac{k_B T}{N A \mu_B^2} \sum_q \left[ A^j_{\text{hf}}(q)^2 \frac{\chi''^j(q,\omega)}{\omega} + A^k_{\text{hf}}(q)^2 \frac{\chi''^k(q,\omega)}{\omega} \right]. \tag{2.24}
\]

Since \(1/T_1\) is seen to be proportional to \(T\), it is common to consider the temperature-normalized relaxation rate \(1/T_1 T\), which is then given by

\[
\left(\frac{1}{T_1 T}\right)_i = \frac{\gamma^2 N}{2} \frac{k_B T}{N A \mu_B^2} \sum_q \left[ A^j_{\text{hf}}(q)^2 \frac{\chi''^j(q,\omega)}{\omega} + A^k_{\text{hf}}(q)^2 \frac{\chi''^k(q,\omega)}{\omega} \right]. \tag{2.25}
\]

This equation, expressing \(1/T_1 T\) in terms of the \(q\)-sum of the dynamical susceptibility, is commonly used in the strongly-correlated electron NMR literature.

What energy scale is probed by NMR? For \(f = \omega/(2\pi) = 50\) MHz, we find \(E = hf = 0.2\) μeV (using Planck’s constant \(h = 4.14 \times 10^{-15}\) eVs). This is a very small energy scale in condensed matter, where typically energy scales are in meV. In fact, the NMR energy scale is often considered the zero-energy limit. Therefore, we can write \(1/T_1 T\), schematically, as

\[
\frac{1}{T_1 T} \propto \lim_{E \to 0} \frac{\chi''(E)}{E}. \tag{2.26}
\]

Now, since \(\chi''\) is an odd function of \(E\), we have \(\chi''(0) = 0\) and it is clear that we can also write \(1/T_1 T\) as

\[
\frac{1}{T_1 T} \propto \left. \frac{d\chi''(E)}{dE} \right|_{E=0}. \tag{2.27}
\]

Therefore \(1/T_1 T\) measures the low-energy slope of \(\chi''(E)\). Typical experimental data for \(\chi''(E)\), measured by inelastic neutron scattering, is shown in Fig. 2.6. It is clear that, through the low-energy slope, \(1/T_1 T\) is sensitive to energy scales well above the μeV scale and is not only sensitive \(\chi''(0.2\) μeV) \(\approx 0\), as one might naively expect. Experiments have consistently demonstrated that NMR is sensitive to the fluctuations relevant for superconductivity on the meV scale (see, for example, Ref. [51]).

\[\text{The units of } |\mu_j(q,\omega)|^2 \text{ are } \mu_B^2 s, \text{ while the units of } \frac{k_B T}{N} \frac{\chi''}{\omega} \text{ are emu}^2 s.\]
The spin-spin relaxation rate $1/T_2$ is also affected by hyperfine field fluctuations due to the electrons. In the most general density-matrix treatment of nuclear spin-lattice relaxation (see Ref. [47] §5.12), $1/T_2$ (measured with the external field in the $z$ direction) can be expressed in terms of hyperfine field fluctuations

$$
\left( \frac{1}{T_2} \right)_z = \frac{\gamma_N^2}{2} \sum_q \left[ |H_{\text{hf}}^z(q, \omega_N)|^2 + |H_{\text{hf}}^z(q, 0)|^2 \right].
$$

The first term is clearly related to $T_1$ processes and is in fact equal to $1/2T_1$. The second term indicates that, unlike $T_1$ which is only sensitive to hyperfine field fluctuations perpendicular to the applied magnetic field (the quantization axis of the nuclear spins), $T_2$ also probes time-averaged longitudinal hyperfine field fluctuations.
2.8 Korringa relation

In §2.5, we found that the spin part of the NMR shift was proportional to the spin susceptibility \(\chi\) of the electrons (Eq. 2.16)

\[
\mathcal{K}_{\text{spin}} = \frac{A_{hf}}{N_A \mu_B} \chi.
\]  

(2.29)

In this expression, the factors of \(N_A\) and \(\mu'_B\) are necessary since \(\chi\) has units of \(\text{cm}^3/\text{mol}\) and \(A_{hf}\) has units of \(\text{Oe}/\mu_B\). In this section, it will be sufficient to use the expression

\[
\mathcal{K}_{\text{spin}} = A_{hf} \chi.
\]  

(2.30)

Here, \(A_{hf}\) has units of \(\text{Oe}/\text{emu} = \text{cm}^{-3}\) and \(\chi = \mu_{\text{tot}}/H\) is the total susceptibility of a particular sample with units of \(\text{cm}^3\). In this expression, then, \(A_{hf} \propto 1/V\) and \(\chi \propto V\), where \(V\) is the volume of the particular sample. If we assume the electron/nucleus coupling is through the Fermi contact interaction, the hyperfine coupling is simply \(A_{hf} = (8\pi/3)\langle |u_k(0)|^2 \rangle\), where \(u_k(r = 0)\) is the periodic part of the Bloch wavefunction evaluated at the nuclear site and \(\langle \rangle\) denotes an average over the Fermi surface. In a simple metal without electronic correlations, \(\chi\) is the Pauli susceptibility given by \(\chi = (g\mu_B)^2 N(E_F)/2\), where \(N(E_F)\) is the electronic density of states at the Fermi energy. Therefore, \(K_{\text{spin}}\) is given by

\[
K_{\text{spin}} = A_{hf} \frac{(g\mu_B)^2}{2} N(E_F).
\]  

(2.31)

In this simple situation \(K_{\text{spin}}\) is simply proportional to \(N(E_F)\). Here, \(N(E_F)\) measures the total number of states in the entire sample (not normalized by volume or moles of formula units), and \(N(E_F)\) has units of states/erg.

Earlier we presented the most general expression for \(1/T_1\) based on the density matrix (Eq. 2.19), which has a simple physical understanding in terms of fluctuations of the hyperfine field at the Larmor frequency. In the special case of nuclei possessing a well-defined spin temperature in a simple uncorrelated metal (Ref. [47] §5.3), we can derive a historically important, straightforward expression for \(1/T_1\):

\[
\frac{1}{T_1} = \pi \hbar A_{hf}^2 (g\mu_B)^2 \gamma_n^2 N^2(E_F) k_B T
\]  

(2.32)
This expression shows that $1/T_1$ is proportional to temperature, with a slope determined by the square of $N(E_F)$. The quantity $1/T_1T$ will be constant with respect to temperature.

Comparing Eqs. 2.31 and 2.32 we see that if we consider the quantity $T_1TK_{\text{spin}}^2$, the factors of $A_{hf}$ and $N(E_F)$ will cancel leaving us with a material-independent result

$$T_1TK_{\text{spin}}^2 = \frac{(g\mu_B)^2}{4\pi\hbar k_B \gamma_n^2} = \frac{\hbar}{4\pi k_B} \left( \frac{\gamma_e}{\gamma_n} \right)^2 \equiv S_n,$$

which is known as the Korringa relation. Here, $\gamma_e = g\mu_B/\hbar$ is the electron gyromagnetic ratio ($\gamma_e/2\pi \sim 28$ GHz/T). Each nucleus has a different value of the Korringa constant $S_n$, depending on its $\gamma_n$.

### 2.9 Electric Quadrupole Interaction

Some nuclei possess an electric quadrupole moment, meaning that the charge distribution of the nucleus is not spherically symmetric but rather prolate or oblate about the quantization axis of its spin. In this case the nucleus has an interaction energy associated with its orientation with respect to its electric field environment. As we shall see, the effect of this coupling is to create multiple “satellite” lines in the NMR spectrum. In addition, resonance can be observed from quadrupolar nuclei even in the absence of an external magnetic field, an effect referred to as Nuclear Quadrupole Resonance (NQR). This is possible because the field $H_1$ can excite transitions between various orientational states of the nuclei.

#### 2.9.1 Nuclear Quadrupole Resonance (NQR)

The Hamiltonian for a quadrupolar nucleus with (dimensionless) total angular momentum $I$ in an electric field environment determined by the electric potential $V(\mathbf{r})$ is conventionally expressed as

$$\mathcal{H} = \frac{(eQ)V_{zz}}{4I(2I-1)} \left[ (3I_z^2 - I^2) + \eta(I_x^2 + I_y^2) \right].$$

In this expression, $eQ$ is the quadrupole moment of the nucleus, the quantity $V_{\alpha\beta} \equiv \partial^2V/\partial x_\alpha \partial x_\beta$ is evaluated at the nuclear site and the asymmetry parameter $\eta$ is given by $\eta = (V_{xx} - V_{yy})/V_{zz}$.
Since the electric field component $E_\alpha$ is simply $-\partial V/\partial x_\alpha$, the second derivative tensor $V_{\alpha\beta}$ is referred to as the electric field gradient (EFG). This expression has been written in the principal axis system of the EFG tensor where $V_{\alpha\beta}$ is diagonal. LaPlace’s equation $\nabla^2 V = 0$ implies that $V_{xx} + V_{yy} + V_{zz} = 0$, and therefore the EFG tensor is traceless. This additional condition ensures that only the two quantities $V_{zz}$ and $\eta$ are needed to fully describe the EFG environment at the site of the nucleus. At nuclear sites with axial symmetry, $\eta$ will be zero, which simplifies the analysis. At nuclear sites of cubic symmetry, we have $V_{xx} = V_{yy} = V_{zz} = 0$ and the quadrupole coupling is not observed. It is conventional to rewrite the prefactor in terms of the quadrupole frequency $\nu_Q$ defined according to

$$\frac{h\nu_Q}{6} = \frac{(eQ)V_{zz}}{4I(2I-1)},$$

so that the Hamiltonian is written as

$$\mathcal{H} = \frac{h\nu_Q}{6} \left[ (3I_z^2 - I^2) + \eta(I_x^2 + I_y^2) \right].$$

(2.36)

Consider a nucleus at a site of axial symmetry such that $\eta = 0$. In the absence of an external magnetic field, the nuclear energy levels for states $|Im\rangle$ are clearly given by

$$E_m = \frac{h\nu_Q}{6} \left[ 3m^2 - I(I + 1) \right].$$

(2.37)

There is a degeneracy between states with $\pm m$, reflecting the fact that flipping the nucleus “end-for-end” does not affect the orientational energy of the nucleus [47]. The energy levels and spectrum for $I = 5/2$ are shown in Fig. 2.7. For $I = 5/2$, the energy differences are $E_{\pm 3/2} - E_{\pm 1/2} = h\nu_Q$ and $E_{\pm 5/2} - E_{\pm 3/2} = 2h\nu_Q$. That is, the quadrupole frequency $\nu_Q$ directly determines the splittings between orientational energy levels. The field $\mathbf{H}_1$ with a frequency $\nu_Q$ or $2\nu_Q$ can induce resonant transitions between these orientational energy levels of the $I = 5/2$ nucleus. This is known as nuclear quadrupole resonance (NQR).

2.9.2 NMR spectrum in the presence of Quadrupole Effects

In the case of an applied laboratory magnetic field $\mathbf{H}_0$, it is usually sufficient to consider the quadrupole Hamiltonian as a perturbation to the usual Zeeman Hamiltonian $\mathcal{H} = -\gamma\hbar\mathbf{I}\cdot\mathbf{H}_0$. Again
Figure 2.7 NQR energy levels and NQR spectrum for a nucleus with $I = 5/2$ ($h = 1$). Credit: [46]

Figure 2.8 NMR spectrum with quadrupole perturbation for $I = 3/2$ nucleus, showing a central transition and two quadrupole satellites. In this example, the $m = \pm 1/2$ energy levels are lowered, while the $m = \pm 3/2$ energy levels are raised. Credit: [46]
considering the simple case \( \eta = 0 \), the total Hamiltonian is written as

\[
\mathcal{H} = -\hbar \nu L z' + \frac{\hbar \nu Q}{6} (3I_z^2 - I^2).
\] (2.38)

Here \( z' \) is along the external magnetic field \( \mathbf{H}_0 \) and \( z \) is along the principal axis of the EFG. According to this Hamiltonian, the NMR spectrum depends on the angle \( \theta \) between the external field and the EFG principal axis. A simple calculation in first-order perturbation theory shows that the perturbed energy levels are given by

\[
E_m = -\hbar \nu_L m + \frac{\hbar \nu Q}{6} \left[ 3m^2 - I(I + 1) \right] \left( \frac{3 \cos^2 \theta - 1}{2} \right). \quad (2.39)
\]

Consider now the case of a nucleus with \( I = 3/2 \) and \( \eta = 0 \). Instead of a single frequency \( \nu_L \) for all three transitions \( (3/2 \leftrightarrow 1/2, 1/2 \leftrightarrow -1/2 \) and \( -1/2 \leftrightarrow -3/2) \), there are now three distinct frequencies (Fig. 2.8). To first order in perturbation theory, the frequency of the \( 1/2 \leftrightarrow -1/2 \) “central” transition is unaffected by the quadrupole perturbation and remains at \( \nu_L \). The remaining two frequencies fall above and below \( \nu_L \) and are referred to as quadrupole satellites. To first order, the quadrupole satellite resonance frequencies are given by

\[
\nu_\pm = \nu_L \pm \frac{\nu Q}{2} (3 \cos^2 \theta - 1). \quad (2.40)
\]

In second order perturbation theory, the central transition frequency also depends on \( \theta \) according to

\[
\nu(\theta) = \nu_L - \frac{3 \nu Q^2}{16 \nu_L} \sin^2 \theta (9 \cos^2 \theta - 1). \quad (2.41)
\]

In practice, the angle \( \theta \) is changed by physically rotating the crystal with respect to the fixed external magnetic field.

### 2.10 Powder Lineshape

As we have seen, according to first order perturbation theory, the positions of the quadrupole satellite frequencies depend on the angle \( \theta \) between the external field and the principle axis of the EFG at the nuclear site:

\[
\nu = \nu_L \pm \frac{\nu Q}{2} (3 \cos^2 \theta - 1). \quad (2.42)
\]
Furthermore, in second order perturbation theory, the central transition line is also shifted according to

$$\nu = \nu_L - \frac{3\nu_Q^2}{16\nu_L^3}(1 - \cos^2 \theta)(9\cos^2 \theta - 1).$$  \hspace{1cm} (2.43)

These formulas apply specifically to an $I = 3/2$ nucleus such as $^{75}$As, with asymmetry parameter $\eta = 0$. In a single crystal sample, peaks will be observed at the specific frequencies corresponding to the orientation $\theta$ of the crystal. However, for metallic samples it is often useful to use a powder sample, consisting of many, randomly-oriented tiny crystal grains. This is done to increase the surface area in order to increase the number of nuclei within one skin-depth of the surface. In a powder sample, crystallites randomly sample all orientations in 3D space. What is the shape of the NMR spectrum in this case?

If we assume all orientations in 3D space are equally probable, the probability of the orientation being in the range $(\theta, \theta + d\theta)$ and $(\phi, \phi + d\phi)$ is given by

$$P(\theta, \phi)d\theta d\phi = \frac{\sin \theta d\theta d\phi}{4\pi}. \hspace{1cm} (2.44)$$

With $\eta = 0$, we can assume axial symmetry and integrate over $\phi$ to obtain

$$P(\theta)d\theta = \frac{\sin \theta d\theta}{2}. \hspace{1cm} (2.45)$$

This equation shows that the probability of a crystallite having $\theta \sim 0$ is nearly zero. This reflects the fact that $\theta$ is the polar angle away from a preferred direction, the direction of the external magnetic field defining the $z$ axis. Crystallites sampling all directions in 3D space are unlikely to select the preferred direction. Mathematically, the surface area of the unit sphere in the range $(\theta, \theta + d\theta)$ is small near $\theta = 0$.

### 2.10.1 Quadrupole Satellite Powder Pattern

We wish to calculate the distribution function $g(\nu)d\nu$, the probability that a nucleus has a resonance frequency in the range $(\nu, \nu + d\nu)$, given that $\nu = \nu(\theta) = \nu_L \pm \frac{\nu_Q}{2} (3\cos^2 \theta - 1)$. The problem is very similar to that of calculating the electronic density of states $N(E)dE$ from the
electronic band structure $E = E(k)$. It is a standard problem in solid state physics to show that

$$N(E) \sim \frac{1}{|\frac{dE}{dk}|}. \hspace{1cm} (2.46)$$

For example, if $E(k)$ is nearly constant at some energy $E_0$, the density of states near $E_0$ will be high. Analogous reasoning applies to the present problem, except an additional factor of $\sin \theta$ is needed to account for the fact that small values of $\theta$ are unlikely, as discussed above:

$$g(\nu) = \frac{\sin \theta}{|\frac{d\nu}{d\theta}|}. \hspace{1cm} (2.47)$$

This can be simply expressed in terms of $u = \cos \theta$ as

$$g(\nu) = \frac{1}{|\frac{d\nu}{du}|}. \hspace{1cm} (2.48)$$

In the present case where $\nu(u) = \nu_L + \frac{\nu Q}{2} (3u^2 - 1)$ we have that $d\nu/du = 3\nu Qu$ and $|u| = \sqrt{2(\nu - \nu_L + \nu Q/2)/(3\nu Q)}$. Thus we obtain

$$g(\nu) = \frac{1}{\sqrt{6\nu Q(\nu - \nu_L + \nu Q/2)}}. \hspace{1cm} (2.49)$$

Similarly, for the other satellite:

$$g(\nu) = \frac{1}{\sqrt{6\nu Q(-\nu + \nu_L + \nu Q/2)}}. \hspace{1cm} (2.50)$$

Both feature divergent peaks at the frequency corresponding to $\theta = 90^\circ$, as shown in Fig. 2.10.

### 2.10.2 Quadrupole Split Central Transition Line Powder Pattern

To obtain the NMR spectrum of the central transition line for a powder sample, we can again use Eq. 2.48. In this case the frequency as a function of $u = \cos \theta$ is given by $\nu = \nu_L - \frac{3\nu Q^2}{16\nu_L}(1 - u^2)(9u^2 - 1)$. Performing the differentiation with respect to $u$ and simplifying we obtain

$$g(u) = \frac{1}{|\frac{d\nu}{du}|} = \frac{1}{\frac{3\nu Q^2}{4\nu_L^2}|u||9u^2 - 5|}. \hspace{1cm} (2.51)$$

The denominator has zeros at $\theta = 90^\circ$ ($u = 0$) and $\theta = \cos^{-1}(\sqrt{5}/3) = 41.8^\circ$ ($u = \sqrt{5}/3$). Therefore the NMR spectrum will have divergent peaks at frequencies corresponding to $\theta = 90^\circ$ and $\theta = 41.8^\circ$. 

In order to obtain the expression for the NMR spectrum as a function of frequency (instead of $u$), it is necessary to solve the expression $\nu = \nu_L - \frac{3\nu_Q^2}{16\nu_L} (1 - u^2)(9u^2 - 1)$ for $|u|$. This is a multivalued function of $\nu$, as shown in Fig. 2.9. The expressions for the two branches are

$$|u|_\pm = \frac{1}{3} \sqrt{5 \pm \frac{4}{\nu^2_Q} \sqrt{3(\nu - \nu_L)\nu_L\nu^2_Q + \nu^4_Q}}.$$ (2.52)

Since multiple $|u|$ values correspond to the same frequency, the NMR spectrum as a function of frequency is a piecewise function

$$g(\nu) = \begin{cases} g(|u|_-) + g(|u|_+) ; \nu_L - \frac{\nu_Q^2}{3\nu_L} < \nu < \nu_L \\ g(|u|_-) ; \nu_L < \nu < \nu_L + \frac{3\nu_Q^2}{16\nu_L} \end{cases},$$ (2.53)

where $g(u)$ is given by Eq. 2.51 and $|u|_\pm$ are given by Eq. 2.52. The central transition line of the NMR spectrum therefore has a discontinuity at $\nu_L$ as shown in Fig. 2.10. This figure also shows the full NMR spectrum including the satellite lines. Note that in the real world, the sharp divergences will be smeared out due to NMR broadening effects. Mathematically, the spectrum shown here will be convoluted with a Gaussian of non-zero width, for example.
Figure 2.9  $|u|$ as a function of $\nu$ for the quadrupole split central transition line in a powder sample. Here, for illustration, $\nu_L = 10$ and $\nu_Q = 3$. The lower blue branch takes the minus sign in Eq. 2.52. The upper orange branch takes the plus sign in Eq. 2.52. The frequency range is between $\nu_L - \frac{\nu_Q^2}{3\nu_L}$ and $\nu_L + \frac{3\nu_Q^2}{16\nu_L}$. 
Figure 2.10  NMR spectrum in a powder sample with quadrupole effects ($I = 3/2$). Here, for illustration, $\nu_L = 10$ and $\nu_Q = 3$. Top: Zoom of the central transition line. The high frequency peak corresponds to $\theta = 90^\circ$, while the low frequency peak corresponds to $\theta = 41.8^\circ$. The frequency range is again between $\nu_L - \frac{\nu_Q^2}{3\nu_L}$ and $\nu_L + \frac{3\nu_Q^2}{16\nu_L}$. Bottom: Full NMR spectrum including satellite lines. The two peaks in the satellite spectrum both correspond to $\theta = 90^\circ$. 
CHAPTER 3. EXPERIMENTAL DETAILS

While the previous chapter focussed on the theory of NMR, this chapter describes some practical details necessary to obtain NMR data in a real-world laboratory. Also included is a discussion of high-pressure cells.

3.1 NMR coil configurations

In order to perform NMR measurements, the NMR coil containing the sample must be a part of a resonant “tank” circuit, whose resonance frequency matches the resonance frequency of the nuclei being studied. In practice, the sample coil is the inductor $L$ in an $LC$ circuit. The resonance frequency of the $LC$ circuit is given by $\omega = 1/\sqrt{LC}$. In addition, the impedance of the tank circuit must be matched to the 50 $\Omega$ output impedance of the RF pulse amplifier. Otherwise the RF pulses output by the amplifier will be reflected back towards the amplifier, instead of being broadcasted to the sample via the tank circuit. Similarly, if the tank circuit impedance is not matched to the input impedance of the NMR receiver, the NMR signal we wish to detect will be reflected away from the receiver. The coil tank circuit therefore must be both correctly “tuned” and correctly “matched”.

The typical $LC$ circuit arrangements are shown in Fig. 3.1. These are the parallel-tuned, series-matched (PTSM, Fig. 3.1(a)) and series-tuned, parallel-matched (STPM, Fig. 3.1(b)). The coil tank circuit is typically mounted on an NMR “probe” which is inserted into the cryostat such that the sample coil sits in the center of the homogeneous magnetic field produced by the superconducting solenoid magnets in our lab. The NMR probes in our laboratory all have at least one built-in variable capacitor, which is typically used for tuning the $LC$ circuit. If space allows, the probe can also have another built-in variable capacitor for matching, enabling the easy implementation of PTSM or STPM. When only one variable capacitor is available on the probe,
the pickup-coil configuration (Fig. 3.1(c)) can be used. In this configuration, there is no direct electrical connection between the pulse amplifier and the sample coil. Rather, the pulse is broadcast into a pickup coil and the pulse reaches the $LC$ circuit through induction, as in a transformer. In this arrangement, the matching can be controlled by varying the mutual inductance (“coupling”) between the pickup and sample coils. In practice, this is accomplished by moving the pickup coil relative to the sample coil until the matching is optimized, and then fixing the pickup coil in that position using glue.

### 3.2 Superconducting Magnets

To produce the large, stable, spatially homogeneous external magnetic field required for NMR measurements, our lab is equipped with three superconducting magnets. These magnets are solenoidal coils of superconducting wire in a completely closed loop. The coils must be maintained at liquid helium temperatures. One station has a fixed magnetic field of 7.4089 T. At the other stations, the magnetic field can be swept continuously from 0 T to approximately 8 T. The field sweep capability is useful for measurement of very broad NMR spectra, because the NMR
The NMR spectrometer has two main functions. First, it must deliver high power radiofrequency (RF) pulses to the NMR coil tank circuit in order to excite nuclei in the sample. The typical pulse NMR spectrometer has an RF pulse amplifier rated for an output power of 300 W to 1 kW, although power above 100 W is seldom needed in my experience. At this output power, a typical saturation pulse has a duration on the order of a few $\mu$s. Second, the spectrometer must receive the tiny spin echo signal which is broadcast by the nuclei in response to the high-power pulses. The spin echo is simply an amplitude modulated (AM) radio signal, with the nuclear Larmor frequency being the “carrier” frequency. The detection functions of the spectrometer are thus entirely analogous to the radio receivers we are all familiar with. The challenge is that the NMR spin echo signal is typically very weak. The precessing nuclear magnetization induces a voltage in the NMR coil tank circuit on the order of $\mu$V. For a particular spin echo signal, the signal-to-noise
ratio (S/N) is often less than one! Thus in order to extract the signal from the noise, the same experiment is repeated many times and digital signal averaging is used. With a sufficient number of trials \( n_{\text{avg}} \), ratios of S/N = 50 are achievable in a reasonable experimental time frame. The noise is reduced by a factor of \( \sqrt{n_{\text{avg}}} \). For the measurements presented in this thesis, \( n_{\text{avg}} \) was typically at least 32 and often greater than 1024.

A schematic block diagram of the “home-made” NMR spectrometers in our lab is shown in Fig 3.2. The NMR pulse parameters (duration, separation, phase, repetition time etc...) are set by the user on a desktop computer, which sends control signals to the pulse generator. The pulse generator then outputs the transistor-transistor logic (TTL) signals to control the other parts of the spectrometer.

The QPSK unit (short for “Quadrature Phase Shift Key”) takes a continuous wave RF signal from the frequency synthesizer and converts it into phase-controlled, low-power RF pulses according to the control TTL signals from the pulse generator. The control TTL signals from the pulse generator are (1) the pulse “gate” signal, which determines the duration and separation of the pulses and (2) the two-bit QPSK inputs, which determine the phase shift of the pulse \( 0, \pi/2, \pi, 3\pi/2 \) relative to the phase of the frequency synthesizer.

The phase-controlled, low-power RF pulses output from the QPSK are fed into the high-power RF pulse amplifier, which is also called the “transmitter”. On the way to the pulse amplifier, the low-power pulses are run through an RF attenuator to control the final output power (the pulse amplifier has a fixed gain). The high-power pulses are then sent to the NMR coil tank circuit. The cross diode in series ensures that low-voltage noise \(< 0.5 \text{ V}\) from the amplifier is not applied to the NMR coil tank circuit.

Note that the pulse generator also sends a TTL gate (or “blanking”) signal to the pulse amplifier. The pulse amplifier is actually kept off most of the time. The pulse amplifier is turned on shortly before the pulse and turned back off again shortly after the pulse, according to the TTL blanking signal from the pulse generator.
Figure 3.2  Block diagram of the NMR spectrometer. See §3.3.1 for an explanation of $f_{\text{ref}}$ and the 750 MHz intermediate frequency.
The next step is to receive and process the NMR spin echo signal. The spin echo signal passes through a pre-amplifier on its way to the receiver. The second cross diode in parallel conducts the high-power pulses (> 0.5 V) to ground, preventing them from reaching the preamp and receiver. The purpose of the receiver is to amplify the tiny signal and remove the Larmor frequency “carrier wave,” to extract the envelope of the AM spin echo signal. The amplified, spin echo envelope is output from the receiver to the computer and oscilloscope for signal averaging and analysis. The computer samples the spin echo envelope with a sample frequency of 10 MHz using an analog-to-digital converter card. The oscilloscope is triggered by a TTL signal from the pulse generator.

The example shown in Fig. 3.2 uses the Thamway N320-9059B, which combines the functions of the QPSK and receiver into a single unit.

3.3.1 What happens inside the receiver

3.3.1.1 Homodyne system

The basic function of the receiver is to amplify the tiny signal and to remove the carrier wave. To understand how the receiver removes the carrier wave, it is necessary to introduce the concept of an RF “mixer”. A mixer (indicated by the cross inside a circle) is a device which takes two incoming signals and gives the product of the two signals as an output. Recall the trigonometric identity $\cos(f_1t) \cos(f_2t) = (\cos((f_1 - f_2)t) + \cos((f_1 + f_2)t))/2$. Therefore, if two signals of frequencies $f_1$ and $f_2$ are sent into a mixer, the mixer output will contain signals with frequencies $|f_1 - f_2|$ and $(f_1 + f_2)$. The output of the mixer can be sent into a low-pass filter (LPF) to remove the high frequency $(f_1 + f_2)$ component, leaving just the difference frequency $|f_1 - f_2|$.

To remove the carrier (Larmor) frequency, the spin echo signal (with frequency $f_L$) is mixed with the reference frequency from the signal generator (with frequency $f_{\text{ref}}$). The output of the mixer/LPF is a signal with frequency $\Delta f = |f_L - f_{\text{ref}}|$. If the signal generator frequency $f_{\text{ref}}$ is exactly on resonance with the true NMR frequency $f_L$, then $\Delta f = 0$ and the carrier frequency has been removed completely. If the NMR spectrum is sharp and $f_{\text{ref}}$ is slightly off resonance, “beats” are clearly visible in the output of the receiver ($\Delta f \neq 0$).
Figure 3.3  The basic principle of quadrature ("phase-sensitive") detection using RF mixers (circle with cross). Low pass filters remove the $f_{\text{ref}} + f_L$ Fourier component emerging from the mixer.

Using this "mixing down" process, the Larmor frequency carrier wave can be removed from the spin echo signal. However, since the output has a frequency $\Delta f = |f_L - f_{\text{ref}}|$, we have lost the information about whether the Larmor frequency is above or below the reference frequency. To overcome this issue, the spin echo signal is actually mixed twice in parallel in a process referred to as "phase-sensitive detection" or "quadrature detection," as shown in Fig. 3.3. The spin echo signal is split in two. One component is mixed directly with the reference signal from the frequency synthesizer. The other component is mixed with a reference signal with a $\pi/2$ phase shift. Therefore the receiver produces two output signals (the "sin" component $s(t)$ and "cos" component $c(t)$) from only one input signal. The sin and cos components are then considered to be the real and imaginary parts of a complex time-domain spin echo signal $e(t) = c(t) + is(t)$. The Fourier transform $\tilde{e}(f)$ has peaks at both $\pm \Delta f$ making it unclear whether $f_L$ is above or below $f_{\text{ref}}$. In contrast, the Fourier transform of the complex signal $\tilde{c}(f)$ has only one peak, correctly indicating whether $f_L$ is above or below $f_{\text{ref}}$. 

\[
\Delta f = f_{\text{ref}} - f_L
\]
In the real world, amplifiers and mixers operate only within characteristic frequency bands. It is not possible to design one circuit which operates over the entire frequency range of relevance to NMR (10-500MHz). Therefore, the receiver requires separate circuitry for each frequency band, and the user must switch between the different frequency bands manually (Fig. 3.4). This is referred to as a “homodyne” system. This necessity of band-switching in the homodyne system is overcome by the “heterodyne” system.

### 3.3.1.2 Heterodyne system

The heterodyne system overcomes this drawback by using an “intermediate” frequency (IF). Using an additional RF mixer, all signals are transformed into the IF band, and the amplifier is optimized for this IF band. After amplification, the signal is mixed again to remove the IF carrier. The example shown in Fig. 3.5 is a heterodyne system with an intermediate frequency of 750 MHz, such as the receiver section of the Thamway N320-9059B.
Figure 3.5 Heterodyne quadrature NMR receiver. All signals are mixed into the intermediate frequency (IF = 750 MHz) band. No band selection switch is needed. BPF: Band-pass filter.

### 3.4 $T_1$ fitting functions

In the simplest case of a nucleus with $I = 1/2$, no quadrupole interaction is present and the nuclear magnetization after saturation will recover according to a single exponential

$$1 - \frac{M(t)}{M(\infty)} = A \exp(-t/T_1). \quad (3.1)$$

This situation applies to $^{77}$Se NMR in FeSe. Here $A$ is a fitting parameter that allows for experimentally imperfect saturation.

The other case which will arise in this thesis is that of $^{75}$As NMR, which is an $I = 3/2$ nucleus. In this case the NMR spectrum consists of three frequencies: the central transition, along with upper and lower satellites. If all three frequencies can be simultaneously irradiated and saturated, the nuclear magnetization will still recover according to a single exponential Eq. 3.1. However, in the more typical case only the central transition line is irradiated and saturated. In this case, the
nuclear magnetization will recover according to

\[
1 - \frac{M(t)}{M(\infty)} = A \left[ \frac{1}{10} \exp(-t/T_1) + \frac{9}{10} \exp(-6t/T_1) \right],
\]

(3.2)

which measures predominantly the rate \( T_1/6 \). Similarly in the case of \(^{75}\)As pure NQR, the nuclear magnetization recovers according to

\[
1 - \frac{M(t)}{M(\infty)} = A \exp(-3t/T_1),
\]

(3.3)

which measures \( T_1/3 \). An understandable explanation and derivation of Eqs. 3.2 and 3.3 is given in Ref. [50].

Typically, the nuclear relaxation time \( T_1 \) is uniform throughout the sample. However, in some cases, there is a distribution of \( T_1 \) values within the sample. In this case, the nuclear relaxation follows the “stretched” exponential form [52; 53; 54]

\[
1 - \frac{M(t)}{M(\infty)} = A \exp[-(t/T_1)^\beta],
\]

(3.4)

where \( 0 < \beta < 1 \) is known as the stretching exponent. Here, \( \beta = 1 \) indicates that there is no distribution of \( T_1 \) (a uniform \( T_1 \) throughout the sample). A value of \( \beta < 1 \) indicates a distribution of \( T_1 \). The smaller the \( \beta \) the larger the width of the distribution of \( T_1 \). Similar stretched forms also apply for the \( I = 3/2 \) cases Eqs. 3.2 and 3.3.

### 3.5 NMR under hydrostatic pressure

In condensed matter physics, it is often enlightening to study how the ground state of the material changes as a function of various tuning parameters, such as chemical doping or applied magnetic fields. Hydrostatic pressure is another common tuning parameter. The term “hydrostatic” is used to indicate that the pressure is applied with the sample immersed in a liquid pressure medium (typically oil-based) so that pressure is applied to the sample isotropically, that is, in all directions equally. This is in contrast to “uni-axial” pressure in which pressure is applied along one particular axis only. Hydrostatic pressure is capable of changing lattice constants and thereby orbital overlaps, leading to changes in the electronic properties of materials. An advantage of hydrostatic pressure
is that it can modify the electronic structure of materials without introducing additional disorder due to chemical dopants.

For the NMR measurements presented here, pressure was applied using a piston-cylinder type pressure cell composed of a CuBe outer shell and NiCrAl inner shell (Fig. 3.6). The diameter of the inner cylinder is 6 mm. Coils for NMR/NQR consist of about 20 turns of thin 40 AWG copper wire, with a coil diameter of a few mm. The wires are fed through an opening in a CuBe “plug” which is subsequently sealed using Stycast to fill the hole. The plug is then inserted into a Teflon tube filled with the Daphne 7373 pressure medium. The plug and teflon tube assembly containing the sample and pressure medium is then slid into the hollow cylinder of the pressure cell and clamped between the upper and lower clamping nuts by way of a tungsten carbide (WC) piston and piston backups. By applying force the upper piston backup using a hydraulic press, the teflon tube is compressed, which pressurizes the liquid medium. The pressure medium converts the uni-axial force applied by the hydraulic press into hydrostatic pressure applied to the sample. The upper clamping nut is then tightened, which locks in the pressure even when the cell is removed from the hydraulic press.

At high pressures and low temperatures, the pressure medium will solidify. In order for the applied pressure to be hydrostatic, the medium must be liquid when the pressure is changed using the hydraulic press. Since this process is done at room temperature, a key property of the pressure medium is the room temperature solidification pressure. Above this pressure, the pressure applied to the sample is no longer hydrostatic. As shown in Fig. 3.6, the Daphne 7373 pressure medium remains liquid at room temperature up to 2.2 GPa. Since this pressure corresponds nicely to the maximum pressure our cell can withstand without irreversible deformations, Daphne 7373 was a natural choice of pressure medium for our experiments.

In order to calibrate the pressure inside the cell, a second NQR coil containing powdered Cu₂O was used in addition to the main NMR/NQR coil containing the sample of interest. The axes of the two coils were oriented perpendicular to one another to avoid interference between the coils. The Cu NQR frequency of Cu₂O at room temperature and ambient pressure is 25.99 MHz. Since
Figure 3.6  Left panel: Schematic of the hybrid CuBe-NiCrAl piston-cylinder clamp cell used for high pressure NMR measurements. (WC: Tungsten Carbide.) Right panel: Phase diagram of the pressure medium Daphne 7373. Credit: [55; 56]

the pressure and temperature dependence of the NQR frequency of Cu₂O is well known in the literature [57], it can be used to measure the pressure conditions inside the cell.

It is important to note that the pressure in the cell is not quite constant as a function of temperature. As the cell is cooled from room temperature to 100 K, the pressure drops by approximately 0.2 GPa. However, below 100 K the pressure remains nearly constant to the lowest measurement temperatures.
CHAPTER 4. COEXISTENCE OF ANTIFERROMAGNETIC AND
FERROMAGNETIC SPIN CORRELATIONS IN SrCo$_2$As$_2$ REVEALED BY
$^{59}$Co AND $^{75}$As NMR


P. Wiecki$^{1,2}$, V. Ogloblichev$^{1,3}$, Abhishek Pandey$^{1,2}$, D. C. Johnston$^{1,2}$, and Y. Furukawa$^{1,2}$

1 The Ames Laboratory, Ames, Iowa 50011, USA
2 Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA
3 Institute of Metal Physics, Ural Division of Russian Academy of Sciences, Ekaterinburg 620990, Russia

4.1 Abstract

In nonsuperconducting, metallic paramagnetic SrCo$_2$As$_2$, inelastic neutron scattering measurements have revealed strong stripe-type $\mathbf{q} = (\pi, 0)$ antiferromagnetic (AFM) spin correlations. Here, using nuclear magnetic resonance (NMR) measurements on $^{59}$Co and $^{75}$As nuclei, we demonstrate that stronger ferromagnetic (FM) spin correlations coexist in SrCo$_2$As$_2$. Our NMR data are consistent with density functional theory (DFT) calculations which show enhancements at both $\mathbf{q} = (\pi, 0)$ and the in-plane FM $\mathbf{q} = 0$ wavevectors in static magnetic susceptibility $\chi(\mathbf{q})$. We suggest that the strong FM fluctuations prevent superconductivity in SrCo$_2$As$_2$, despite the presence of stripe-type AFM fluctuations. Furthermore, since DFT calculations have consistently revealed similar enhancements of the $\chi(\mathbf{q})$ at both $\mathbf{q} = (\pi, 0)$ and $\mathbf{q} = 0$ in the iron-based superconductors and parent compounds, our observation of FM correlations in SrCo$_2$As$_2$ calls for detailed studies of FM correlations in the iron-based superconductors.
4.2 Introduction

The interplay between magnetism and superconductivity is one of the central issues in unconventional superconductors (SCs) such as high $T_c$ cuprates and iron pnictide-based SCs. Among the iron pnictide-based SCs, the “122” class of compounds, $A$Fe$_2$As$_2$ ($A =$ Ca, Ba, Sr, Eu), has been one of the most widely studied systems in recent years. [16; 58; 59; 60; 18; 19; 61] These systems undergo coupled structural and magnetic phase transitions at a system-dependent Néel temperature $T_N$, below which long-range stripe-type antiferromagnetic (AFM) order emerges. Suppression of the AFM order by doping or pressure results in a SC ground state with $T_c$ ranging from a few K to more than 50 K. Continued doping ultimately results in the suppression of the stripe-type AFM spin fluctuations, which correlates with the suppression of SC.[16; 58; 59; 60; 18; 19; 61] Although the Cooper pairing is widely believed to originate from the residual stripe-type AFM spin fluctuations, the origin of the large variability of $T_c$ is still not well understood.

Tetragonal, metallic paramagnetic (PM) SrCo$_2$As$_2$ is the end member of the electron-doped Sr(Fe$_{1-x}$Co$_x$)$_2$As$_2$ family of compounds, which displays superconductivity in the range from $x = 0.07$ to $x = 0.17$ with a maximum $T_c$ of 19 K.[62; 63] The $x = 0$ parent compound, SrFe$_2$As$_2$, is an AFM showing stripe-type spin density wave order below 220 K.[64; 65] In SrCo$_2$As$_2$, on the other hand, no long range magnetic ordering is observed down to 1.8 K.[66] The Sommerfeld coefficient ($\gamma = 37.8 \text{ mJ mol}^{-1} \text{K}^{-2}$) is significantly enhanced relative to SrFe$_2$As$_2$ in the stripe AFM state.[66] Angle-resolved photoemission spectroscopy and electronic structure calculations show no clear nesting features of the Fermi surface which drive the stripe-type AFM order and SC in the parent and modestly doped compounds.[66] Nevertheless, AFM spin correlations are suggested from the temperature ($T$) dependence of magnetic susceptibility $\chi$ which exhibits a broad maximum around 115 K, a characteristic of short-range dynamic AFM correlations in low-dimensional spin systems. [66] Subsequent inelastic neutron scattering (INS) measurements on SrCo$_2$As$_2$ revealed strong AFM spin fluctuations at the stripe-type wavevector.[67] Similar physical properties are reported in the SC compound KFe$_2$As$_2$, the end member of the hole-doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ family. This compound also has an enhanced $\gamma = 103 \text{ mJ mol}^{-1} \text{K}^{-2}$ and a broad peak in $\chi$ around 100 K.[68]
along with strong stripe-type AFM fluctuations.[69] The similarity between SC KFe$_2$As$_2$ and non-SC SrCo$_2$As$_2$ raises the important question of why superconductivity does not arise in SrCo$_2$As$_2$.

In this paper, we report $^{59}$Co and $^{75}$As nuclear magnetic resonance (NMR) measurements to examine the local microscopic properties of SrCo$_2$As$_2$. Our analysis, based on the modified Korringa relation, reveals strong ferromagnetic (FM) spin fluctuations within the Co layer coexisting with the stripe-type AFM fluctuations observed by INS. Based on these results, we suggest that the low-energy FM fluctuations observed by NMR compete with the stripe-type AFM fluctuations, resulting in the suppression of SC in SrCo$_2$As$_2$. Furthermore, our observation of coexisting stripe AFM and FM fluctuations in SrCo$_2$As$_2$ is consistent with density functional theory (DFT) calculations which show peaks in the static susceptibility, $\chi(q)$, at both the FM and stripe AFM in-plane wavevectors.[67] This theoretically predicted enhancement of $\chi(q)$ at both wavevectors is not unique to SrCo$_2$As$_2$ but in fact applies more generally to iron-pnictide based superconductors and parent compounds.[16; 71; 72; 73; 74; 75] Our NMR data provide the first microscopic confirmation of spin susceptibility enhanced at both wavevectors in the iron-pnictide family, indicating that FM fluctuations may play an important role in determining $T_c$ in iron-pnictide based SCs.

NMR measurements were performed on $^{75}$As ($I = 3/2, \gamma/2\pi = 7.2919$ MHz/T) and $^{59}$Co ($I = 7/2, \gamma/2\pi = 10.03$ MHz/T) using a homemade phase-coherent spin-echo pulse spectrometer. The $^{59}$Co and $^{75}$As spin-lattice relaxation rates ($1/T_1$) were measured with a recovery method using a single $\pi/2$ saturation pulse.[70] The single crystal used in this study was grown with Sn flux and is same as that in our previous study [66] where preliminary $^{75}$As-NMR results were reported.

4.3 Results

Figure 4.1(a) shows field-swept $^{59}$Co-NMR spectra at various values of $T$ for magnetic fields parallel to the $c$ axis ($H \parallel c$ axis) and to the $ab$ plane ($H \parallel ab$ plane). The typical spectrum for a nucleus with spin $I = 7/2$ with Zeeman and quadrupolar interactions can be described by a nuclear spin Hamiltonian $\mathcal{H} = -\gamma h \mathbf{I} \cdot \mathbf{H}_{\text{eff}} + \frac{\hbar q}{6} [3I_z^2 - I(I + 1)]$, where $\mathbf{H}_{\text{eff}}$ is the effective field at the nuclear site and $h$ is Planck’s constant. The nuclear quadrupole frequency for $I = 7/2$ nuclei is
Figure 4.1 (Color online) (a) Field-swept $^{59}$Co-NMR spectra at frequency $f = 66.3$ MHz for magnetic fields $H \parallel c$ axis (black) and $H \parallel ab$ plane (red) to at various values of $T$. The vertical dashed line represents the zero-shift position ($K = 0$). (b) $T$ dependence of the $^{59}$Co-NMR shifts $K_c$ and $K_{ab}$. The black and red dashed lines are corresponding to $K_0$ for $K_c$ and $K_{ab}$, respectively. Inset: $K$ vs $\chi$ plots for each field direction where we used $\chi$ data reported in Ref. [66]. The thick solid lines are fitting results and two thin lines above and below the thick line give an error for our estimate of $K_0$ for each $H$ direction. (c) $T$ dependence of the full width at half maximum (FWHM) of the spectra for each field direction.

given by $\nu_Q = e^2 Q V_{ZZ}/14h$, where $Q$ is the nuclear quadrupole moment and $V_{ZZ}$ is the electric field gradient at the nuclear site. For $I = 7/2$ nuclei, this Hamiltonian produces a spectrum with a sharp central transition line flanked by three satellite peaks on either side. The observed $^{59}$Co NMR spectra, however, do not show the seven distinct lines but rather exhibit a single broad line due to inhomogeneous broadenings. From the line width, we estimate $\nu_Q \sim 0.14$ MHz at 4.2 K with $V_{ZZ}$ parallel to the $c$ axis, close to the value of 0.13 MHz for $^{59}$Co in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ with $x = 0.02$ and 0.04.[76]
Figure 4.2 (Color online) $T$ dependence of $1/T_1T$ for both magnetic field directions, $H \parallel c$ axis [$1/(T_1T)_{H\parallel c}$] and $H \parallel ab$ plane [$1/(T_1T)_{H\parallel ab}$]. Inset: Recovery curves at $T = 2.4$ K for both $H$ directions. The solid lines are fits by the relaxation function described in the text.

Figure 4.1(b) shows the $T$ dependence of the NMR shift for $H \parallel c$ axis ($K_c$) and $H \parallel ab$ plane ($K_{ab}$). The NMR shift has contributions from the $T$-dependent spin part $K_{\text{spin}}$ and a $T$-independent orbital part $K_0$. $K_{\text{spin}}$ is proportional to the spin susceptibility $\chi_{\text{spin}}$ through the hyperfine coupling constant $A_{hf}$ giving $K(T) = K_0 + \frac{A_{hf}}{N_A} \chi_{\text{spin}}(T)$, where $N_A$ is Avogadro’s number. The anisotropic spin susceptibilities $\chi_{ab}$ and $\chi_c$ in SrCo$_2$As$_2$ were reported in Ref. [66]. The inset of Fig. 4.1(b) plots $K_{ab}$ and $K_c$ against $\chi_{ab}$ and $\chi_c$, respectively, with $T$ as an implicit parameter. $T$ is chosen to be above 20 K to avoid upturns in $\chi$ due to impurities.[66] $K_{ab}$ and $K_c$ vary with the corresponding $\chi$ as expected, although one can see a slight deviation from the linear relationship. We estimated the hyperfine coupling constants $A_c = (-110 \pm 5)$ kOe/$\mu_B$ and $A_{ab} = (-22.9 \pm 1.0)$ kOe/$\mu_B$ by fitting the data (shown by the thick lines in the inset). $A_c$ is comparable to the value of $-105$ kOe/$\mu_B$ for isotropic $d$ electron core polarization, while $A_{ab}$ is much smaller. The small value of $A_{ab}$ could be
due to anisotropic and positive orbital and/or dipolar hyperfine coupling contributions which cancel
a part of the negative core polarization hyperfine field. Similar reductions in the hyperfine coupling
constant have been observed in several Co compounds, which have been well explained by taking
the orbital contributions into consideration.[77; 78; 79] The orbital shifts $K_{0,ab} = (1.31 \pm 0.10)\%$
and $K_{0,c} = (1.51 \pm 0.13)\%$ were estimated from the fittings. In order to estimate the error in $K_0$, we
change the $K_0$ while keeping the same slope to cover all data points. The two thin lines correspond
to the fitting lines with minimum and maximum $K_0$ for each $H$ direction. The $T$ dependences of
$K_{ab}$ and $K_c$ are similar to the behaviors reported for $^{75}\text{As-NMR}$ in Ref. [66], which show broad
maxima at $T \sim 115$ K. These maxima are observed as minima in the $^{59}\text{Co NMR shift}$ data due to
the negative hyperfine coupling constant. The broad minima in $K_{ab}$ and $K_c$ suggest the presence
of low-dimensional dynamic short-range AFM correlations below 115 K. In Fig. 4.1(c), we plot the
full width at half maximum (FWHM) of the spectra as a function of $T$ for $H \parallel c$ axis and $H \parallel ab$
plane. With decreasing $T$, the FWHM decreases gradually and starts to increase below $\sim 30$ K
where $\chi$ shows $T$-independent behavior, suggesting inhomogeneities of the dynamic short-range
AFM order below 30 K.

To investigate the dynamical magnetic properties, we have measured $1/T_1$ versus $T$ (Fig. 4.2).
In both field directions $1/T_1T$ is roughly constant over the entire temperature range. The inset
shows nuclear magnetization recovery curves for the two magnetic field directions together with
fitting results. To examine the character of the spin fluctuations in more detail, we perform a
modified Korringa relation analysis. Within a Fermi liquid picture, $1/T_1T$ is proportional to the
square of the density of states at the Fermi energy $D(E_F)$ and $K_{\text{spin}}(\propto \chi_{\text{spin}})$ is proportional to
$D(E_F)$. In particular, $T_1K_{\text{spin}}^2 = \frac{\hbar}{4\pi k_B} \left(\frac{\chi}{T_1}\right)^2 = S$, which is the Korringa relation. Deviations from
$S$ can reveal information about electron correlations in the material [80; 81], which are expressed
via the parameter $\alpha = S/(T_1K_{\text{spin}}^2)$. For instance, enhancement of $\chi(q \neq 0)$ increases $1/T_1T$ but
has little or no effect on $K_{\text{spin}}$, which probes only the uniform $\chi$ with $q = 0$. Thus $\alpha > 1$ for AFM
correlations and $\alpha < 1$ for FM correlations.
Application of the Korringa relation to SrCo$_2$As$_2$ requires some care due to the anisotropy of $K_{\text{spin}}$ and $1/T_1 T$. Since $1/T_1 T$ probes magnetic fluctuations perpendicular to the magnetic field,[82] it is natural to consider the Korringa ratio $1/(T_{1,\perp} T K_{\text{spin}, ab}^2)$ where $1/(T_{1,\perp} T) = 1/(T_1 T)_{H\parallel c}$, when examining the character of magnetic fluctuations in the $ab$ plane. Similarly, we consider the Korringa ratio $1/(T_{1,\parallel} T K_{\text{spin}, c}^2)$ for magnetic fluctuations along the $c$ axis. Here $1/(T_{1,\parallel} T)$ is estimated from $2/(T_1 T)_{H\parallel ab} - 1/(T_1 T)_{H\parallel c}$.

In the top panel of Fig. 4.3, we show the $T$ dependence of the Korringa ratios for magnetic fluctuations in the $ab$ plane and along the $c$ axis, along with the corresponding values of the parameter $\alpha$ in the bottom panel. We find that $\alpha \ll 1$ in each case, with the value of $\alpha$ remaining constant throughout the range of $T$. The low values of $\alpha$ indicate that the fluctuations have predominantly FM character. It should be emphasized that the $\alpha$ values strongly depend on $K_{\text{spin}}$.
Figure 4.4 (Color online) (a) $T$ dependence of the $^{75}$As NMR shift for both field directions in SrCo$_2$As$_2$ (black) and BaCo$_2$As$_2$ (red) [83]. (b) $T$ dependence of $1/T_1 T$ at the $^{75}$As sites for both field directions in SrCo$_2$As$_2$ (black) and BaCo$_2$As$_2$ (red).

and the $\alpha_{\perp}$ greater than $\alpha_{\parallel}$ could be due to the small $K_{\text{spin}}$ values arising from the small $A_{ab}$. In addition, it should be noted that the observed $1/T_1 T$ is the sum of four contributions: the $s$ electron Fermi contact, $d$ orbital, $d$ core polarization, and $d$ dipole relaxation rates. As a result, the estimated values for $\alpha$ for both directions can be considered to be upper limits on $\alpha$, indicating even stronger FM fluctuations in SrCo$_2$As$_2$ than expected from the above $\alpha$ values. On the other hand, the increase of $1/T_{1,\parallel} T K^2_{\text{spin,c}}$ below 50 K clearly indicates the presence of AFM correlations along the c axis coexisting with the dominant FM fluctuations.
The suggested FM spin correlations can be confirmed by $^{75}\text{As}$ NMR in SrCo$_2$As$_2$. In Fig. 4.4(a), we show the $T$ dependence of the $^{75}\text{As}$ NMR shifts $K_{ab}$ and $K_c$. For comparison, Fig. 4.4 also shows our analogous data from isostructural BaCo$_2$As$_2$ reported in Ref. [83], which are in agreement with those reported in Ref. [84]. The NMR shifts measured at the $^{75}\text{As}$ sites of SrCo$_2$As$_2$ display broad maxima at $T \sim 115$ K, consistent with the NMR shift measured at the $^{59}\text{Co}$ sites, although with opposite sign of the hyperfine coupling. The broad peak observed in SrCo$_2$As$_2$ contrasts sharply with the NMR shift in BaCo$_2$As$_2$, which increases with decreasing $T$ and then levels off at low $T$.

The $T$ dependence of $1/T_1 T$ of $^{75}\text{As}$, measured in both field directions, is shown in Fig. 4.4(b) for both SrCo$_2$As$_2$ and BaCo$_2$As$_2$. For SrCo$_2$As$_2$, $1/T_1 T$ for both field directions shows a broad peak around $T \sim 115$ K. This $T$ dependence is very similar to that of the NMR shift. Also in BaCo$_2$As$_2$, $1/T_1 T$ shows a very similar $T$ dependence to that of the corresponding NMR shift. This similar $T$ dependence of $1/T_1 T$ and $K$ for BaCo$_2$As$_2$ was also noted in Ref. [84]. Ahilan et al. contrasted this behavior to that of the PM state in optimally-doped Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$, where $1/T_1 T$ increases with decreasing $T$ below 100 K, while $K$ slowly decreases.[84] This behavior is clear evidence for the presence of fluctuations with $\mathbf{q} \neq 0$. In contrast, the similar $T$ dependence of $1/T_1 T$ and $K$ in BaCo$_2$As$_2$ rules out strong fluctuations with $\mathbf{q} \neq 0$, since these would increase $1/T_1 T$ but not $K$. Ahilan et al. therefore concluded the correlations in BaCo$_2$As$_2$ are primarily FM in nature. By a similar argument, our data on SrCo$_2$As$_2$ offer clear evidence for dominant FM fluctuations. In fact, the FM fluctuations can be shown by the modified Korringa relation analysis using the $^{75}\text{As}$ NMR data. Figure 4.5 shows the Korringa ratios for both field directions in SrCo$_2$As$_2$ and BaCo$_2$As$_2$ along with the corresponding Korringa parameters $\alpha$. In each case we find $\alpha \ll 1$, again consistent with strong FM fluctuations in both materials, consistent with dominant FM correlations as found above for $^{59}\text{Co}$ in SrCo$_2$As$_2$. The slightly higher value of the $\alpha_{||}$ for SrCo$_2$As$_2$ than the other three cases suggests that the $c$ axis component of the magnetic fluctuations in SrCo$_2$As$_2$ would be less FM than in BaCo$_2$As$_2$. The above analysis is based on a simple model that the nuclear relaxation is due to the local $D(E_F)$ at the As sites, through on-site hyperfine interactions, where As-4$p$ bands hybridize with Fe-3$d$ bands. On the other hand, if the relaxations are induced by only localized Fe
Figure 4.5 (Color online) Top panel: $T$ dependence of the Korringa ratios $1/T_{\perp}K_{\text{spin,ab}}^2$ (open symbols) and $1/T_{\parallel}K_{\text{spin,c}}^2$ (closed symbols) for spin correlations in the $ab$ plane and along the $c$ axis, respectively, for SrCo$_2$As$_2$ (black) and BaCo$_2$As$_2$ (red). Lower panel: $T$ dependence of $\alpha_\perp$ and $\alpha_\parallel$ for SrCo$_2$As$_2$ and BaCo$_2$As$_2$.

electronic spins through isotropic transferred hyperfine interactions, the $\alpha$ value would be modified by a factor of 4 due to the $q$ dependent hyperfine form factor;[85] FM spin correlations would then be expected for $\alpha < 0.25$. Regardless of the model, the $\alpha$ values in both systems are consistent with FM spin correlations.

According to DFT calculations in Ref. [67], the $\chi(q)$ in SrCo$_2$As$_2$ shows enhancements of similar strength at both the FM and stripe AFM wavevectors. Furthermore, the DFT results indicate that the stripe-type AFM fluctuations have a higher energy scale than the FM fluctuations, suggesting that FM fluctuations may be dominant at low energies. From the NMR point of view, which probes energies very near the ground state, we find that the fluctuations are indeed predominantly FM in character. We also find evidence for weak AFM fluctuations coexisting with the dominant FM
fluctuations, which can be attributed to the contribution in $\chi(q)$ at the stripe AFM wave vector revealed by the DFT calculations and INS measurements.

4.4 Conclusions

In summary, our $^{59}$Co and $^{75}$As NMR data demonstrate that the low energy spin fluctuations in paramagnetic SrCo$_2$As$_2$, the end member of the electron-doped Sr(Fe$_{1-x}$Co$_x$)$_2$As$_2$ family, are predominantly FM in character. We also found clear evidence of coexisting weak stripe-type AFM fluctuations that also appear at the higher INS energy scale. In the standard phenomenology of the iron-arsenide SCs, optimum SC is expected if strong stripe-type AFM fluctuations are present in the absence of long-range AFM order. We suggest that the competing low energy FM fluctuations interfere with the stripe-type AFM fluctuation-based pairing mechanism, thus suppressing superconductivity in SrCo$_2$As$_2$ even though the standard requirements are satisfied. Finally, several theoretical calculations have shown enhancements of $\chi(q)$ at both the FM and stripe-type AFM wavevectors in iron-based superconductors and parent compounds, similar to the case of SrCo$_2$As$_2$. Experimentally, a Korringa parameter $\alpha$ from $^{77}$Se-NMR data on the iron-chalcogenide superconductor K$_{0.8}$Fe$_2$Se$_2$ seems to be consistent with FM fluctuations in the high $T$ paramagnetic phase.[86] These results suggest that strong FM correlations and fluctuations may be important to determining $T_c$ in the iron-based superconductors. Due to the partial cancellation of the influences of FM and AFM fluctuations in NMR measurements, polarized inelastic neutron scattering measurements are needed to definitively measure the relative strengths of FM and AFM fluctuations in SrCo$_2$As$_2$ and other iron-based superconductors.

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CHAPTER 5. COMPETING MAGNETIC FLUCTUATIONS IN IRON PNICTIDE SUPERCONDUCTORS


P. Wiecki, B. Roy, D. C. Johnston, S. L. Budko, P. C. Canfield, and Y. Furukawa

The Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA

5.1 Abstract

In the iron pnictide superconductors, theoretical calculations have consistently shown enhancements of the static magnetic susceptibility at both the stripe-type antiferromagnetic (AFM) and in-plane ferromagnetic (FM) wavevectors. However, the possible existence of FM fluctuations has not yet been examined from a microscopic point of view. Here, using $^{75}$As NMR data, we provide clear evidence for the existence of FM spin correlations in both the hole- and electron-doped BaFe$_2$As$_2$ families of iron-pnictide superconductors. These FM fluctuations appear to compete with superconductivity and are thus a crucial ingredient to understanding the variability of $T_c$ and the shape of the superconducting dome in these and other iron-pnictide families.

5.2 Introduction

The role of magnetic fluctuations in iron pnictide superconductors (SCs) has been extensively studied since their discovery. As the parent materials have antiferromagnetic (AFM) ground states, attention has been understandably focused on stripe-type AFM fluctuations, which are widely believed to give rise to the Cooper pairing in these systems. In the standard picture, carrier doping or pressure application results in suppression of the AFM order and the emergence of a SC state, with $T_c$ ranging from a few K to 56 K [16]. However, as of yet, there is no accepted theory for $T_c$
in these materials with which to explain the large variability in maximum $T_c$ between different iron arsenide families and the different shapes of the SC dome with electron and hole doping.

Recent nuclear magnetic resonance (NMR) measurements on non-SC, paramagnetic (PM) SrCo$_2$As$_2$, the $x = 1$ member of the electron-doped Sr(Fe$_{1-x}$Co$_x$)$_2$As$_2$ family, revealed strong ferromagnetic (FM) spin fluctuations in the Co layer coexisting with stripe-type AFM fluctuations [87; 67]. Since stripe-type AFM fluctuations are a key ingredient to SC in the iron pnictides, this result suggested that FM fluctuations might compete with the stripe-type AFM fluctuations, suppressing SC in SrCo$_2$As$_2$. FM correlations were also observed in isostructural BaCo$_2$As$_2$ [87; 84]. Similarly, CaCo$_{1.86}$As$_2$ has an A-type AFM ground state with in-plane FM order [88]. These results also raise the question of whether similar FM correlations exist generally in the SC $A$(Fe$_{1-x}$Co$_x$)$_2$As$_2$ compounds, not just at the $x = 1$ edges of their phase diagrams.

According to density functional theory calculations [71; 72; 73; 74; 75], the generalized static magnetic susceptibility $\chi(q)$ is enhanced at both the FM and stripe-type AFM wavevectors in all the iron-based SCs and parent compounds. Experimentally, the uniform $\chi(q = 0)$ of the parent compounds is enhanced by a factor of order five over band structure values, which is consistent with FM correlations [16]. Nevertheless, FM fluctuations have not been investigated microscopically, perhaps because low-energy FM fluctuations are difficult to observe via inelastic neutron scattering (INS). The peak in the inelastic structure factor at $q = 0$ coincides with the elastic Bragg diffraction peaks, and the energy scale of thermal neutrons is relatively high. The study of low-energy FM fluctuations therefore requires cold, polarized neutrons. NMR, in contrast, is a microscopic probe uniquely sensitive to low-energy FM fluctuations via the modified Korringa ratio.

In this Letter, using $^{75}$As NMR measurements, we present clear evidence for FM fluctuations in the tetragonal, PM phase of both the hole- and electron-doped BaFe$_2$As$_2$ families of iron pnictide SCs. Furthermore, we suggest that these FM fluctuations compete with SC, and that this competition between FM and AFM fluctuations may be a key ingredient to a theory of $T_c$ in the iron pnictides.
For this study, we chose $x = 4.7\%$ ($T_N \sim 50$ K and $T_c \sim 15$ K) and $x = 5.4\%$ ($T_N \sim 35$ K and $T_c \sim 20$ K) in single-crystalline Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ as representative superconducting samples in which to look for FM correlations. We also used our existing data on BaCo$_2$As$_2$, reported elsewhere [83; 87] and other data from the literature. The $^{75}$As NMR shift and spin-lattice relaxation rates $1/T_1$ were measured under magnetic fields parallel to the $c$ axis ($H \parallel c$) and to the $ab$ plane ($H \parallel ab$).

**5.3 Results**

Figures 5.1(a) and 5.1(b) show the existing NMR data ($T$ dependence of NMR shift $K$ and $1/T_1T$, respectively) for both the electron-doped Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ and hole-doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ families of iron-pnictide SCs. The NMR shift consists of a $T$-independent orbital shift $K_0$ and a $T$-dependent spin shift $K_{\text{spin}}(T)$ due to the uniform magnetic spin susceptibility $\chi(q = 0)$. The NMR shift can therefore be expressed as $K(T) = K_0 + K_{\text{spin}}(T) = K_0 + A_{hf}\chi_{\text{spin}}/N_A$, where $N_A$ is Avogadro’s number, and $A_{hf}$ is the hyperfine coupling, usually expressed in units of kOe/$\mu_B$. In order to extract $K_{\text{spin}}(T)$, we plot $K(T)$ against the corresponding bulk static uniform magnetic susceptibility $\chi(T)$ with $T$ as shown in Fig. 5.1(c). From the y-intercept of the linear fit curve we can estimate the orbital shift $K_0$, and extract $K_{\text{spin}}(T)$ needed for the following Korringa ratio analysis.

To extract the character of spin fluctuations in the iron pnictides from $^{75}$As NMR data, we employ a modified Korringa ratio analysis. Within a Fermi liquid picture, both $1/T_1T$ and $K_{\text{spin}}$ are determined primarily by the density of states at the Fermi energy $\mathcal{D}(E_F)$, leading to the Korringa relation $T_1TK^2_{\text{spin}} = (\hbar/4\pi k_B)(\gamma_e/\gamma_N)^2 \equiv S$. For the $^{75}$As nucleus ($\gamma_N/2\pi = 7.2919$ MHz/T), $S = 8.97 \times 10^{-6}$ Ks. Deviations from $T_1TK^2_{\text{spin}} = S$, which are conveniently expressed via the Korringa ratio $\alpha \equiv S/(T_1TK^2_{\text{spin}})$, can reveal information about electron correlations in the material [82; 81]. For uncorrelated electrons, we have $\alpha \sim 1$. However, enhancement of $\chi(q \neq 0)$ increases $1/T_1T$ but has little or no effect on $K_{\text{spin}}$, which probes only the uniform $\chi(q = 0)$. Thus $\alpha > 1$ for AFM correlations. In contrast, $\alpha < 1$ for FM correlations. The Korringa ratio $\alpha$, then, reveals whether the magnetic correlations in the material have predominantly FM or AFM character.
Figure 5.1  (Color online) (a) $T$ dependence of the NMR shift $K$ for a variety of indicated samples. (b) $T$ dependence of NMR spin-lattice relaxation rate $1/T_1 T$ for the same samples. Here, and throughout, filled (open) symbols are used for $H\parallel ab$ ($H\parallel c$). (c) $K_i(T)$ vs. $\chi_i(T)$ ($i = ab,c$) for a variety of samples. Data are from Refs. [51; 103; 38; 104; 69; 61; 60; 105]. For KFe$_2$As$_2$, $K_c$ is nearly $T$ independent making a $K$ vs. $\chi$ analysis impossible. From the relative values of $K_{ab}$ and $K_c$, we estimate $K_{0,c} \sim 0.21\%$. For BaFe$_2$As$_2$, $K_{0,ab} = 0.14\%$ and $K_{0,c} = 0.21\%$ are from Ref. [38]. For the 8% Co doped sample, $K_{0,c} = 0.22\%$ from Ref. [51].
To perform the Korringa ratio analysis, one needs to take the anisotropy of $K_{\text{spin}}$ and $1/T_1 T$ into consideration. The $1/T_1$ probes hyperfine field fluctuations at the NMR Larmor frequency, $\omega_N$, perpendicular to the external magnetic field according to $(1/T_1)_{H||i} = \gamma_N^2 \left[ |H^{\text{hf}}(\omega_N)|^2 + |H^{\text{hf}}(\omega_N)|^2 \right]$, where $(i, j, k)$ are mutually orthogonal directions and $|H^{\text{hf}}(\omega)|^2$ represents the power spectral density of the $j$-th component of the hyperfine magnetic field at the nuclear site. Thus, defining $H^{\text{hf}}_{ab} \equiv H^{\text{hf}}_a = H^{\text{hf}}_b$, which is appropriate for the tetragonal PM state, we have $(1/T_1)_{H||c} = 2\gamma_N^2 |H^{\text{hf}}_{ab}(\omega_N)|^2 \equiv 1/T_{1,\perp}$. The Korringa parameter $\alpha_{\perp} \equiv S/T_{1,\perp} T K^2_{\text{spin},ab}$ will then characterize fluctuations in the $ab$-plane component of the hyperfine field. By analogy, we should pair $K_{\text{spin},c}$ with $2\gamma_N^2 |H^{\text{hf}}_c(\omega_N)|^2 \equiv 1/T_{1,\parallel}$, so that the Korringa parameter $\alpha_{\parallel} = S/T_{1,\parallel} T K^2_{\text{spin},c}$ characterizes fluctuations in the $c$-axis component of the hyperfine field. Since $(1/T_1)_{H||ab} = \gamma_N^2 \left[ |H^{\text{hf}}_{ab}(\omega_N)|^2 + |H^{\text{hf}}_c(\omega_N)|^2 \right]$, we estimate the quantity $1/T_{1,\parallel} T$ from $1/T_{1,||} T = 2(1/T_1 T)_{H||ab} - (1/T_1 T)_{H||c}$.

The $T$ dependences of the Korringa ratios $\alpha_{\perp} = S/T_{1,\perp} T K^2_{\text{spin},ab}$ and $\alpha_{\parallel} = S/T_{1,\parallel} T K^2_{\text{spin},c}$ are shown in Fig. 5.2(a). In BaCo$_2$As$_2$, both $\alpha_{\perp}$ and $\alpha_{\parallel}$ are nearly independent of $T$ and much less than 1, consistent with FM correlations. For the remaining samples, $\alpha_{\parallel}$ is generally greater than 1 indicating AFM correlations throughout the $T$ range. In addition, both $\alpha_{\perp}$ and $\alpha_{\parallel}$ increase as $T$ is lowered, showing the growth of AFM spin fluctuations at low $T$. In contrast, we find that $\alpha_{\perp} \sim 0.3 < 1$ for the parent and Co-doped samples in the high-$T$ PM phase. The hole-doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ also display $\alpha_{\perp} \leq 1$ in the PM phase, suggesting FM correlations, although less strong than in the Co-doped samples.

Careful consideration is required to interpret the value of the Korringa ratio. In comparing the $\alpha$ value to the crossover $\alpha_0 = 1$ between dominant FM and AFM fluctuations, one is assuming a simple model in which the nuclear relaxation is due to the local $D(E_F)$ at the As sites through on-site hyperfine interactions, where As-4p bands hybridize with Fe-3d bands [38]. If, on the other hand, the nuclear relaxation is induced only by the localized Fe spins through isotropic transferred hyperfine interactions, the value of $\alpha$ would instead be compared to the crossover $\alpha_0 = 1/4$, assuming no contributions to $1/T_1$ from AFM correlations due to form factor effects [89; 85; 90]. In the highly overdoped $x = 26\%$ Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$, however, AFM fluctuations are known to
be absent from INS measurements [91]. Accordingly, Refs. [16] and [51] find $\alpha \sim 1.2$, suggesting weak correlation. If the crossover were $\alpha_0 = 1/4$, this value of 1.2 for the Korringa ratio must be associated with dominant AFM fluctuations, in conflict with observations. These results suggest that the factor of 4 change to $\alpha_0 = 1/4$ proposed by Ref. [85] for iron pnictides is too large. In fact, the FM correlations have been also pointed out in $(La_{0.87}Ca_{0.13})FePO$ with $\alpha = 0.37$ by $^{31}$P NMR [92]. In addition, in the case of Na$_x$CoO$_2$ for $x > 0.65$, FM correlations are known to be present [90] and the measured Korringa ratio takes the value $\alpha \sim 0.3$ [93]. It is also noted that the Wilson ratio for BaFe$_2$As$_2$ is mildly enhanced ($R_W \sim 3$) [94], consistent with FM correlations. Thus we conclude that value we observe, $\alpha_\perp \sim 0.3$, can be reasonably attributed to FM fluctuations.

To discuss the magnetic correlations based on the values of $\alpha_\perp$ and $\alpha_\parallel$ in the iron pnictides in more detail, it is helpful to consider the hyperfine field at the $^{75}$As site, which is determined by the spin moments on the Fe sites through the hyperfine coupling tensor [69]. In this case, there
are two sources of hyperfine field pointing along the $c$ axis [38]: stripe-type AFM fluctuations at $\mathbf{q} = (\pi,0)/(0,\pi)$ with the spins pointing within the $ab$ plane [as illustrated in Fig. 5.3(a)] or FM fluctuations at $\mathbf{q} = 0$ with the spins pointing along the $c$ axis [Fig. 5.3(b)]. Similarly, hyperfine field fluctuations in the $ab$ plane can result from FM fluctuations at $\mathbf{q} = 0$ with the spins pointing within the $ab$ plane [Fig. 5.3(c)], or from AFM fluctuations at $\mathbf{q} = (\pi,0)/(0,\pi)$ with the spins pointing along the $c$ axis [Fig. 5.3(d)]. Thus, the value of $\alpha_\parallel$ reflects the competition between (a)- and (b)-type correlations: type (a) AFM correlations will increase $\alpha_\parallel$ above 1, while type (b) FM correlations will lower $\alpha_\parallel$ below 1. Similarly, $\alpha_\perp$ reflects the competition between (c)- and (d)-type correlations: type (d) AFM correlations will increase $\alpha_\perp$, while type (c) FM correlations will lower $\alpha_\perp$. In what follows, we will refer to the correlations depicted in Fig. 5.3(a) as “type (a)” correlations (similarly for the others). Since $\alpha_\parallel$ reflects the character of the $c$-axis component hyperfine field fluctuations, the AFM value of $\alpha_\parallel$ in Fig. 5.2 can be attributed to type (a) correlations, i.e., stripe-type AFM correlations with the Fe spins in-plane. These must dominate type (b) fluctuations in order to have an AFM value of $\alpha_\parallel$. Similarly, since $\alpha_\perp$ reflects the character of the $ab$-plane component of hyperfine field fluctuations, the FM value of $\alpha_\perp$ in the high-$T$ region can be attributed to type (c) in-plane FM fluctuations. On the other hand, the increase of $\alpha_\perp$ as the temperature is lowered reflects the increasing dominance of type (d) stripe-type AFM correlations with a $c$-axis component to the spin. This clearly indicates the simultaneous coexistence of FM and AFM fluctuations. Furthermore, the dominance of type (a) and (c) spin fluctuations in the high-$T$ region suggests that both the AFM and FM fluctuations are highly anisotropic in the iron pnictides, favoring the $ab$ plane.
Finally it is interesting to isolate the FM fluctuations and extract their $T$ dependence. We adopt the simple phenomenological model of Refs. [51; 95; 96] to decompose $1/T_1 T$ into inter- and intraband components according to $1/T_1 T = (1/T_1 T)_{\text{inter}} + (1/T_1 T)_{\text{intra}}$. The $T$ dependence of the interband term is assumed to follow the Curie-Weiss form appropriate for 2D AFM fluctuations: $(1/T_1 T)_{\text{inter}} = C/(T - \Theta_{\text{CW}})$. For the Co-doped samples, we use $(1/T_1 T)_{\text{intra}} = \alpha + \beta \exp(-\Delta/k_B T)$, while for the K-doped samples we simply use $(1/T_1 T)_{\text{intra}} = \text{const}$, as in Ref. [69]. The Curie-Weiss parameter $C$ measures the strength of AFM fluctuations, and $\Theta_{\text{CW}}$ corresponds to the distance in $T$ from the AFM instability point. Here, we decompose the quantities $1/T_{1,\parallel} T$ and $1/T_{1,\perp} T$ into their inter- and intraband components. Our results for the CW parameters $C_{\perp}$, $C_{\parallel}$ and $\Theta_{\text{CW}}$, shown in Fig. 5.4, are consistent with the results of Refs. [69] and [51]. Similar carrier doping dependence of $\Theta_{\text{CW}}$ is reported in P-doped BaFe$_2$As$_2$ [97] and in LaFeAsO$_{1-x}$F$_x$ [98]. We use the intraband components to calculate the Korringa ratios $\alpha_{\parallel}^{\text{intra}}$ and $\alpha_{\perp}^{\text{intra}}$. The results are shown in Fig. 5.2(b). Both $\alpha_{\parallel}^{\text{intra}}$ and $\alpha_{\perp}^{\text{intra}}$ remain roughly constant through the $T$ range. The deviations at low $T$ are due to imperfect subtraction of the interband part, arising from our simplistic Curie-Weiss fitting. We notice that $\alpha_{\parallel}^{\text{intra}}$ for several compounds are greater than 1, suggesting AFM correlations in the intraband component. On the other hand, the value of $\alpha_{\perp}^{\text{intra}}$ is consistent with FM fluctuations, as discussed above, for all samples.

What then is the role of these FM fluctuations in the iron pnictide superconductors? In Fig. 5.4, we summarize our results across the combined hole- and electron-doped phase diagram of BaFe$_2$As$_2$. First of all, $C_{\parallel}$ is always greater than $C_{\perp}$ in the entire phase diagram, indicating that type (a) spin fluctuations are stronger than type (d) spin fluctuations. On the electron-doped side, AFM spin fluctuations die out beyond the SC dome at $x \sim 15\%$ [91]. In contrast, the AFM spin fluctuations become very strong on the hole-doped side relative to the electron-doped side. The doping dependences of $C_{\perp}$ and $C_{\parallel}$ are reminiscent of the doping dependence of the mass enhancement [99]. For a measure of the strength of the FM fluctuations, we plot in Fig. 5.4(a) the average values of $\alpha_{\parallel}^{\text{intra}}$ and $\alpha_{\perp}^{\text{intra}}$ above 150 K except for BaCo$_2$As$_2$ where we average over all data. We find that $\alpha_{\perp}^{\text{intra}}$ has a FM value throughout the phase diagram, consistent with in-plane FM [type (c)] spin fluctuations.
Figure 5.4 (Color online) Potential relevance of FM spin fluctuations to iron pnictide phase diagram: (a) Doping dependence of the nearly $T$-independent values of $\alpha_{\text{intra}}^{\parallel}$ and $\alpha_{\text{intra}}^{\perp}$, which parameterize the strength of FM fluctuations [106]. We also show the doping dependence of the Curie-Weiss parameters $C_{\perp}$ and $C_{\parallel}$, which parameterize the strength of 2D AFM fluctuations. (b) The doping dependence of the Curie-Weiss temperature $\Theta_{\text{CW}}$. Solid lines are guides to the eye.

In contrast, $\alpha_{\text{intra}}^{\parallel}$ shows an AFM value at 8% Co doping, but exhibits a dramatic decrease towards FM values when hole doped or electron doped beyond 8%. The FM fluctuations are thus strongest at the maximally-doped edges of the phase diagram. The disappearance of AFM spin fluctuations beyond 15% Co doping coincides with the appearance of FM fluctuations, suggesting a competition between FM and AFM fluctuations. On the hole-doped side, AFM correlations clearly increase in strength. Paradoxically, this increase in strength of AFM correlations is accompanied by a decrease of $T_c$, as noted in Ref. [68]. Our analysis offers a possible explanation. FM correlations also increase in strength on the hole-doped side, as seen from the rapidly decreasing values of $\alpha_{\text{intra}}^{\parallel}$ and $\alpha_{\text{intra}}^{\perp}$ and the increasing value of the NMR shift [Fig. 5.1(a)] with increasing hole doping. We suggest that the growth of competing FM correlations results in the reduction of $T_c$ despite the increase in AFM correlation strength. In KFe$_2$As$_2$, then, FM and AFM correlations coexist with neither
dominating the other, leading to the Korringa parameters $\alpha_\perp \sim 1$ and $\alpha_\parallel \sim 1$ that we observe in Fig. 5.2(a). Finally, it is noted that structural parameters have been pointed out to play an important role for controlling the ground state of iron pnictides [100]. Although we discussed our NMR data based on the well-known phase diagram where the tuning parameter is carrier doping, the observed trends should not be attributed to carrier concentration alone.

5.4 Conclusions

In conclusion, using an anisotropic modified Korringa ratio analysis on $^{75}$As NMR data, we have provided clear evidence for the existence of FM spin correlations in both hole- and electron-doped BaFe$_2$As$_2$. The FM fluctuations are strongest in the maximally-doped BaCo$_2$As$_2$ and KFe$_2$As$_2$, but are still present in the BaFe$_2$As$_2$ parent compound, consistent with its enhanced $\chi$ [16]. While we consider here only the Ba122 system, similar results are found for other iron-pnictide based superconductors. In particular, FM values of $\alpha$ were also observed in the PM phase of LaO$_{0.9}$F$_{0.1}$FeAs ($\alpha = 0.55 < 1$) [101], K$_{0.8}$Fe$_2$Se$_2$ ($\alpha = 0.45 < 1$) [86] and Ca(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [102]. These FM fluctuations appear to compete with superconductivity and are thus a crucial ingredient to understand the variability of $T_c$ and the shape of the SC dome. Our results indicate that theoretical microscopic models should include FM correlations to capture the phenomenology of the iron pnictides. Polarized INS experiments examining magnetic response at the FM wavevector will be needed to further understand the interplay between FM and AFM spin correlations in the iron pnictides.

5.5 Acknowledgments

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CHAPTER 6. KFe$_2$As$_2$: PRESSURE DEPENDENCE OF COHERENCE—INCOHERENCE CROSSOVER BEHAVIOR OBSERVED BY RESISTIVITY AND $^{75}$As-NMR/NQR


P. Wiecki$^1$, V. Taufour$^{1,2}$, D. Y. Chung$^3$, M. G. Kanatzidis$^3$, S. L. Bud’ko$^1$, P. C. Canfield$^1$ and Y. Furukawa$^1$

1 The Ames Laboratory, U.S. DOE and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA

2 Department of Physics, University of California, Davis, Davis, CA 95616, USA

3 Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

6.1 Abstract

We present the results of $^{75}$As nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), and resistivity measurements in KFe$_2$As$_2$ under pressure ($p$). The temperature dependence of the NMR shift, nuclear spin-lattice relaxation time ($T_1$) and resistivity show a crossover between a high-temperature incoherent, local-moment behavior and a low-temperature coherent behavior at a crossover temperature ($T^*$). $T^*$ is found to increase monotonically with pressure, consistent with increasing hybridization between localized 3$d$ orbital-derived bands with the itinerant electron bands. No anomaly in $T^*$ is seen at the critical pressure $p_c = 1.8$ GPa where a change of slope of the superconducting (SC) transition temperature $T_c(p)$ has been observed. In contrast, $T_c(p)$ seems to correlate with antiferromagnetic spin fluctuations in the normal state as measured by the NQR $1/T_1$ data, although such a correlation cannot be seen in the replacement effects of A in the AFe$_2$As$_2$ (A= K, Rb, Cs) family. In the superconducting state, two $T_1$ components are observed at low temperatures, suggesting the existence of two distinct local electronic environments. The
temperature dependence of the short $T_{1s}$ indicates nearly gapless state below $T_c$. On the other hand, the temperature dependence of the long component $1/T_{1L}$ implies a large reduction in the density of states at the Fermi level due to the SC gap formation. These results suggest a real-space modulation of the local SC gap structure in KFe$_2$As$_2$ under pressure.

6.2 Introduction

The iron-based superconductors (SCs) continue to be the focus of intense research in condensed matter physics, due to their unique interplay of magnetic, orbital and charge degrees of freedom [18; 16; 32; 23; 22]. Among the iron-based SCs, the heavily hole-doped iron-pnictide superconductor KFe$_2$As$_2$, with a SC transition temperature of $T_c \sim 3.5$ K, shows several unique properties. The Sommerfeld coefficient ($\gamma \sim 102$ mJ/molK$^2$) is significantly enhanced, and the magnetic susceptibility exhibits a broad peak around 100 K [68]. Nuclear magnetic resonance (NMR) spin-lattice relaxation rates ($1/T_1$) are strongly enhanced, evidencing antiferromagnetic spin fluctuations. Curie-Weiss fits to the NMR data have demonstrated the proximity of KFe$_2$As$_2$ to a quantum critical point (QCP) [69; 107; 108]. These results indicate a heavy quasiparticle effective mass and strong electronic correlations [68; 107]. Recent NMR investigations have also pointed out the importance of ferromagnetic spin correlations in this material [107].

Furthermore, the SC properties of KFe$_2$As$_2$ are also unique. Whereas two full SC gaps are reported in the hole-doped series Ba$_{1-x}$K$_x$Fe$_2$As$_2$ for $x < \sim 0.8$ [109], a nodal SC gap structure in KFe$_2$As$_2$ ($x = 1$) has been suggested by several experiments [110; 111; 112; 113; 114; 115]. A large full gap accompanied by several very small gaps has also been proposed based on specific heat measurements [116]. In addition, $T_c$ shows non-monotonic behavior under pressure, with a minimum at $p_c \sim 1.8$ GPa, which has been suggested to be caused by a change in the SC gap structure [117; 118; 119]. Measurements of the pressure dependence of the upper critical field $H_{c2}$ suggested the appearance of a $k_z$ modulation of the SC gap above $p_c$ [119].

Analogous behavior has also been found in the related alkali metal compounds RbFe$_2$As$_2$ and CsFe$_2$As$_2$ [120; 121; 122; 123; 124; 125; 126], which show even greater mass enhancements with
\( \gamma \sim 127 \text{ mJ/molK}^2 \) and \( \gamma \sim 184 \text{ mJ/molK}^2 \), respectively [127]. The unusual properties of the AFe\(_2\)As\(_2\) (A = K, Rb, Cs) family have been pointed out [68; 127; 128] to be quite similar to f-electron heavy fermion materials [129; 130], which display a crossover between a high-temperature incoherent, local-moment behavior and a low-temperature coherent behavior, with the crossover occurring at a temperature \( T^* \). In this picture, the importance of dual role of Fe \( d \) electrons has been pointed out theoretically [131; 132] where the two aspects of the itinerant and localized electrons may originate from different 3\( d \) orbitals of the iron ions. Recently, experimental [133; 128] and theoretical [68] studies suggest that the bands derived from the Fe 3\( d_{xy} \) orbitals would play the role of the local moments. This orbital-selective localization is due to the strong Hund coupling in these materials [37].

Recent NMR measurements have pointed out a possible \( d \)-electron heavy fermion behavior in the AFe\(_2\)As\(_2\) (A = K, Rb, Cs) family at ambient pressure [127]. \( T^* \) is reported to increase from 85 K for Cs, to 125 K for Rb and to 165 K for KFe\(_2\)As\(_2\). Thermal expansion measurements on this family also find the lowest \( T^* \) for Cs and highest \( T^* \) for K, although the reported crossover temperatures are lower [134]. Since the so-called chemical pressure effects would increase when one moves from Cs to Rb to K due to the decrease in size of the alkali metal ion, this suggests that \( T^* \) increases with increasing the chemical pressure. Furthermore, two empirical relationships involving \( T^* \) have been discussed [127]. First, the superconducting transition temperature \( T_c \) is generally proportional to \( T^* \), that is \( T_c \propto T^* \), reflecting the correlation of \( T_c \) to local magnetic coupling \( J \) as pointed out in Ref. [135] in the context of \( f \)-electron heavy fermion SCs. Second, the Sommerfeld coefficient \( \gamma \), and thus the effective mass \( m^* \), is inversely proportional to \( T^* \), that is \( \gamma^{-1} \propto T^* \) (see also Ref. [68]).

The \( T_c \propto T^* \) relationship for the AFe\(_2\)As\(_2\) (A = K, Rb, Cs) naively suggests that the non-monotonic behavior of \( T_c \) in these materials under pressure could be due to a non-monotonic behavior of \( T^* \) under pressure. This motivates an experimental investigation of the relationship between \( T_c \) and \( T^* \) under pressure. Here, we have carried out NMR and nuclear quadrupole resonance (NQR) measurements under high pressure up to 2.1 GPa and resistivity measurements
up to ∼ 5 GPa in order to investigate the pressure dependence of $T^*$ and to test its relationship with $T_c$. Based on the NMR and resistivity data, we find that $T^*$ increases monotonically with increasing pressure with no anomaly associated with crossing $p_c \sim 1.8$ GPa. These results indicate that $T^*$ is not the primary driver of the pressure dependence of $T_c$ in KFe$_2$As$_2$. On the other hand, $1/T_1$ measurements demonstrate that spin fluctuations are suppressed with increasing pressure up to the $p_c$ and then start to be enhanced above $p_c$, suggesting that $T_c$ is related to spin fluctuations in the normal state. In the superconducting state, two-component NQR relaxation is observed below $T = 1$ K, suggesting real space variation of the superconducting gap structure. One of the two components, the short $T_1$ component, shows no change in the slope of $1/T_1$ across $T_c$ above 1.5 GPa, indicating these nuclei see a gapless local electronic environment in the SC state under these pressure conditions. Only the second component, the long $T_1$ component, shows a large reduction of the density of states at the Fermi energy due to the SC gap.

### 6.3 Experimental Details

Highly pure KFe$_2$As$_2$ crystal sample was obtained by recrystallization of pre-reacted KFe$_2$As$_2$ polycrystalline powder in KAs flux as follows. KFe$_2$As$_2$ polycrystalline powder was prepared by annealing a stoichiometric mixture of K/Fe/As (0.27/0.77/1.03 g) contained in an alumina crucible which was subsequently sealed in a sealed silica tube under vacuum, at 700 °C for one day. KAs was prepared by heating a stoichiometric 1/1 ratio of K/As (0.94/1.80 g) in an alumina tube sealed in a silica tube at 250 °C for 12 h. The obtained KFe$_2$As$_2$ powder was then thoroughly mixed with KAs at a ratio of 1/4 (1.10/1.67 g) and heated to 1,050 °C for 12 h, followed by cooling slowly to room temperature at 5 °C/h. Isolation of KFe$_2$As$_2$ crystals from excess KAs flux was performed by dissolving KAs in ethanol for two days under nitrogen gas flow, which produces very shiny thin plate KFe$_2$As$_2$ crystals. The quality of KFe$_2$As$_2$ crystals was confirmed by a very sharp superconducting transition at 3.4 K from the magnetic susceptibility measurement.

$^{75}$As-NMR/NQR ($I = 3/2; \gamma/2\pi = 7.2919$ MHz/T; $Q = 0.29$ barns) measurements were performed using a lab-built, phase-coherent, spin-echo pulse spectrometer. The KFe$_2$As$_2$ sample
was a fine powder in order to maximize the surface area for NMR/NQR measurements. The total mass of powder used in the high-pressure NMR/NQR measurements was $\sim 15$ mg. The $^{75}$As-NMR spectra were obtained either by sweeping the magnetic field $H$ at a fixed frequency $f = 54.8756$ MHz or by Fourier transform of the NMR echo signals at a constant magnetic field of $H = 7.41$ T. $^{75}$As-NQR spectrum in zero field was measured in steps of frequency by measuring the intensity of the Hahn spin-echo. For our measurements at ultra-low temperatures below 1 K, we used a dilution refrigerator (Oxford Instruments, Kelvinox 100) where the pressure cell was mounted.

The $^{75}$As NMR/NQR $1/T_1$ was measured with a recovery method using a single $\pi/2$ saturation pulse. For NMR measurements, the $1/T_1$ at each $T$ was determined by fitting the nuclear magnetization $m$ versus time $t$ using the exponential function

$$1 - \frac{m(t)}{m(\infty)} = 0.1 \exp(-t/T_1) + 0.9 \exp(-6t/T_1),$$

where $m(t)$ and $m(\infty)$ are the nuclear magnetization at time $t$ after the saturation and the equilibrium nuclear magnetization at $t \to \infty$, respectively. For NQR measurements, the recovery curve was fit to

$$1 - \frac{m(t)}{m(\infty)} = \exp(-3t/T_1).$$

Pressure was applied at room temperature using a hybrid CuBe/NiCrAl piston-cylinder-type high pressure clamp cell [136; 55]. Daphne 7373 was chosen as the pressure transmitting medium. Pressure calibration was accomplished by $^{63}$Cu-NQR in Cu$_2$O [137; 57] at 77 K. In our pressure cell, the sample pressure decreases by $\sim 0.2$ GPa when cooled from room temperature to 100 K, but remains constant below 100 K. The NMR coils inside the pressure cell consisted of $\sim 20$ turns of 40AWG copper wire. The sample and calibration coils were oriented with their axes perpendicular to each other to avoid interference between coils.

The single-crystal electrical resistivity measurements were performed using the four-probe method with current in the $ab$ plane [119]. Pressure was applied at room temperature using a modified Bridgman cell [138] with a 1:1 mixture of n-pentane/isopentane as a pressure medium, with the pressure determined using the superconducting transition of Pb.
6.4 Results and Discussion

6.4.1 $T_c$ and critical pressure

The superconducting transition temperature $T_c$ of the KFe$_2$As$_2$ powder was determined by measuring the $T$ dependence of the NMR coil tank circuit resonance frequency, $f(T)$, under zero magnetic field. The frequency $f$ is a measure of the ac-susceptibility $\chi_{ac}(\omega_{\text{NMR}})$ since $f = 1/2\pi\sqrt{LC}$ and $L = L_0(1 + \chi_{ac})$. The onset of the Meissner effect therefore results in a sharp change of $f(T)$ as shown in the inset of Fig. 6.1. At ambient pressure, we find $T_c \sim 3.3$ K, as expected. The pressure dependence of $T_c$ is shown in Fig. 6.1 together with the data reported previously [117; 119; 118; 108; 139; 140]. $T_c$ decreases with $p$ below the critical pressure $p_c \sim 1.8$ GPa with a rate of 0.97 K/GPa, while $T_c$ shows weak pressure dependence above $p_c$.

6.4.2 NMR spectrum

Figure 6.2 shows a representative field-swept NMR spectrum of the KFe$_2$As$_2$ powder measured at 10 K and $p = 1.9$ GPa. The spectrum is typical for an $I = 3/2$ nucleus in a powder sample with Zeeman interaction greater than quadrupole interaction. A central transition is flanked by two satellite lines split by the quadrupole interaction of the As nucleus with the local electric field gradient (EFG). In addition, the central transition line is split by the second-order quadrupole perturbation.

The situation is described by the spin Hamiltonian [47]

$$\mathcal{H} = -\hbar\nu_L(1 + K_z')I_z' + \frac{\hbar\nu_Q}{6}(3I_z^2 - I^2),$$

appropriate for tetragonal crystals. Here $z'$ is the direction of the applied field ($H_{\text{ext}}$) and $z$ is the direction of the principal axis of the EFG. $\nu_L = \gamma H_{\text{ext}}/2\pi$ is the Larmor frequency and $K_z'$ represents the NMR shift. The quadrupole frequency for an $I = 3/2$ nucleus can be expressed as $\nu_Q = e^2QV_{zz}/2h$, $e$ is the electron charge, $Q$ is the nuclear quadrupole moment, $V_{zz}$ is the EFG and $h$ is Planck’s constant. According to this Hamiltonian, the NMR spectrum depends on the angle $\theta$ between the external field and the EFG principal axis. To first order, the quadrupole satellite
Figure 6.1  Superconducting transition temperature $T_c$ as a function of pressure determined by onset of Meissner effect measured by \textit{in situ} ac-susceptibility. $p_c \sim 1.8$ GPa marks the critical pressure where $T_c$ changes slope. Previously reported data are shown for comparison: Terashima \textit{et al.} Ref. [118]; Wang \textit{et al.} Ref. [108]; Tafti \textit{et al.} Ref. [117]; Taufour \textit{et al.} Ref. [119]; Grinenko \textit{et al.} Ref. [139].

Inset shows the typical temperature dependence of the change in the NMR coil tank circuit resonance frequency, $\Delta f$, under different pressures.

resonance frequencies are given by

$$\nu_{\pm} = \nu_L (1 + K_z') \pm \frac{\nu_Q}{2} (3 \cos^2 \theta - 1)$$  \hspace{1cm} (6.4)

In second order perturbation theory, the central transition frequency depends on $\theta$ according to

$$\nu(\theta) = \nu_L (1 + K_z') - \frac{3\nu_Q^2}{16 \nu_L} \sin^2 \theta (9 \cos^2 \theta - 1).$$  \hspace{1cm} (6.5)

In a powder sample, crystallites with all values of $\theta$ are present. Under these conditions the quadrupole satellites appear as sharp peaks at $\nu_L (1 + K_z') \pm \nu_Q/2$ which correspond to $\theta = 90^\circ$. For a powder, sharp peaks are observed in the central transition for $\theta = 90^\circ$ and $\theta = \cos^{-1}(\sqrt{5}/9) = 41.8^\circ$, as shown by the calculated powder-pattern spectrum in Fig. 6.2. The calculated spectrum assumes no preferential orientation of crystal grains, which is reasonable because the solidifications
Figure 6.2 Representative field-swept $^{75}$As NMR spectrum of KFe$_2$As$_2$ powder measured at $T = 10$ K and $p = 1.9$ GPa. The central transition line is split into two lines by the second order quadrupole effect. $\theta$ is the angle between the external field and the principal axis of the electric field gradient (see text). The red curve is a simulated powder spectrum with $\nu_Q = 12.66$ MHz.

of the pressure medium prevent the crystal grains from re-orienting. In a field-swept spectrum, the $\theta = 90^\circ$ peak occurs at lower field, as indicated in Fig. 6.2. Since the EFG principal axis is along the $c$ direction in KFe$_2$As$_2$, the $\theta = 90^\circ$ peak arises from those crystallites that experience an external field in the crystal $ab$ plane. We conducted our NMR shift and $1/T_1$ measurements at this peak of the central transition.

The quadrupole resonance frequency $\nu_Q$ was obtained by a direct measurement of the NQR spectrum at zero magnetic field. The typical NQR spectrum is shown in the inset of Fig. 6.3, where the full-width-at-half-maximum (FWHM) of the NQR spectrum is $\sim 250$ kHz at $T = 4.2$ K, which is consistent with the value reported previously [108] and is sharper than early NQR data measured at ambient pressure [110]. The temperature and pressure dependence of $\nu_Q$ is summarized in Fig. 6.3. As a function of temperature, $\nu_Q$ is nearly constant below 50 K, and increases slowly
Figure 6.3  Nuclear quadrupole resonance (NQR) frequency as a function of temperature for indicated pressures. Upper inset: Representative NQR spectrum at $p = 2.1$ GPa and $T = 4.2$ K, shown with a Lorentzian fit. Lower inset: NQR frequency as a function of pressure at $T = 4.2$ K. Lines are guides to the eye.

above 50 K, which is not simply explained by the so-called $T^{3/2}$-law originating from the thermal vibrations of the lattice [141]. A similar increase of $\nu_Q$ at the Fe site is observed by Mössbauer measurements [142]. It is interesting to note that the value and temperature dependence of $\nu_Q$ in KFe$_2$As$_2$ is very similar to the $\nu_Q$ measured at the As(1) site near the K layer in the recently discovered superconductor CaKFe$_4$As$_4$, where magnetic fluctuations are involved to explain the temperature dependence [143]. As a function of pressure at constant temperature, $\nu_Q$ increases quickly up to 1.5 GPa, but increases slowly thereafter as in seen in the inset to Fig. 6.3. Similar pressure dependence of $\nu_Q$ in KFe$_2$As$_2$ has been reported [108]. No sharp anomalies are seen in $\nu_Q$, indicating no structural phase transitions in the measured pressure and temperature range.

In order to precisely determine the NMR shift with external field applied in the $ab$ plane, we performed Fourier transform measurements of the $\theta = 90^\circ$ peak of the NMR central transition line
at a constant magnetic field. In general, the central transition frequency is given by

\[ \nu(\theta) = \nu_L \left( 1 + \frac{2K_{ab} + K_c}{3} \right) + \frac{\nu_L}{3} (K_c - K_{ab})(3\cos^2 \theta - 1) - \frac{3\nu_Q^2}{16\nu_L} \sin^2 \theta(9\cos^2 \theta - 1). \]  

(6.6)

where \(K_{ab}\) and \(K_c\) are Knight shifts for \(H \parallel ab\) plane and \(H \parallel c\) axis, respectively. In the present case, since \(\frac{3\nu_Q^2}{16\nu_L} \gg \frac{\nu_L}{3} (K_c - K_{ab})\) (Ref. [69] gives \(|K_c - K_{ab}| \sim 0.001\)), Eq. 6.6 can be simplified as

\[ \nu(\theta = 90^\circ) = \nu_L (1 + K_{ab}) + \frac{3\nu_Q^2}{16\nu_L} \]  

(6.7)

when \(\theta = 90^\circ\). We therefore obtain \(K_{ab}\) by subtracting \(3\nu_Q^2/16\nu_L\) from the measured resonance frequency, \(\nu(\theta = 90^\circ)\).

The obtained NMR shifts are shown in Fig. 6.4. At ambient pressure, the NMR shift is nearly constant at low temperature and shows a broad peak near 150 K, before decreasing at high temperature. The behavior of \(K_{ab}\) is qualitatively similar under pressure, with the broad peak shifting to slightly higher temperature.

6.4.3 Crossover temperature \(T^*\)

The NMR shift data in Fig. 6.4 are consistent with a coherence/incoherence crossover behavior in \(\text{KFe}_2\text{As}_2\) at all measured pressures. The broad peak in the NMR shift has been interpreted as the crossover from the high-temperature local-moment (Curie Weiss) behavior to the low temperature coherent state [68; 127]. We could not reliably extract the crossover temperature \(T^*\) from the NMR shift data alone because of the weak temperature dependence of the NMR shift and also the broad quadrupole powder lineshape, although the data suggest a small increase of \(T^*\) under pressure.

The coherence/incoherence crossover temperature in \(\text{KFe}_2\text{As}_2\) can also be estimated from the nuclear spin-lattice relaxation rate \(1/T_1\) data, shown in Fig. 6.5. Our results for \(1/T_1\) at ambient pressure are quantitatively consistent with Ref. [69]. At low temperature, \(1/T_1\) shows a power law behavior \(1/T_1 \sim T^{0.75}\) for all pressures, as seen in Fig. 6.5. An obvious reduction in the
Figure 6.4 NMR shift with external field aligned in the $ab$ plane ($K_{ab}$) for indicated pressures. The dashed lines are guides to the eye. The arrows represent the crossover temperature $T^*_{\text{NMR}}$ as determined by NMR $1/T_1$ measurements (see text and Fig. 6.5). The horizontal bars denote the uncertainty in estimation of $T^*_{\text{NMR}}$ ($\pm 20$ K).

slope of $1/T_1$ is seen at high temperature, however. Similar temperature dependence of $1/T_1$ is often observed in heavy fermion systems, where $1/T_1$ shows a power law behavior of $1/T_1 \propto T^\alpha$ (i.e. $\alpha = 0.25$ in CeCoIn$_5$ [144] and $\alpha = 1$ in URu$_2$Si$_2$ [145]) at low temperatures due to coherent metallic heavy fermion states and levels off at higher temperatures due to incoherent local moment behaviors. Thus the change in slope of the temperature dependence of $1/T_1$ gives an estimate of the coherence/incoherence crossover temperature (defined as $T^*_{\text{NMR}}$). From the $T_1$ data, we find $T^*_{\text{NMR}} \sim 145 \pm 20$ K at ambient pressure, $T^*_{\text{NMR}} \sim 170 \pm 20$ K at 1.5 GPa and $T^*_{\text{NMR}} \sim 180 \pm 20$ K at 2.1 GPa, indicating that $T^*_{\text{NMR}}$ increases under pressure. The uncertainty in $T^*_{\text{NMR}}$ is due primarily to uncertainty in the high-$T$ slope (see below). These values of $T^*_{\text{NMR}}$ seem to be consistent with the high-temperature end of the broad peak of $K_{ab}$ (arrows in Fig. 6.4). The increase of $T^*_{\text{NMR}}$ under
Figure 6.5  NMR spin-lattice relaxation rate $1/T_1$ as a function of temperature. The coherence/incoherence crossover temperature $T_{NMR}^*$ is found by the change of slope of $1/T_1$. The uncertainty in estimation of $T_{NMR}^*$ is $\pm 20$ K (see text).

pressure is reasonable, as the application of pressure should increase the hybridization between localized and itinerant electrons, thus increasing the local magnetic coupling $J$ [135].

We also note that $1/T_1$ constant behavior above the coherent/incoherent crossover temperature $T^*$ is observed in CsFe$_2$As$_2$ [127], which has the highest effective mass of the AFe$_2$As$_2$ (A = K, Rb, Cs) family and therefore most localized electrons. However, as seen in Fig. 6.5, in KFe$_2$As$_2$ at ambient pressure $1/T_1$ does not level off completely above $T_{NMR}^*$ but rather increases much more slowly, following roughly $1/T_1 \sim T^{0.25\pm0.1}$. Furthermore, as $T_{NMR}^*$ increases under pressure, so does the slope of $1/T_1 \sim T^{0.4\pm0.1}$. It would be interesting if the high-temperature slope correlates with extent of the localization.
Figure 6.6  (a) Resistivity of KFe$_2$As$_2$ single crystals [119] for selected pressures. (b) Resistivity plotted as a function of $T/t^*$ where the scaling coefficient $t^*$ is chosen so as to merge each curve with the ambient pressure curve. For ambient pressure, $t^* \equiv 1$. Upper inset: pressure dependence of the unitless scaling factor $t^*$. Lower inset: Comparison of pressure dependence of $T^*$ as measured by resistivity ($T^*_R$; filled symbols) and NMR ($T^*_\text{NMR}$; open symbols). For resistivity $T^*_R = (157 \text{ K})t^*$, where $T^*_R$ at 0 GPa is determined by the crossing of two tangent lines, as proposed in Ref. [127] (see text).
To corroborate our estimate of \( T^* \) and expand the results to pressures higher that those attainable in our NMR pressure cell, we also present and re-analyze single-crystal resistivity data up to \( \sim 5 \) GPa [119], as shown in Fig. 6.6(a). In heavy fermion systems, one expects a decrease of the resistivity below the coherence temperature, often showing a broad maximum at \( T^* \) [146; 68]. While the NMR data provide incontrovertible evidence for coherence-incoherence crossover, the resistivity contains contributions from phonon scattering which complicate the interpretation of the data. The decrease in resistivity observed in Fig. 6.6(a) could, in principle, be due to the small Debye temperature and not electronic coherence effects. However, in the AFe\(_2\)As\(_2\) (A = K, Rb, Cs) family, a strong correlation has been observed between \( T_{NMR}^* \) (as observed by NMR) and the cross point of two approximately linear trends in the resistivity [127]. This method, then, appears to give a reasonable estimate of \( T^* \) in these materials. Here we also apply this method to estimate \( T^* \) (defined as \( T_{R}^* \)) in KFe\(_2\)As\(_2\) using the resistivity data. We note that our resistivity curves for different pressures can be scaled by a pressure dependent scaling factor \( t^* \) (defined dimensionless), as shown in Fig. 6.6(b). The pressure dependence of \( t^* \) is shown in the upper inset. To estimate \( T_{R}^* \) from the resistivity data, we use the cross point of two approximately linear trends as shown in Fig. 6.6(b) where \( T_{R}^* \) is estimated to be \( T_{R}^* = 157 \) K for the ambient pressure data. Then, the pressure dependence of \( T_{R}^* \) can be obtained by using the pressure dependence of \( t^* \). As shown in the lower inset of Fig. 6.6(b), \( T_{R}^* \) increases with increasing pressure. While the values of \( T_{R}^* \) extracted from the resistivity data up to 2.1 GPa are slightly higher than the \( T_{NMR}^* \) values identified by NMR data, both techniques show the increase of the coherent/incoherent crossover temperature \( T^* \) with applied pressure. It is clear that \( T_{R}^* \) evolves continuously, showing no anomaly at \( p_c \sim 1.8 \) GPa. It is interesting to note that the resistivity data for the Rb- and Cs-samples [127] can also be scaled to our ambient pressure data with \( t^* = 0.78 \) (\( T_{R}^* = 123 \) K) and \( t^* = 0.52 \) (\( T_{R}^* = 82 \) K) respectively.

We now consider the empirical relation that \( T_c \) is proportional to \( T^* \) observed in the AFe\(_2\)As\(_2\) (A = K, Rb, Cs) family at ambient pressure [127]. Figure 6.7 plots our results for \( T_c \) as a function of \( T^* \) along with the results of Ref. [127]. In the AFe\(_2\)As\(_2\) (A= Cs, Rb, K) family at ambient pressure, \( T_c \) moves in proportion to \( T^* \), suggesting that the change of \( T^* \) is the primary factor
in determining $T_c$. In contrast, for pressurized KFe$_2$As$_2$ we find that $T_c$ decreases sharply as a function of $T^*$ below $p_c \sim 1.8$ GPa and then becomes roughly independent of $T^*$ above $p_c$. These results indicate that $T^*$ is not the primary driver of the pressure dependence of $T_c$ in KFe$_2$As$_2$. Instead, as will be described in the next section, we show the antiferromagnetic spin fluctuations play an important role for the pressure dependence of $T_c$.

Finally, it is interesting to discuss the second empirical relation that $\gamma^{-1} \propto T^*$ under pressure. Quantum oscillation experiments under high pressure found that the effective mass $m^*$ decreases under pressure [118]. In addition, the coefficient $A$ in the low-temperature resistivity $\rho = \rho_0 + AT^2$ decreases smoothly, which is also consistent with a decreasing $m^*$ under pressure [119]. The decreasing $m^* \sim \gamma$ accompanied by the increase of $T^*$ suggest that the $\gamma^{-1} \propto T^*$ relationship seems to hold under pressure, similar to the case of AFe$_2$As$_2$ ($A = \text{K, Rb, Cs}$). As one moves from CsFe$_2$As$_2$ to RbFe$_2$As$_2$ to KFe$_2$As$_2$, the chemical pressure increases due to the decreasing size of the alkali metal ion [108]. Simultaneously, $T^*$ increases [127]. Consequently, the increase of $T^*$ in KFe$_2$As$_2$ under physical pressure could be considered an extension of the chemical pressure trend. However, it is noted that the $\gamma^{-1} \propto T^*$ relationship does not appear to hold the case of carrier doping in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ as seen in Ref. [134].

### 6.4.4 NQR Spin-Lattice Relaxation Rate

Since $T^*$ evolves smoothly across the critical pressure $p_c$, the pressure dependence of the coherence/incoherence crossover behavior cannot explain the non-monotonic behavior of $T_c$ under pressure in KFe$_2$As$_2$. To address this question, we have also performed NQR $1/T_1$ measurements in both the PM and SC states. No external magnetic field is required to measure NQR $1/T_1$, making this technique ideal for investigation of the SC state.

#### 6.4.4.1 Paramagnetic State

First, we consider the NQR $1/T_1 T$ in the PM state at ambient pressure. As seen in Fig. 6.8, the NQR $1/T_1 T$ at ambient pressure follows a power law above $T_c$: $1/T_1 = 4T^{0.8} \iff 1/T_1 T = 4T^{-0.2}$
Figure 6.7 Plot of $T_c$ vs $T^*$ for AFe$_2$As$_2$ (A = K, Rb, Cs) family at ambient pressure [127] (black). The orange arrow illustrates the increase of chemical pressure from CsFe$_2$As$_2$ to KFe$_2$As$_2$. The green data plots $T_c$ vs $T^*$ for KFe$_2$As$_2$ with indicated pressure as an implicit parameter, using $T^*_\text{NMR}$ extracted from NMR measurements (see Fig. 6.5). Similarly, the red data shows $T_c$ vs $T^*$ for KFe$_2$As$_2$ using $T^*_R$ extracted from resistivity measurements (see Fig. 6.6).

(Shown by the red solid curve in Fig. 6.8). This power law is consistent with previously reported NQR results at ambient pressure [110], and also NMR $1/T_1$ data ($1/T_1 \propto T^{0.75}$) described in the previous section. In general, the nuclear spin-lattice relaxation rate measures the $q$-summed dynamical susceptibility at the Larmor frequency perpendicular to the quantization axis of nuclear spin,

$$\frac{1}{T_1 T} \sim \gamma^2 k_B \sum_q A_\perp^2(q) \frac{\text{Im} \chi_\perp(q,\omega_L)}{\omega_L}. \quad (6.8)$$

Therefore, since the NMR shift $K$, which reflects the $q = 0$ component of $\chi$, shows a weak temperature dependence, the increase of $1/T_1 T$ at low temperatures reflects the enhancement of low-energy $q \neq 0$ AFM spin fluctuations.

As shown in Fig. 6.8, the enhancements of $1/T_1 T$ at low temperatures seems to be suppressed up to $p_c$ and then starts to increase above $p_c$ with increasing pressure, although the pressure
dependence of $1/T_1 T$ becomes less clear at high temperatures above $\sim 10$ K due to our experimental uncertainty. To see clearly the pressure dependence of low temperature $1/T_1 T$ data, we plot the $1/T_1 T$ values at 4.2 K as a function of pressure in the inset of Fig. 6.8. Here we took the $1/T_1 T$ values at 4.2 K because enhancements of $1/T_1 T$ due to the AF spin fluctuations are more significant at low temperatures and also the temperature is close to the lowest temperature above $T_c$ in the paramagnetic state for all pressures measured. The value of $1/T_1 T$ at 4.2 K clearly decreases with increasing pressure below $p_c$ and then increases again above $p_c$. Since the value of $1/T_1 T$ reflects the strength of low-energy AFM spin fluctuations, we conclude that spin fluctuations at low temperatures are suppressed below $p_c$ and enhanced again above $p_c$. This trend is very similar to the pressure dependence of $T_c$. Therefore, we may conclude that AFM spin fluctuations are involved in the superconducting pairing both above and below $p_c$, consistent with the high-field NMR results [108].
Figure 6.9  $T$ dependence of the ratio $R \equiv T_{1,c}/T_{1,ab}$ for different pressures where NQR-$T_1$ data are used for $T_{1,c}$, in addition to $R$ obtained from $T_{1,c}/T_{1,ab}$ at ambient pressure from Ref. [69]. NQR $1/T_1 T$ above $T_c$ for various pressures. The inset shows the $T$ dependence of $1/T_1$ for $H||c$ and $H||ab$ from Ref. [69], together with NQR $1/T_1$ data.

However, it should be noted that the values of $1/T_1 T$ decrease for the replacement of A from Cs to K in AFe$_2$As$_2$, despite the fact that $T_c$ increases due to the replacement [127]. The relationship between $T_c$ and $1/T_1$ therefore appears to be different in the pressure and replacement cases. Although at present the origin of the different behavior of $T_c$ between the pressure and replacement cases is not understood well, we here discuss a few possibilities to explain the difference.

One possible difference between the pressure and replacement cases may relate to the anisotropy of magnetic fluctuations. According to Zhang et al. [147], based on their NMR data, the anisotropy of the low-temperature AFM fluctuations is found to significantly decrease with the replacement from Cs to K in AFe$_2$As$_2$. That is, the Cs sample with the lowest $T_c$ in the family has the greatest anisotropy, suggesting that $T_c$ may correlate with the anisotropy of the AFM fluctuations. Zhang
et al. also suggested that the difference of the anisotropy may relate to quantum criticality and that the Cs sample is the closest to a QCP.

It is interesting to compare this to the behavior of the magnetic fluctuation anisotropy in KFe$_2$As$_2$ under pressure which can be obtained by taking a look at the ratio of $1/T_1$ for the two field directions, $R \equiv (1/T_1)_{ab}/(1/T_1)_c$. According to the previous NMR studies performed on Fe pnictide SCs [148; 149; 69], the ratio $R$ depends on the nature of magnetic fluctuations and also anisotropy of the magnetic fluctuations as

$$R = \begin{cases} 
0.5 + \left( \frac{S_{ab}}{S_c} \right)^2 & \text{for the stripe AFM fluctuations} \\
0.5 & \text{for the Néel-type spin fluctuations}
\end{cases} \quad (6.9)$$

where $S_\alpha$ is the amplitude of the spin fluctuation spectral density at NMR frequency along the $\alpha$ direction. Unfortunately, since we used a powder sample to improve the signal intensity, only $H \parallel ab$ plane $1/T_1$ NMR measurements are feasible. Nevertheless, we can obtain some information about the anisotropy of the AFM spin fluctuations using our NQR $1/T_1$ data. Since the quantization axis of the electric field gradient is parallel to the $c$ axis, the NQR $1/T_1$ should reflect magnetic fluctuations perpendicular to the $c$ axis. These are the same fluctuations observed by NMR $1/T_1$ for $H \parallel c$ axis, where the quantization axis is determined by the magnetic field. Indeed, we confirmed that our NQR $1/T_1$ data coincide almost perfectly with the NMR $1/T_1$ data under $H \parallel c$ axis reported previously at ambient pressure [69], as shown in the inset of Fig. 6.9. This also indicates no magnetic field effects on $1/T_1$. Therefore, using both the NQR $1/T_1$ and NMR $1/T_1$ data under pressure, we can estimate how the anisotropy of magnetic fluctuations changes with pressure. The estimated $R$ values using both the NQR $1/T_1$ and NMR $1/T_1$ data are shown in Fig. 6.9 as a function of temperature for different pressures. All $R$ values are greater than unity, consistent with the stripe-type spin fluctuations. As shown, $R$ does not show any significant change with pressure. This indicates that the anisotropy of spin fluctuations is almost independent of pressure, in contrast to the case of replacement effects on AFe$_2$As$_2$. We suggest that the different behaviors of the spin fluctuation anisotropy between the pressure and replacement cases may be related to the different behavior of $T_c$ in the two cases. It is also interesting to note that several papers have
proposed that, in the proximity of a QCP, the critical fluctuations may actually be detrimental to superconductivity in these systems [125; 68; 147]. Since CsFe$_2$As$_2$ is considered to be the closest to the QCP, it would be expected to have a low $T_c$.

It is also interesting to note in this context that in the hole-overdoped region of the Ba$_{1-x}$K$_x$Fe$_2$As$_2$ phase diagram, the AFM spin fluctuations and Sommerfeld coefficient determined by specific heat measurements are both enhanced with increasing $x$ while $T_c$ decreases, similar to the case of AFe$_2$As$_2$ (A = K, Rb, Cs). One possible explanation for the decrease of $T_c$ in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ is the growth of competing ferromagnetic (FM) spin fluctuations, which coexist with the AFM spin fluctuations [107]. As demonstrated by Wiecki et al., the growth of the AFM fluctuations with increasing $x$ in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ is accompanied by the simultaneous growth of FM fluctuations. These FM fluctuations may interfere with the AFM-fluctuation-based Cooper-pairing mechanism, thus lowering $T_c$ despite the enhancement of AFM fluctuations. It is possible such physics could apply to the AFe$_2$As$_2$ (A=K, Rb, Cs) system also.

6.4.4.2 Superconducting State

The $T$ dependence of NQR $1/T_1$ below $T_c$ is shown in Fig. 6.10. At ambient pressure, $1/T_1$ follows the power law $1/T_1 \sim T^{0.8}$ in the PM state as discussed above (red dashed line in Fig. 6.10). A clear kink is seen at $T_c$, and the data follow a new power law $1/T_1 \sim T^{1.3}$ below $T_c$ (red solid line in Fig. 6.10). This behavior is consistent with previous ambient pressure NQR results [110]. However, in contrast to Ref. [110], a long $T_1$ component is found to appear below $T = 1$ K at ambient pressure and also under pressure. The upper inset of Fig. 6.10 shows the typical two-component exponential behavior of the nuclear magnetization recovery curve observed at low temperature ($T = 0.4$ K; $p = 1.5$ GPa), together with a single exponential behavior at $T = 3.73$ K and $p = 1.5$ GPa. Then, we fit the recovery curves according to

$$1 - \frac{m(t)}{m(\infty)} = A \exp\left(-\frac{3t}{T_{1S}}\right) + (1 - A) \exp\left(-\frac{3t}{T_{1L}}\right),$$  \hspace{1cm} (6.10)$$

where $T_{1S}$ and $T_{1L}$ are the short and long relaxation times, respectively. The parameter $A$, representing the fraction of nuclei relaxing with the shorter relaxation time $T_{1S}$, is shown in the lower
inset of Fig. 6.10, demonstrating that the long $T_{1L}$ component fraction increases with decreasing temperature.

The existence of two $T_1$ components implies the existence of two distinct local electronic environments, which are physically separated in real space. Similar two-component relaxation has been observed by NQR in the closely-related sample RbFe$_2$As$_2$, in which the two-component behavior was argued to be associated with a charge order of nanoscale periodicity [126]. While we find no direct evidence for charge order in KFe$_2$As$_2$ in this study, charge ordering in KFe$_2$As$_2$ at 2.4 GPa (above our maximum pressure) was proposed by high pressure NMR [108]. Two-component relaxation has also been reported in CsFe$_2$As$_2$ under magnetic field in Refs. [127] (Supplemental Information), [128] and [150]. At present, although the origin of the two $T_1$ components in KFe$_2$As$_2$ is not clear, the similar behavior in closely related systems would suggest that the two-component behavior observed here is intrinsic. Further studies will be needed to clarify the origin.

NQR $1/T_1$ is a sensitive probe of the reduction of the density of states (DOS) at the Fermi energy $N(E_F)$ due to the opening of the SC gap. In general, $1/T_1$ in the SC state is given by [50]

$$\frac{1}{T_1} \sim \int_0^\infty \left[ N_s^2(E) + M_s^2(E) \right] f(E)(1 - f(E))dE, \quad (6.11)$$

where $N_s(E)$ is the DOS and $f(E)$ is the Fermi distribution function. $M_s(E)$ is the anomalous DOS arising from Cooper pair coherence. Due to the lack of a coherence peak just below $T_c$, we neglect the coherence term, as has been done in previous NMR/NQR studies of FeAs superconductors.

The very weak decrease of the short component $1/T_{1S}$ below $T_c$ ($1/T_{1S} \sim T^{1.3}$), implies a very small SC gap. Using a simple full gap model for $N_s(E)$, we estimate a gap of $\Delta(0) \sim 0.07$ meV ($2\Delta(0)/k_BT_c \sim 0.5$) from the short component, consistent with $2\Delta(0)/k_BT_c \sim 0.51$ reported by previous NQR measurements [110]. For all but the lowest temperatures measured, the relaxation is dominated by the short component, as shown by the inset of Fig. 6.10. This implies that a large number fraction of nuclei see a nearly gapless electronic environment below $T_c$. This may correspond to a large ungapped DOS below $T_c$ in KFe$_2$As$_2$ observed by scanning tunneling spectroscopy (STS) [133]. The large ungapped DOS was attributed to a Van Hove singularity just below the Fermi level seen by angle resolved photoemission spectroscopy (ARPES) [133]. It is also worth mentioning
that a residual DOS in SC state has been reported in SrFe$_2$As$_2$ under high pressure [151] and also in Co doped BaFe$_2$As$_2$ by specific heat measurements [152]. It is also suggested theoretically that the residual DOS is due to a possible formation of domain walls inherent to antiferromagnetism in iron pnictide SCs [153].

In contrast, the long component $1/T_{1L}$ shows a large reduction relative to the $1/T_1$ in the PM state, implying a large reduction in $N_s(E_F)$ due to the SC gap. Although the experimental uncertainty is large, $1/T_{1L}$ seems to be proportional to $T^{2\pm 1}$ as shown by the solid line in Fig. 6.10. The sizable depletion of $N_s(E_F)$ only below $T \sim 1$ K has been observed by the STS and ARPES experiments [133]. The co-existence of one large gap and at least one very small gap has also been reported with specific heat [116] and small angle neutron scattering [112] experiments. However, from the two-component relaxation behavior, our NQR data suggest a real-space modulation of the local gap structure, which has not been reported previously.

Under high pressure of 1.5 GPa and above, no obvious change of the slope of the short $T_1$ component occurs across $T_c$ within our experimental uncertainty. This indicates that the nuclei relaxing according to $1/T_{1S}$ see a gapless local electronic environment above 1.5 GPa. Therefore the small gap seen by $1/T_{1S}$ at ambient pressure is thought to be suppressed to zero near $p_c$, and is not recovered above $p_c$. Similarly, muon spin rotation ($\mu$SR) measurements [154] on the closely-related RbFe$_2$As$_2$ with $p_c \sim 1$ GPa [123] reported that the smaller of two SC gaps is suppressed to zero near 1 GPa. As for the long $T_1$ component under high pressure, as shown in Fig. 6.10, no obvious change in $1/T_{1L}$ can be found, suggesting no dramatic change in the magnitude of the larger SC gap upon pressure application. According to Ref. [119], the SC gap structure changes above $p_c$, where the SC gap is modulated along $k_z$. However, we did not observe a clear change in gap symmetry across $p_c$ from our $1/T_1$ measurements.

6.5 Conclusions

We have presented $^{75}$As-NMR, NQR and resistivity data which clearly show an increase of the coherence/incoherence crossover temperature $T^*$ in KFe$_2$As$_2$ under pressure. This increase of $T^*$
is expected due to the increase in hybridization between localized and conducting bands caused by pressure application. We find that the relation $\gamma^{-1} \sim T^*$ observed in ambient pressure AFe$_2$As$_2$ ($A = K, Rb, Cs$) continues to hold under pressure. However, the proportionality between $T^*$ and $T_c$ is clearly broken under pressure. The non-monotonic behavior of $T_c$ under pressure is therefore unrelated to the coherence-incoherence crossover behavior in the paramagnetic state. However, the strength of AFM spin fluctuations in the paramagnetic state is found to correlate with $T_c$, evidencing clearly that the AFM spin fluctuations play an important role for the appearance of superconductivity in KFe$_2$As$_2$, although such a correlation cannot be seen in the replacement effects of $A$ in the AFe$_2$As$_2$ ($A= K, Rb, Cs$) family. In the superconducting state, two $T_1$ components are observed at low temperatures, suggesting the existence of two distinct local electronic environments. The temperature dependence of the short $T_{1s}$ indicates nearly gapless state below $T_c$. On the other hand, the temperature dependence of the long component $1/T_{1L}$ implies a large reduction in the density of states at the Fermi level due to the SC gap formation. These results suggest a real-space modulation of the local SC gap structure in KFe$_2$As$_2$ under pressure.

6.6 Acknowledgments

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Figure 6.10 NQR $1/T_1$ for indicated pressures. The arrows denote $T_c$ at each pressure. The dashed lines are power law fits to the PM state data for each pressure. The red solid line below $T_c$ shows the power law with $1/T_{1S} \propto T^{1.3}$ at ambient pressure. Below $T \sim 1$ K, a component with long $T_1$ appears. The solid pink line represents $1/T_{1L} \propto T^2$ behavior. Upper inset: The typical two exponential behavior (black squares) of the nuclear magnetization recovery curve observed at low temperature ($T = 0.4$ K; $p = 1.5$ GPa), together with a single exponential behavior (red circles) at $T = 3.73$ K and $p = 1.5$ GPa. Lower Inset: Fraction $A$ of nuclei relaxing with the short $T_1$ (see text).
CHAPTER 7. NMR EVIDENCE FOR STATIC LOCAL NEMATICITY AND ITS COOPERATIVE INTERPLAY WITH LOW-ENERGY MAGNETIC FLUCTUATIONS IN FeSe UNDER PRESSURE


P. Wiecki, M. Nandi, A. E. Böhmer, S. L. Bud’ko, P. C. Canfield, and Y. Furukawa

The Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA

7.1 Abstract

We present $^{77}$Se-NMR measurements on single-crystalline FeSe under pressures up to 2 GPa. Based on the observation of the splitting and broadening of the NMR spectrum due to structural twin domains, we discovered that static, local nematic ordering exists well above the bulk nematic ordering temperature, $T_s$. The static, local nematic order and the low-energy stripe-type antiferromagnetic spin fluctuations, as revealed by NMR spin-lattice relaxation rate measurements, are both insensitive to pressure application. These NMR results provide clear evidence for the microscopic cooperation between magnetism and local nematicity in FeSe.

7.2 Introduction

Much attention in recent research on iron-based superconductivity (SC) has been paid to understanding the nature of the electronic nematic phase, which breaks rotational symmetry while preserving time-reversal symmetry [155; 32]. In the archetypical “122” compounds AFe$_2$As$_2$ (A=Ca, Sr, Ba) [18; 16], the nematic phase is closely tied to the stripe-type antiferromagnetic (AFM) phase in the phase diagram, suggesting a magnetic origin for the nematic state. Among the Fe-based SCs, FeSe is known to be an exception. At ambient pressure, FeSe undergoes a transition to the nematic
phase at a bulk structural phase transition temperature $T_s \sim 90$ K, as well as to SC below $T_c \sim 8$ K, but has no stripe-type AFM ordered phase. Under pressure ($p$), $T_s$ is suppressed to $\sim 20$ K at $p \sim 1.7$ GPa [156; 157; 158] and an AFM ordered state emerges above $\sim 0.8$ GPa [159; 160; 161; 162]. In addition, $T_c$ is enhanced from 8 K at ambient pressure to $\sim 37$ K at $p \sim 6$ GPa [163]. The decrease of $T_s(p)$ and increase of $T_N(p)$ under pressure suggests competition between nematic and magnetic orders. Furthermore, NMR measurements [164; 165] showed Korringa behavior above $T_s$, consistent with an uncorrelated Fermi liquid, while AFM spin fluctuations (SFs) were found to be strongly enhanced only below $T_s$. These observations suggested that SFs are not the driver for nematic order and therefore pointed to an orbital mechanism for the nematicity [165]. An orbital mechanism was also suggested by Raman spectroscopy [166].

In contrast, several recent studies have suggested cooperation between nematicity and magnetism in FeSe. High-energy x-ray diffraction measurements [158] found that the orthorhombic distortion is enhanced in the magnetic state at $p = 1.5$ GPa. Furthermore, above 1.7 GPa $T_s(p)$ and $T_N(p)$ were found to coincide as a simultaneous first-order magneto-structural transition. These observations are consistent with a spin-driven mechanism for nematic order in FeSe. Similarly, inelastic neutron scattering (INS) measurements at ambient pressure [167; 168] showed that commensurate stripe-type AFM SFs are in fact present well above $T_s$, which could possibly drive the nematic transition. These SFs were not seen by NMR [164; 165] due to a spin gap above $\sim 90$ K. In addition, $^{77}$Se-NMR data under pressure [169] revealed a first-order transition to a stripe-type magnetic ordered state, and suggested a magnetic driven nematicity. Therefore, the origin of nematicity in FeSe is still under intense debate, motivating further study of the microscopic properties of the nematic state in FeSe.

Here, we present $^{77}$Se-NMR measurements on FeSe under pressures up to 2 GPa, focusing our attention on the local, microscopic properties of the paramagnetic and nematic phases. We found clear evidence that a static, local nematic ordering exists well above $T_s$. Both the local nematic order and the low-energy stripe-type antiferromagnetic spin fluctuations, are found to be robust against
pressure application, providing clear evidence for the microscopic cooperation between magnetism and local nematicity in FeSe.

7.3 Results

$^{77}$Se-NMR ($I = 1/2; \gamma/2\pi = 8.118 \text{ MHz/T}$) spectra have been measured on a single crystal (24 mg) of FeSe in the temperature ($T$) range of 4–300 K with a fixed field of $H = 7.4089 \text{ T}$ applied along the [110] direction in the high-$T$ tetragonal phase. The crystal was grown using chemical vapor transport as outlined in Ref. [170]. The experimental details are described in Supplemental Material (SM) [171]. At room temperature, the spectra are very narrow with the full-width-at-half-maximum (FWHM) reaching as low as $\sim 1.5 \text{ kHz}$, which is half of $3 \text{ kHz}$ reported previously [169], indicative of the high quality of our single crystal. Typical NMR spectra below 100 K for all measured pressures are shown in Fig. 7.1. At ambient pressure, a clear splitting of the spectrum was observed in the orthorhombic structural phase below $T_s$, consistent with previous data [164; 165; 172; 169]. The spectral splitting arises from the presence of two types of nematic domains in the twinned sample, one of which experiences $H \parallel a$ axis and the other $H \parallel b$ axis, combined with the anisotropy of the in-plane Knight shift ($K_a$ and $K_b$) in the nematic ordered phase [164; 165]. The difference of the Knight shift $\Delta K = |K_a - K_b|$ is, therefore, a measure of the local microscopic nematic order parameter [165; 172]. Under pressure, we observed similar clear splittings of the spectra below the bulk $T_s$ as shown in Fig. 7.1. However, we found that the splitting of the spectrum exists even above $T_s$ at all measured pressures. This was not reported in the previous NMR study [169]. A similar splitting of the spectrum above the bulk $T_s$ was reported at ambient pressure due to random local strains produced by gluing of the crystal [172]. The asymmetric spectra observed for $T > T_s$ originates from the difference in the FWHM of the lower- and higher-frequency peaks. This provides evidence of the existence of the two peaks above $T_s$, although the origin of the different FWHM of the two lines is not clear at present. The existence of two peaks above $T_s$ under pressure is also shown by the $T$ and $p$ dependence of the coefficient of determination ($R^2$) of a single-peak fit shown in SM [171].
Figure 7.1 Representative NMR spectra at indicated $T$ for all measured pressures. The two peaks arise from inequivalent nematic domains with $H \parallel a$ and $H \parallel b$. The solid red line is the bulk $T_s$, as determined by a kink in the NMR shift (see Fig. 7.2). The dashed blue line is $T_N$ and the dot-dash dark yellow line is $T_c$. $T_N$ and $T_c$ were determined from data shown in shown in [171]. The colors of the spectra correspond to different phases: black for the paramagnetic state, dark yellow for below $T_c$, blue for below $T_N$, and red for the bulk nematic ordered state.
In order to extract $\Delta K$, we have fit the spectrum to a sum of two Lorentzian peaks. From the fitting, we determined the position of each peak, providing the $T$ and $p$ dependence of $K_a$ and $K_b$ as shown by orange triangles and teal circles in the upper panels of Fig. 7.2. Note that the NMR data alone do not determine which of the two peaks corresponds to $K_a$ [164; 165]. Also displayed is the average value $K_{\text{avg}} = \frac{1}{2}(K_a + K_b)$, shown by black squares. $K_{\text{avg}}$ decreases monotonically with decreasing $T$. The bulk $T_s$ is identified by kinks in $K_a$, $K_b$ and $K_{\text{avg}}$ as can be seen in the upper panel of Figs. 7.2. The observed $T_s$ agree well with values reported previously [162; 161; 158].

Figure 7.3 shows the $T$ dependence of $\Delta K$ under different pressures, where the vertical lines indicate the corresponding bulk $T_s$ for each pressure. At ambient pressure, $\Delta K$ increases sharply below $T_s$ and shows a broad peak near $\sim 50$ K before decreasing at low $T$, consistent with the previous NMR results [164; 165]. A peak near $\sim 60$ K is also seen in the $T$ dependence of the resistivity anisotropy [173]. As seen from Fig. 7.3, $\Delta K$ remains non-zero within our experimental uncertainty above $T_s$ up to a temperature we define as $T_K^*$. At ambient pressure, we find $T_K^* \sim T_s$. Under pressure, on the other hand, it is clearly seen that $T_K^*$ exceeds $T_s$. It is also found that $T_K^*$ is nearly constant as a function of $p$, despite the decrease of $T_s$. Given the fact that recent x-ray diffraction measurements [158] indicated that the bulk tetragonal symmetry of the crystal is broken only below $T_s$, our NMR results imply that a short-range nematic order exists above $T_s$ in the bulk tetragonal phase, and is surprisingly resistant to pressure application. Since the NMR spectrum probes static electronic properties, these results indicate that the local nematic short-range order is static at the NMR time scale ($\sim$ MHz). A similar local static nematic state has been observed in the BaFe$_2$(As$_{1-x}$P$_x$)$_2$ system [174; 175] in which NMR spectrum measurements on the $x = 0.04$ ($T_s = 120$ K) compound revealed the existence of nearly static nematic fluctuations up to 250 K [174].

Evidence for nematicity above $T_s$ is also seen in the FWHM of the spectra (Fig. 7.2 lower panels). In the PM state, the FWHM displays a strong upturn at a pressure-dependent temperature $T_{\text{FWHM}}^*$, indicated by black arrows in Fig. 7.2. Since $^{77}\text{Se}$ has $I = 1/2$, the broadening cannot be attributed to quadrupole effects. In normal circumstances of magnetic broadening of NMR lines in
Upper panels: NMR shift $K$ as a function of $T$ as obtained from a two-Lorentzian fit for indicated pressures. Orange triangles and teal circles represent $K_a$ and $K_b$, while the black squares are the average of the two, $K_{av}$. The black vertical lines indicate the corresponding bulk $T_s$ for each pressure. $T_c$ and $T_N$ for different pressures are also shown by the vertical broken lines. Lower panels: Full-width-at-half-maximum (FWHM) of NMR spectral peaks for two $ab$ plane orientations: $\theta = 0^\circ$ (filled symbols) and $\theta \sim 25^\circ$ (open symbols). Below $T_s$, the FWHM of each of the two peaks is shown separately. The low-frequency peak (teal) has consistently greater FWHM than the high-frequency peak (orange). Above $T_s$, the FWHM of a single-peak model is shown (black). Arrows denote $T_{*}$. 
a paramagnetic (PM) phase, the FWHM is expected to have the same $T$ dependence as the NMR shift $K$, which measures the uniform spin-susceptibility of the electrons. In FeSe, we find that $K$ decreases monotonically with decreasing temperature [171], consistent with [176; 164; 165]. The observed increase in the FWHM is therefore quite unexpected for a PM state, and cannot be due to normal magnetic broadening effects.

To get further insight into the origins of the increase in FWHM we also measured the spectrum with the crystal rotated by $\theta \sim 25^\circ$ away from tetragonal [110] within the $ab$ plane. At ambient pressure, Baek [165] has shown explicitly that $\Delta K$ below $T_s$ vanishes at $\theta = 45^\circ$, since then both types of domains experience symmetry-equivalent magnetic field directions. Indeed, we find that $\Delta K$ below $T_s$ is much reduced at $\theta \sim 25^\circ$ [171]. Remarkably, we find that the FWHM above $T_s$ is also drastically reduced at $\theta \sim 25^\circ$. However, below $T_s$ the FWHM of the two individual peaks shows no $ab$ plane orientation dependence. $T^*_\text{FWHM}$ also has no $ab$ plane orientation dependence. These results, together with the asymmetric shape of the spectra described above, clearly indicate that the broadening above $T_s$ is due to local nematicity and not local magnetism. We conclude that above $T_s$ the NMR spectrum consists of two nematic peaks (of orientation independent FWHM) with a small, unresolved, orientation-dependent splitting. $T^*_\text{FWHM}$ is understood as a crossover
between magnetic- and nematic-dominated broadening. Local nematicity may therefore be present even above \( T_{FWHM}^* \) where the nematic splitting would be less than the magnetic broadening.

We now discuss the AFM SFs based on the \(^{77}\text{Se} \) spin-lattice relaxation rate \( 1/T_1 \) and \( K \) data. For all pressures measured, as shown in SM [171], \( 1/T_1 T \) shows a similar \( T \) dependence in which \( 1/T_1 T \) decreases with decreasing \( T \) from room temperature to around \( T \sim 80 \text{ K} \) then increases, which indicates enhancements of low-energy AFM SFs at low \( T \) [176]. Within a Fermi liquid picture, the spin part of the NMR shift \( K_s (\propto \chi_{\text{spin}}) \) is proportional to the density of states at the Fermi energy \( D(E_F) \), whereas \( 1/T_1 T \) is proportional to the square of \( D(E_F) \). Therefore, in order to examine electron correlation effects, it is useful to estimate the quantity \( T_1 T K_s^2 \) [82; 81].

The so-called Korringa ratio \( \alpha = \hbar \gamma_e^2 / ( T_1 T K_s^2 4\pi k_B \gamma_n^2) \) is unity for uncorrelated metals. Here we plot \( \sqrt{1/T_1 T} \) vs. \( K(T) \) with \( T \) as an implicit parameter, for which a straight line is expected for the Korringa behavior. Under ambient pressure, the Korringa behavior is observed above \( T_s \) and \( \alpha \) is estimated to be \( \sim 1 \), suggesting no significant AFM correlations above \( T_s \). On the other hand, below \( T_s \), enhancements of AFM SFs are observed via the deviation of \( \sqrt{1/T_1 T} \) from the high-\( T \) linearity [164].

The \( \sqrt{1/T_1 T} \) vs. \( K(T) \) plots for all measured pressures are shown in Fig. 7.4 where, for reference, the \( T \) for each point is indicated. At 0.5 GPa, the \( \sqrt{1/T_1 T} \) vs \( K(T) \) behavior is similar to the case for ambient pressure, but one can see a deviation of \( \sqrt{1/T_1 T} \) from the high-\( T \) linearity slightly above \( T_s \), indicating that AFM SFs are enhanced slightly above \( T_s \). This effect is much more apparent at higher pressures. We define \( T_{spin}^* \) as the temperature below which low-energy SFs are enhanced. At ambient pressure, \( T_{spin}^* \sim T_s \) [164]. At 1 GPa, we find \( T_{spin}^* \sim 80 \text{ K} \) which differs significantly from \( T_s = 48 \text{ K} \). A similar behavior is also observed at 1.5 GPa with \( T_s = 32 \text{ K} \) and \( T_{spin}^* \sim 85 \text{ K} \). At 2 GPa, we find \( T_{spin}^* \sim 90 \text{ K} \).

As seen in the phase diagram of Fig. 7.5, \( T_{spin}^* \) is nearly pressure independent. This behavior is reminiscent of the robustness of \( T_K^* \) (and \( T_{FWHM}^* \)) to pressure application, suggesting a correlation between the local nematicity and low-energy magnetic fluctuations. While local nematicity is also present above \( T_K^* \), its \( \Delta K \) is too small to detect directly. It is possible that a corresponding
Figure 7.4 $\sqrt{1/T_1 T}$ versus $K(T)$ plot with $T$ as an implicit parameter for indicated pressures. $T^*_{\text{spin}}$, the onset of low-energy spin fluctuations, is determined by the deviation of the data from high-$T$-linear behavior shown by solid lines (see text). Bulk $T_s$ is indicated for comparison.
small low-energy SF contribution to $1/T_1T$ exists above $T^*_{\text{spin}}$ which cannot be detected within experimental uncertainty.

According to the INS measurements at ambient pressure [167], stripe-type AFM SFs exist above $T^*_{\text{spin}}$, despite not being observed in our NMR measurements. Since NMR detects SFs in the very low-energy region (of order $\mu$eV) while INS probes mainly high-energy spin dynamics (of order meV), the AFM SFs must have no spectral weight in the low-energy region which NMR can detect. In fact, the INS measurements point out the existence of a spin gap of $\sim 2.5$ meV at 110 K [167]. The INS measurements also indicate that the spin gap is closed below $T_s$ at ambient pressure. This picture is consistent with the NMR data at ambient pressure [164]. Since we continue to observe Korringa behavior above $T^*_{\text{spin}}$ for all measured pressures, the high-$T$ spin gap which exists at ambient pressure remains present up to at least 2 GPa. Therefore, $T^*_{\text{spin}}(p)$ may be attributed to the closing of a spin gap. Since the argument for orbital-driven nematicity from the ambient pressure NMR data [165; 164] is based on the lack of SFs above $T_s$, our observation of SFs above $T_s$ under pressure, combined with the ambient pressure INS results, does not exclude the possibility

Figure 7.5  Phase diagram of pressurized FeSe incorporating microscopic details of the paramagnetic phase as revealed by NMR.
of spin-driven nematic order. Further studies are highly required to shed light on the nature of the spin gap in FeSe.

7.4 Conclusions

In summary, from our measurements of the splitting and FWHM of $^{77}\text{Se}-\text{NMR}$ spectra, we find that a static, local nematic order exists above $T_s$ in FeSe under pressure, which has not been detected in previous studies. The local nematic order and the low-energy stripe-type antiferromagnetic spin fluctuations are both nearly independent of pressure, suggesting a cooperation between the magnetic fluctuations and local nematicity in pressurized FeSe.

Note added.—After submission of our manuscript, a similar NMR study, consistent with our results, was posted to the arXiv by Wang et al. [177].

7.5 Acknowledgements

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7.6 Supplemental Information

7.6.1 Experimental Details

$^{77}\text{Se}-\text{NMR}$ ($I = 1/2; \gamma/2\pi = 8.118 \text{ MHz/T}$) measurements on a 24 mg single crystal of FeSe were performed using a lab-built, phase-coherent, spin-echo pulse spectrometer at a fixed field of $H = 7.4089 \text{ T}$ (calibrated by $^{31}\text{P}-\text{NMR}$ in $\text{H}_3\text{PO}_4$ solution). Nuclear spin-lattice relaxation rate $1/T_1$ at each $T$ for different pressures was determined by fitting the nuclear magnetization $M$ versus time $t$ using the exponential function $1 - M(t)/M(\infty) = e^{-t/T_1}$, where $M(t)$ and $M(\infty)$ are the nuclear magnetization at time $t$ after saturation and the equilibrium nuclear magnetization at $t \to \infty$, respectively.
Figure 7.6  (Color online) Representative recovery curves at $p = 0.5$ GPa. Single component behavior is observed even at 25 K, deep in the nematic ordered state.

For $T_1$ measurements in the nematic ordered state, the entire spectrum was irradiated and no attempt was made to resolve the $T_1$ of each peak separately. Under these conditions, one might expect to observe two-component relaxation in the nematic state if the $ab$-plane anisotropy of $1/T_1$ is large. However, all recovery curves were well fit with the single component model above to within experimental error, as shown in Fig. 7.6 for 0.5 GPa. The small $ab$ plane anisotropy of $1/T_1$ in the nematic state is in line with Ref. [164].

Pressure was applied using a hybrid CuBe/NiCrAl piston-cylinder-type high pressure clamp cell [136; 55]. Daphne 7373 was chosen as the pressure transmitting medium. Pressure calibration was accomplished by $^{63}$Cu-NQR in Cu$_2$O [137; 57] at 77 K. In our pressure cell, the sample pressure decreases by $\sim 0.2$ GPa when cooled from room temperature to 100 K, but remains constant below 100 K. The NMR coils inside the pressure cell consisted of $\sim 20$ turns of 40AWG copper wire. The sample and calibration coils were oriented their axes perpendicular to each other to avoid interference between coils.
7.6.2 Ambient Pressure Results

For comparison, we provide our NMR results at ambient pressure, as shown in Fig. 7.7. Our ambient pressure measurements were conducted outside of the pressure cell and without applying any varnish to the sample to ensure no external stresses, since this has been shown to affect the spectrum [172]. The NMR shift of the two split peaks is consistent with Refs. [165; 172].

$K_{avg}$ decreases monotonically with decreasing $T$. We note that no sharp drop of $K_{avg}$ is seen below $T_c$. This indicates no sharp reduction in spin susceptibility in the SC state, suggesting a strong spin-orbit coupling of the $3d$ electrons of iron ions. A similar $T$ dependence of the Knight shift was observed previously [164; 165].
Figure 7.8  (Color online) Upper panel: Coefficient of determination $R^2$ for a single-peak–
model fit of the NMR spectrum as a function of temperature. At high temperature, we find that $R^2$ is nearly independent of temperature (dotted horizontal
line). Deviation from this temperature-independent behavior is observed at low
$T$ due to the appearance of two resolvable peaks in the spectrum (see text).
Vertical dashed lines indicate the bulk $T_s$. Lower panels: Detail of the $R^2$ re-
results above $T_s$ (indicated by vertical lines). Dotted horizontal lines denote an
average of the $R^2$ values between 100 K and 200 K.
The FWHM data for ambient pressure has not been reported previously. It is similar to our data under pressure and shows an upturn below \( T_{\text{FWHM}}^* \sim 200 \text{ K} \) and a peak at \( T_s = 90 \text{ K} \). Below \( T_s \) the low-frequency peak of the spectrum has a greater FWHM, consistent with our results under pressure.

### 7.6.3 Single Lorentzian fit results

In order to objectively determine the temperature at which the transition from two-peak to single-peak behavior occurs, we fit all the spectra to a single-Lorentzian model. As the \( R^2 \) of the single-peak fit is very sensitive to a small asymmetry of the spectrum due to presence of two overlapping peaks of unequal FWHM, one can expect reduction of \( R^2 \) if the observed spectra consist of two peaks. A simple symmetric broadening of a single-peak spectrum would not produce such a decrease of \( R^2 \). Since we kept the S/N ratio of our spin-echo measurements constant, changes in \( R^2 \) can be attributed solely to changes in the shape of the measured spectrum.

As shown in Fig. 7.8, the \( R^2 \) values are nearly independent of temperature at high temperatures. On lowering \( T \), the \( R^2 \) values decrease slightly above the bulk \( T_s \) and exhibit steep decreases below \( T_s \), before increasing again at low \( T \) due to broadening of the spectral lines. At ambient pressure, \( R^2 \) is almost constant just above \( T_s \). Under pressure, however, \( R^2 \) clearly begins to decrease well above the \( T_s \) for 0.5, 1 and 1.5 GPa. At 2 GPa, where a bulk \( T_s \) is no longer observed, \( R^2 \) continues to show a clear decrease at low \( T \). These data justify the use of a two-peak model fit of the spectrum above the bulk \( T_s \). When \( R^2 \) is less than its high-\( T \) average value, we consider the two peaks to be resolved.

### 7.6.4 In-plane anisotropy of spectrum splitting

In the main text, we show FWHM data with the external magnetic field applied in the \( ab \) plane at an angle \( \theta \sim 25^\circ \) from the [110] direction of the tetragonal phase. Fig. 7.9 shows \( \Delta K \) measured at this orientation, along with the \( \theta \sim 0^\circ \) data for 0.5 GPa for comparison. As expected, the absolute magnitude of \( \Delta K \) is drastically reduced. The temperature dependence of \( \Delta K \) is identical
Figure 7.9  NMR spectral splitting $\Delta K$ as a function of $T$ with the external magnetic field applied in the $ab$ plane at an angle $\theta \sim 25^\circ$ from the [110] direction of the tetragonal phase, with the 0.5 GPa data at $\theta \sim 0^\circ$ for comparison.

to the $\theta \sim 0^\circ$ data, however. We still resolve a splitting above $T_s$ and for 2 GPa according to our $R^2$ test. These data illustrate that even if one considers the spectrum at 2 GPa to be a single broad peak, the broadening of the spectrum as a function of $\theta$ decreases exactly in proportion to $\Delta K$. These data strongly support our conclusions of local nematicity, and rule out other possible explanations for the broadening above $T_s$, such as a charge density wave scenario.

7.6.5 Additional Data

Figure 7.10 shows the NMR shift under pressure for the entire range of $K$ values to emphasize that $K$ decreases monotonically when cooled from room temperature. Thus the drastic increase of the FWHM is unexpected within a magnetic broadening scenario.

Figure 7.11 shows the $T$ and $p$ dependence of $^{77}\text{Se}$ spin-lattice relaxation rate $1/T_1T$. For all pressures measured, $1/T_1T$ shows a similar $T$ dependence in which $1/T_1T$ decreases with decreasing $T$ from room temperature to around $T \sim 80$ K then increases, which indicates enhancements of low-energy AFM SFs at low $T$ [176]. The sudden decreases in $1/T_1T$ observed below $T_c$ or $T_N$ indicate
rapid suppression of low-energy SFs in the SC and AFM ordered states, respectively, consistent with previous NMR data [176; 178].

Here $T_c$ and $T_N$ at our NMR measurement field of 7.4 T were determined from the $T$ dependence of the the NMR coil tank circuit resonance frequency $f$, as shown in Fig. 7.12. $f$ is a measure of the ac-susceptibility $\chi_{ac}(\omega_{NMR})$ since $f = 1/2\pi\sqrt{LC}$ and $L = L_0(1 + \chi_{ac})$. The sharp increase at low $T$ is due to the diamagnetism of the SC state, and we use this to extract $T_c(p, H)$. At 1.5 GPa and 2 GPa, we observe an anomaly in $f$, which is attributed to the bulk magnetic state. We use this anomaly to determine $T_N(p)$. With a sweep rate of 1 K/min, we observe a small hysteresis of the magnetic transition, consistent with a first-order transition [178].

Beginning just above $T_N$, we observed a suppression of the NMR signal intensity consistent with Refs. [176; 178]. Given the fact that our observed spectrum is still very sharp ($< 10$ kHz), our signal should be understood as originating from a paramagnetic fraction of the sample which coexists with the magnetic state in the transition region, as seen in Ref. [158]. Therefore, the small decrease of $\Delta K$ observed below $T_N$ in the main text does not indicate that nematic order is suppressed within the magnetic ordered state. At 1 GPa, $T_N$ is not seen in our $\chi_{ac}$ measurement, but we estimate $T_N$ from the onset of the suppression of the NMR signal intensity.
Figure 7.11 $^{77}\text{Se}$ spin-lattice relaxation rate divided by temperature, $1/T_1 T$, for indicated pressures.

Figure 7.12 NMR coil tank circuit resonance frequency $f$ as a function of $T$ for all pressures (see text). Data are offset vertically for clarity.
CHAPTER 8. CORRELATION BETWEEN SUPERCONDUCTIVITY AND MAGNETIC FLUCTUATIONS IN FeSe$_{1-x}$S$_x$ REVEALED BY $^{77}$Se NMR

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P. Wiecki$^1$, K. Rana$^1$, A. E. Böhmer$^{1,2}$, Y. Lee$^1$, S. L. Buď'ko$^1$, P. C. Canfield$^1$, Y. Furukawa$^1$

$^1$The Ames Laboratory, U.S. DOE and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA

$^2$Karlsruhe Institute of Technology, Institut für Festkörperphysik, 76021 Karlsruhe, Germany

8.1 Abstract

We present $^{77}$Se-NMR measurements on FeSe$_{1-x}$S$_x$ samples with sulfur content $x = 0, 9, 15$ and 29%. Twinned nematic domains are observed in the NMR spectrum for all samples except $x = 29\%$. The NMR spin-lattice relaxation rate shows that magnetic fluctuations are initially enhanced between $x = 0\%$ and $x = 9\%$, but are strongly suppressed for higher $x$ values. The observed behavior of the magnetic fluctuations parallels the superconducting transition temperature $T_c$ in these materials, providing strong evidence for the primary importance of magnetic fluctuations for superconductivity, despite the presence of nematic quantum criticality in this system.

8.2 Introduction

Critical fluctuations of an ordered phase found in the proximity to unconventional superconductivity have frequently been discussed as a source of superconducting pairing [179; 180; 181; 182]. In the iron-based superconductors [18; 16], superconductivity (SC) is found in the vicinity of two types of long-range order: the stripe-type antiferromagnetic (AFM) order and the nematic order, which breaks the in-plane rotational symmetry while preserving time reversal symmetry. While
dynamical AFM fluctuations are well known to support SC, experimental and theoretical studies have suggested that nematic fluctuations may also be important for high-$T_c$ SC [183; 184; 185].

In this context, FeSe has emerged as a key material since it undergoes a nematic phase transition from a tetragonal to an orthorhombic structure at $T_s \approx 90$ K and develops superconductivity below $T_c \approx 8.5$ K, but does not display static magnetic ordering [186; 187; 188]. This suggests an opportunity to study the behavior of $T_c$ near a nematic quantum critical point (QCP) isolated from a magnetic QCP. The nematic phase can be suppressed by pressure application, with $T_s$ reaching 32 K at $p = 1.5$ GPa. However, an AFM ordered state emerges above $p = 0.8$ GPa [157; 159] and merges with the nematic state above $p = 1.7$ GPa [158]. Non-monotonic behavior of $T_c$ is seen near the onset of the magnetic order [161], but overall $T_c$ is strongly enhanced up to 37 K at $p = 6$ GPa [189; 190; 191]. While early nuclear magnetic resonance (NMR) measurements connected the enhancement of $T_c$ to enhanced spin fluctuations under pressure [176], the recently revealed complexity of the phase diagram raises new questions. Notably, the role of nematic fluctuations in the superconductivity remains unclear.

The nematic phase can also be suppressed by S substitution in FeSe$_{1-x}$S$_x$ at ambient pressure, with the nematic phase disappearing around $x \approx 17\%$. Importantly, no long-range magnetic order can be observed at ambient pressure, which implies an isolated nematic QCP [192]. $T_c$ initially increases slightly to $T_c \approx 10$ K at $x \approx 10\%$ [193] from $T_c \approx 8.5$ K at $x = 0$, but then decreases, reaching $T_c \approx 5$ K by $x = 29\%$. The application of pressure induces magnetic order in S substituted samples [194; 195].

Recent results have highlighted the rich interplay between magnetic, nematic and superconducting orders in the FeSe$_{1-x}$S$_x$ system. Elastoresistivity measurements found that nematic fluctuations are divergently enhanced near the nematic QCP near $x \approx 17\%$ [192]. The full three-dimensional $T$-$p$-$x$ dependent phase diagram revealed strongly enhanced $T_c$ in regions lacking both nematic and AFM long-range orders [195]. Furthermore, several studies have suggested that $T_c$ does not appear to correlate with nematicity in FeSe$_{1-x}$S$_x$ [192; 195; 196; 197]. On the other hand, no direct measurements of the concentration dependence of magnetic fluctuations have been reported yet.
Since magnetic fluctuations are considered to be one of the key ingredients for the appearance of SC in iron pnictides, it is crucial to reveal how magnetic fluctuations vary with S substitution in FeSe$_{1-x}$S$_x$. NMR is an ideal tool for the microscopic study of low-energy magnetic fluctuations in correlated electron systems. Here, we carried out $^{77}$Se NMR measurements to investigate static and dynamic magnetic properties of FeSe$_{1-x}$S$_x$. Our NMR data clearly show that stripe-type AFM fluctuations are initially slightly enhanced by S doping up to $x \approx 10\%$ from $x = 0$ but are strongly suppressed thereafter, particularly beyond the nematic dome above $x \approx 17\%$. This behavior shows a strong correlation with $T_c$, providing clear evidence for the primary importance of AFM fluctuations over critical nematic fluctuations for SC in the FeSe$_{1-x}$S$_x$ system.

### 8.3 Results

$^{77}$Se NMR measurements have been carried out under a fixed magnetic external field of $H = 7.4089$ T applied either along the $c$ axis or in the $ab$ plane ([110] tetragonal direction). The crystals were grown using chemical vapor transport as outlined in Ref. [170; 198]. The four different S-content crystals used in this study are $x = 0$ ($T_s = 90$ K, $T_c = 8.5$ K), $x = 0.09$ ($T_s = 68$ K, $T_c = 10$ K), $x = 0.15$ ($T_s = 45$ K, $T_c = 8$ K), and $x = 0.25$ ($T_c = 5$ K). Further experimental details are described in the Supplemental Material (SM) [198].

In pure FeSe, the single peak observed in the $H||ab$ NMR spectrum at high $T$ splits into two peaks below $T_s$ due to nematic order, where the two peaks arise from the presence of twinned nematic domains [165; 164; 199]. Representative NMR spectra at $T = 20$ K for both field directions are shown in Fig. 8.1. Splittings of the $H||ab$ spectra below $T_s$ are also observed in FeSe$_{1-x}$S$_x$ except for $x = 29\%$ where only a single peak is observed down to the lowest temperature, consistent with the lack of nematic order seen by resistivity [198].

The $T$ dependence of the NMR shift $K$ for all samples and both $H$ directions is shown in Fig. 8.2. As in pure FeSe, all $K$ values increase monotonically with increasing $T$. $K_{ab}$ is greater than $K_c$ for all samples with almost no $x$ dependence at low $T$. On the other hand, the high temperature value of $K$ shows a large concentration dependence, where $K$ decreases with increasing $x$. 
The inset of Fig. 8.2 shows the $T$ and $x$ dependence of the $H || ab$ spectral splitting $\Delta K$ (the difference of the Knight shifts of the two peaks), which is a measure of the local nematic order parameter [165]. For the pure sample, $\Delta K$ increases sharply below $T_s$ and shows a broad maximum near $\sim 50$ K, as reported previously [165; 169; 199]. In contrast to pure FeSe, $\Delta K$ for $x = 9\%$ and $x = 15\%$ does not exhibit this maximum. While the $\Delta K$ of the $x = 0\%$ and $x = 9\%$ samples show no clear kinks at $T_c$, the $x = 15\%$ sample shows a noticeable drop in the SC state. In the S-doped samples, we could not resolve the splitting all the way up to the bulk $T_s$ identified by resistivity measurements [198], likely due to the broadening of the two individual lines (see Fig. 8.1) by microscopic disorder from dopants and/or small variations in the local S composition. Due to the broad spectra relative to pure FeSe, no clear evidence for the local nematicity above $T_s$, observed in pure FeSe from FWHM measurements [199; 177], could be found.

We now discuss the behavior of the low-energy magnetic fluctuations based the NMR spin-lattice relaxation rate ($1/T_1$) data. $1/T_1 T$ for all samples and both $H$ directions are shown in Fig. 8.3 [200]. In general, $1/T_1 T$ is related to the dynamical magnetic susceptibility as $1/T_1 T \sim \gamma_N^2 k_B \sum_q |A(q)|^2 \chi''(q, \omega_N)/\omega_N$, where $A(q)$ is the wave-vector $q$ dependent form factor and $\chi''(q, \omega_N)$ is the imaginary part of the dynamic susceptibility at the Larmor frequency.
Above $\sim 100$ K, $1/T_1$ shows a similar $T$ dependence as the NMR shift $K(T)$ which measures the uniform susceptibility $\chi(q = 0)$. In contrast, below $\sim 100$ K a strong upturn of $1/T_1$ is observed which is not seen in $K(T)$. The enhancement of $1/T_1$ at low $T$ is therefore attributed to the growth of AFM spin fluctuations with $q \neq 0$. The AFM fluctuations appear below $\sim 100$ K for all samples, but the enhancement of the AFM fluctuations shows a strong $x$ dependence.

In order to characterize the AFM fluctuations, we plotted the ratio of $1/T_1$ for the two field directions, $R \equiv (1/T_1)_ab/(1/T_1)_c = T_{1,c}/T_{1,ab}$. According to previous NMR studies performed on Fe pnictides and related materials [148; 149; 69; 202; 66; 203], $R$ depends on the wavevector of the spin correlations. Assuming isotropic spin correlations, one expects $R = 1.5$ for stripe-type, $R = 0.5$ for Néel-type. As plotted in the inset of Fig. 8.3(b), $R \approx 1$ at high $T$ and increases to $R > 1.5$ starting below $\sim 100$ K. The value of $R$ observed here at low $T$ is consistent with stripe-
Figure 8.3 $T$ dependence of NMR spin-lattice relaxation rate $1/T_1T$ for $H||ab$ (upper panel) and $H||c$ (lower panel) for indicated S concentrations $x$. Arrows denote observed $T_c(H)$ as determined from in situ ac-susceptibility [198] (not shown for $x = 0\%$ $H||ab$). For S-doped samples, missing arrows indicate $T_c(H) < 4.0$ K. Inset: The $T$ dependence of the anisotropy ratio $R = T_{1,c}/T_{1,ab}$ above $T_c$ (see text). Data for $x = 0\%$ ($ab$ plane average $1/T_1T$ and ratio $R$ at $H = 9$ T) are from Ref. [164]. Data for $x = 0\%$ ($H||c$ at $H = 7$ T) are from Ref. [209].

type spin correlations. The $T$ dependence of $R$ is independent of doping $x$ within experimental error, indicating no change in the character of magnetic fluctuations with doping.

To discuss magnetic fluctuations in more detail, it is convenient to isolate the component-resolved hyperfine field (HF) fluctuations from the measured $1/T_1$ data. $1/T_1$ probes the $\mathbf{q}$ sum of fluctuations of HF at $\omega_N$ perpendicular to the applied field according to $(1/T_1)_{H||i} = \gamma_N^2 \sum_{\mathbf{q}} \left[ |H_{j}^{hf}(\mathbf{q},\omega_N)|^2 + |H_{k}^{hf}(\mathbf{q},\omega_N)|^2 \right]$, where $(i,j,k)$ are mutually orthogonal directions and $|H_{j}^{hf}(\mathbf{q},\omega)|^2$ represents the $\mathbf{q}$-dependent power spectral density of the $j$-th component of HF at the nuclear
We have (1/T)\textsubscript{1,\perp} susceptibility according to (1/T\textsubscript{1,\perp}) = 2\gamma\textsubscript{N} \sum_{\mathbf{q}} |H_{\text{c}}^{\text{hf}}(\mathbf{q},\omega_N)|^2 [107]. Note that, for simplicity, we have neglected any ab-plane anisotropy due to nematicity (H_{\text{a}}^{\text{hf}} = H_{\text{b}}^{\text{hf}} \equiv H_{\text{ab}}^{\text{hf}}). Thus defined, 1/T\textsubscript{1,\perp} (1/T\textsubscript{1,\parallel}) directly measures the ab (c) component of HF fluctuations \sum_{\mathbf{q}} |H_{\text{ab}}^{\text{hf}}(\mathbf{q},\omega_N)|^2 (\sum_{\mathbf{q}} |H_{\text{c}}^{\text{hf}}(\mathbf{q},\omega_N)|^2).

In Fermi liquid systems, one expects that 1/T\textsubscript{1} \propto K_{\text{spin}}\textsuperscript{2}. Here K_{\text{spin}} = K - K_0, where K_0 is the T-independent chemical shift. K_{\text{spin}} probes the uniform \mathbf{q} = 0 susceptibility according to K_{\text{spin},i} = A_{ii}\chi_i(0), where A_{ii} is the hyperfine coupling constant. Therefore, to examine the contribution of \mathbf{q} \neq 0 correlations one can compare 1/T\textsubscript{1} to K_{\text{spin}}\textsuperscript{2}. The quantities 1/T\textsubscript{1,\parallel} and 1/T\textsubscript{1,\perp} should be compared to K_{\text{spin},c}\textsuperscript{2} and K_{\text{spin,ab}}\textsuperscript{2}, respectively [107]. The experimentally observed 1/T\textsubscript{1} can then be decomposed into \mathbf{q} = 0 and AFM (\mathbf{q} \neq 0) components as 1/T\textsubscript{1} = (1/T\textsubscript{1})\textsubscript{AFM} + (1/T\textsubscript{1})\textsubscript{q=0}. We have (1/T\textsubscript{1})\textsubscript{q=0} = CK_{\text{spin}}\textsuperscript{2}, where C is a proportionality constant determined empirically from the high T data [198].
Figure 8.5 (a) Band dispersion of pure FeSe in the tetragonal phase, with bands of $d_{xy}$ orbital character indicated. (b) Cross-sections of the Fermi surface in the tetragonal phase at $k_z = 0$ for $x = 0\%$ (red) and $x = 9\%$ (blue). (c) Comparison of AFM fluctuations in pure FeSe under pressure [199] (left panel) and the FeSe$_{1-x}$ system (right panel). Here, the AFM contribution to $1/T_1$ is defined by $(1/T_1)^{AFM} = (1/T_1) - (1/T_1)^0_{q=0}$ using $H_{ab}$ data [188]. Solid lines show $T_N$, $T_c$ determined from resistivity [161; 157; 204; 194], and $T_\alpha$ (orange), $T_N$ (green) and $T_c$ (red) determined from NMR (this work and [199]).
In Fig. 8.4, we compare the angle-resolved pairs of $1/T_1 T$ and $CK_{\text{spin}}^2$. Above $\sim 100$ K, it is clear that $1/T_1 T \approx CK_{\text{spin}}^2$, indicating that the $T_1$ relaxation is being driven primarily by the $q = 0$ component. In contrast, the difference between $1/T_1 T$ and $CK_{\text{spin}}^2$ can be clearly seen below $\sim 100$ K and is attributed to the contribution from the stripe-type AFM fluctuations, $(1/T_1 T)_{\text{AFM}}$. Relative to pure FeSe, spin fluctuations are enhanced at $x = 9\%$, slightly suppressed at $x = 15\%$ and strongly suppressed for $x = 29\%$. The $x$ dependence of the magnetic-fluctuation enhancement closely parallels the $x$ dependence of $T_c$, which shows a slight enhancement between $x = 0\%$ and $x = 9\%$ and is suppressed at higher doping levels. The suppression of magnetic fluctuations for $x \geq 15\%$ is consistent with ARPES data [204].

In all cases, we find that $1/T_{1,||} > 1/T_{1,\perp}$ at low $T$, indicating that $\sum_q |H_{c}^{\text{hf}}(q, \omega_N)|^2$ is greater than $\sum_q |H_{ab}^{\text{hf}}(q, \omega_N)|^2$. The hyperfine field at the Se nuclear site is determined from the magnetic moments on the Fe sites by the hyperfine coupling tensor. Since the stripe-type AFM fluctuations produce the HF fluctuations at the Se site though off-diagonal components of the hyperfine coupling tensor [38; 16], the fact that $|H_{c}^{\text{hf}}|^2$ is greater than $|H_{ab}^{\text{hf}}|^2$ shows that the $ab$-plane polarized stripe-type AFM fluctuations are more developed than the corresponding $c$-axis polarized fluctuations, similar to the BaFe$_2$As$_2$-based superconductors [107].

Within an itinerant picture, the change in the AFM spin correlations with doping would be associated with a change in the nesting condition due to modification of the Fermi surface with S substitution. To understand the band structure of FeSe$_{1-x}$S$_x$, we performed electronic structure calculations [205] using the full-potential linearized augmented plane wave method [206] with a generalized gradient approximation [207]. Here we calculate the band structure for the tetragonal phases in FeSe$_{1-x}$S$_x$ using an FeSe unit cell, adopting chemical pressure effects on the $a$ and $c$ lattice parameters. The calculated band dispersion is shown in Fig. 8.5(a), which is in good agreement with the previous report [196]. The calculated Fermi surface has three hole pockets around the $\Gamma$ point and two electron pockets at the $M$ point along the [110] direction (Fig. 8.5(b)). We find that the size of the smallest of the three hole pockets, originating from the $d_{xy}$ orbital, is increased by S doping. In contrast, the other pockets, originating from $d_{yz}$ and $d_{zx}$ orbitals, do not change. These
results continue to hold for a 1% reduction of the chalcogen height, which also occurs by S doping [195]. Thus the $d_{xy}$ orbital can be considered to play an important role in AFM spin correlations and also in the appearance of SC in FeSe$_{1-x}$S$_x$.

Finally let us comment on the temperature dependence of $1/T_1$ observed in $x = 9\%$ and $x = 15\%$ (see Fig. 8.3). For $x = 0\%$, the maximum of $1/T_1$ has been reported to occur close to $T_c$ [165; 169]. However, for $x = 9\%$ and $x = 15\%$, we find that the maximum of $1/T_1$ instead occurs well above $T_c(H)$ as determined by our in situ ac-susceptibility measurements [198]. At $x = 9\%$, we find $T_c(H||ab) = 7.8$ K and $T_c(H||c) = 5.0$ K, while $1/T_1$ peaks at $\sim 9$ K for both $H$ directions. At $x = 15\%$, we find $T_c(H||ab) = 7.25$ K and $T_c(H||c) \leq 4.0$ K. However, for both $H$ directions, $1/T_1$ peaks at $\sim 12 - 15$ K. These results imply a suppression of magnetic fluctuations just above $T_c$ in the S-doped samples. The effect is more apparent for $H||c$ data. Furthermore, the $T$ difference between $T_c$ and the peak of $1/T_1$ appears to increase with doping. It is interesting to point out that similar behavior has been observed in pure FeSe and discussed in terms of a possible superconducting fluctuation effect [208; 209]. Detailed field-dependent measurements on the S-doped samples will be needed to confirm this scenario.

### 8.4 Conclusions

Our main results are summarized in the phase diagram of Fig. 8.5(c), which shows a contour plot of the AFM contribution to $1/T_1$ as a function of $x$ and $T$. For comparison, a similar plot for pure FeSe under pressure is also shown. In both cases, the bulk nematic order is suppressed. In pure FeSe, the magnetic fluctuations are roughly independent of pressure or slightly enhanced. In contrast, magnetic fluctuations are ultimately strongly suppressed by S doping, after an initial slight enhancement for $x \approx 9\%$. Magnetic fluctuations are strongly correlated with $T_c$ in the FeSe$_{1-x}$S$_x$ system. In contrast, nematic fluctuations are most strongly enhanced near the nematic critical quantum point at $x \approx 17\%$ [192] and show no correlation with $T_c$. These NMR results demonstrate the primary importance of magnetic fluctuations to superconductivity in the FeSe system, and
help to disentangle the roles of magnetic and nematic fluctuations in iron-based superconductors in general.

8.5 Acknowledgements

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8.6 Supplementary Information

8.6.1 Sample growth and characterization

The Fe(Se$_{1-x}$S$_x$) crystals were grown using chemical vapor transport similar to the description in Ref. [170]. Fe, Se and S powder were mixed in a ratio of 1.5:(1-$x_{\text{nom}}$):$x_{\text{nom}}$ and sealed in a quartz ampoule together with a eutectic mix of AlCl$_3$ and KCl. The materials were let to react at 390$^\circ$C for 1-2 days before the ampoules were placed under a temperature gradient and chemical vapor transport was initiated. The sulfur content $x$, which varied from the nominal sulfur content $x_{\text{nom}}$, of several batches (shown as a full symbol in Fig. 8.6) was determined by energy-dispersive x-ray spectroscopy on 3-5 freshly cleaved crystals with an average of 4 different spots per crystal. The error bar indicates one standard deviation. Some early batches in which the initial reaction at 390$^\circ$C was omitted show quite substantial variations in sulfur content. The average lattice parameters of each batch were determined by powder x-ray diffraction in a Rigaku Miniflex diffractometer with Cu Kα radiation. A minority hexagonal phase could sometimes be identified, however, the phase majority always was consistent with the tetragonal P4/nmm space group. The variation of lattice parameters with sulfur content is presented in Fig. 8.6. The results are consistent with findings in Ref. [195]. Furthermore, a linear extrapolation to $x = 1$ yields almost perfectly the lattice parameters of FeS reported in Ref. [210], indicating that Vegard’s law is obeyed for the whole series.
Figure 8.6  Change of $a$- and $c$-axis lattice parameters of FeSe$_{1-x}$S$_x$ with sulfur content $x$ from room-temperature powder diffraction data. For each batch shown as a full symbol, $x$ was determined by energy-dispersive x-ray spectroscopy (EDS). Open symbols have been placed by interpolating both $a$ and $c$ lattice parameters. Literature data from Ref. [195] has been added for comparison.

Figures 8.7 and 8.8 show the phase diagram of Fe(Se$_{1-x}$S$_x$) and the resistance data characterizing the NMR samples, respectively. The phase diagram reflects the variation in $x$ within some of the batches as individual samples of the same batch can exhibit varying $T_s$. To determine the sulfur content of the NMR samples as accurately as possible, we refer to the phase diagram, the EDS results and the average lattice parameters of the respective batches. The structural transition temperature $T_s$ of the samples was determined from resistivity measurements by the midpoint of the step in $dR/dT$ as in Refs. [161; 194]. For the $x = 0.09$ sample, EDS of a selection of samples from the same batch indicates $x = 0.12(2)$. However, the resistance measurement in Fig. 8.8 reveals that $T_s = 68$ K for this sample. Thus, from the phase diagram, the specimen selected for NMR seems to be more accurately described by $x = 0.09$. The four samples with $x \sim 0.15$ show $T_s = 41 - 48$ K in Fig. 8.8, located at $x = 0.15$ in the phase diagram. The interpolation of lattice parameters for the batch yields $x = 0.16$, in good agreement. For the samples with highest sulfur
content, resistivity measurements do not find the signature of the structural phase transition and indicate $T_c \sim 5$ K at zero field. The sulfur content $x = 0.29$ is determined by interpolation of its lattice parameters, since the transition temperature $T_c$ barely varies with $x$ in this range and can therefore not be used as an indicator of sulfur content.

### 8.6.2 Methods

#### 8.6.2.1 NMR experimental details

We conducted $^{77}$Se NMR ($I = 1/2; \gamma / 2\pi = 8.118$ MHz/T) measurements under a fixed external field of $H = 7.4089$ T applied either in the $ab$ plane or along the $c$ axis. The external field in the $ab$-plane was applied along the in-plane [110] tetragonal direction in order resolve the splitting of the NMR spectrum below $T_s$ for $H \parallel ab$. Measurements at $x = 9\%$ were conducted on a single crystal of mass $\sim 2$ mg, with $T_s \sim 68$ K and $T_c \sim 10$ K. However, low NMR signal intensity prevented measurements above $\sim 80$ K. To improve the signal intensity for the $x = 15\%$ measurements, four single crystals of total mass $\sim 10$ mg were each cleaved into 2 to 3 pieces. The samples were co-
Figure 8.8 Electrical resistance of the investigated FeSe$_{1-x}$S$_x$ samples normalized at room temperature. A single sample with $x = 0.09$, 4 samples with $x = 0.15$ and a collection of $\sim 30$ samples with $x = 0.29$ were studied by NMR. For this highest sulfur content, the resistance of two representative samples is shown. For comparison, the resistance of an undoped FeSe single crystal [173] is added. The upper inset shows the temperature derivative which is used to define $T_s$, the lower inset shows the low-temperature resistance on a magnified scale. $T_c$ is defined as the zero-resistance temperature.

aligned by eye based on exterior faces of the crystals and affixed to a glass plate with GE varnish. There was some variation of $T_s$ among this batch of crystals used for NMR measurements due to slight variations in sulfur content, with the average being $T_s = 45 \pm 3$ K, see Figure 8.8. The variation is to be expected because the dependence of $T_s$ on doping is quite steep in this concentration range. All the samples showed $T_c \sim 8$ K at zero field. For the $x = 29\%$ measurements, $\sim 30$ individual single crystals of total mass $\sim 35$ mg were fixed to a glass plate with GE varnish. The $ab$ plane orientation of the $x = 29\%$ samples was not precisely controlled as no nematicity was expected.

The $^{77}$Se NMR spin-lattice relaxation rate $1/T_1$ was measured with a recovery method using a single $\pi/2$ saturation pulse. The $1/T_1$ at each $T$ was determined by fitting the nuclear magnetization $m$ versus time $t$ using the exponential function $1 - m(t)/m(\infty) = \exp(-t/T_1)$, where $m(t)$ and $m(\infty)$ are the nuclear magnetization at time $t$ after the saturation and the equilibrium nuclear
magnetization at $t \to \infty$, respectively. In the nematic state, no attempt was made to resolve the $T_1$ of the two peaks separately. We have measured only the $ab$ plane average $1/T_1$. NMR spectra were measured by FFT of the NMR spin echo.

The superconducting transition temperature $T_c(H)$ at the NMR measurement field ($H = 7.4089$ T) was determined by in situ ac-susceptibility measurements down to $T = 4.0$ K, as shown in Fig 8.9. The stronger suppression of $T_c$ for $H||c$ is consistent with Ref. [193]. No superconductivity was observed above $T = 4.0$ K at $H = 7.4089$ T for $x = 29%$ samples.

### 8.6.2.2 Scaling analysis of $1/T_1T$ and $K_{\text{spin}}^2$

In the main paper we decomposed $1/T_1T = (1/T_1T)_{\text{AFM}} + (1/T_1T)_{q=0}$. The $q = 0$ term will show Korringa behavior

$$
(1/T_1T)_{q=0} = CK_{\text{spin}}^2.
$$

(8.1)
To obtain $K_{\text{spin}} = K - K_0$ one needs the chemical shift $K_0$, which is obtained from a $K$ vs. $\chi$ plot analysis (see below). The proportionality constant in Eq. 8.1 is given by $C = \alpha S^{-1}$, where $S$ is the Korringa constant $S = (\hbar/4\pi k_B) (\gamma_e/\gamma_N)^2$ ($S = 7.23 \times 10^{-6}$ Ks for $^{77}$Se) and the Korringa ratio $\alpha$ parameterizes deviations of $C$ from the theoretical value $S^{-1}$ [107].

The necessary scaling factors $C$ were empirically determined from a plot of $(1/T_1 T)_i$ against $K_{\text{spin},i}^2$ ($i = \perp, ||$) with $T$ as an implicit parameter. The points above $T = 90$ K showed linear behavior, the slope of which determines $C$. Since we measure $K_{\text{spin}}$ in units of $\%$, this analysis determines $C$ in units of $(\%)^{-2}(Ks)^{-1} = 10^4(Ks)^{-1}$, as reported in the main paper. For the $x = 9\%$ sample, we assumed the same values of $C$ and $K_0$ as for $x = 15\%$ since we lack the high-$T$ data due to low signal intensity.

### 8.6.3 Additional data

#### 8.6.3.1 $(1/T_1 T)_{AFM}$ Contour Plot

In the final plot of the main paper, we compared the AFM contribution to $1/T_1 T$ in pressurized and sulfur-doped FeSe. Obviously, we would like to compare the same quantity for both
systems. However, in the case of pressurized FeSe, we lack data for $H \parallel c$ making the full analysis involving $1/T_{1,\parallel}T$ and $1/T_{1,\perp}T$ impossible. We therefore simply used the definition $(1/T_{1}T)_{AFM} \equiv (1/T_{1}T)_{H\parallel ab} - CK_{\text{spin},ab}^{2}$ for the comparison. However, as we describe in the paper, it is preferable to define $(1/T_{1}T)_{AFM} \equiv (1/T_{1}T)_{\parallel} - CK_{\text{spin},c}^{2}$, which consistently compares the susceptibility of the $c$-axis component of the hyperfine field. We include this contour plot here for comparison in Fig 8.10. The plot is qualitatively similar to the one used in the main text and thus the definition of $(1/T_{1}T)_{AFM}$ has no effect on our physical conclusions.

### 8.6.3.2 NMR Shift in FeSe under pressure

Fig. 8.11 shows the NMR shift with $H \parallel ab$ in pure FeSe under pressure. Here, for simplicity, we show the $ab$-plane average $K_{ab} = (K_{a} + K_{b})/2$ in the orthorhombic phase. As in the case of S doping in the main paper, $K_{ab}$ is pressure independent at low $T$, but depends on pressure at high $T$. Here, the high-$T$ value of $K_{ab}$ decreases with increasing pressure, similar to the behavior with increasing S doping.
8.6.3.3 $K$ vs $\chi$ Analysis

We performed a $K$ vs $\chi$ plot analysis to determine the $T$-independent chemical shift $K_0$ and hyperfine coupling constants $A_{ab}$ and $A_c$. In Fig. 8.12, we plot $K$ as a function of $\chi$ with $T$ as an implicit parameter. The $T$ range is chosen so as to avoid low-$T$ upturns of $\chi$ due to magnetic impurities to which NMR, a local probe, is insensitive. For $x = 9\%$, such an analysis is not possible because we lack data over the entire $T$ range due to signal intensity problems at high $T$. In these plots, $K_0$ is the $y$-intercept. The hyperfine coupling constants are determined by the slope. For $x = 0\%$, we obtain $A_{ab} = 3.585$ T/$\mu_B$ and $A_c = 4.37$ T/$\mu_B$. For $x = 15\%$, we obtain $A_{ab} = 3.3$ T/$\mu_B$ and $A_c = 3.56$ T/$\mu_B$. For $x = 29\%$, we obtain $A_{ab} = 2.97$ T/$\mu_B$ and $A_c = 3.7$ T/$\mu_B$. 
Figure 8.12  $K$ vs $\chi$ plot analysis for $x = 0$, $x = 15\%$ and $x = 29\%$. 
CHAPTER 9. CONCLUSIONS

Let us conclude by returning to the questions which motivated this research (§1.7), to assess the progress which has been made. Before our research, the idea that AFM spin fluctuations are involved in the Cooper pairing mechanism was widely acknowledged in the community. However, the role of FM and nematic fluctuations in the superconductivity was still unclear. This thesis has provided additional insights into the role of both FM and nematic correlations in the superconductivity. First of all, in Chs. 4 and 5 we demonstrated that FM spin correlations appear to compete with AFM spin fluctuations, causing a suppression of $T_c$. Thus we were able to explain why SrCo$_2$As$_2$ is not a superconductor (Ch. 4), even though AFM spin fluctuations have been observed in this compound by inelastic neutron scattering measurements. The explanation is that dominant low-energy FM fluctuations, observed via the NMR Korringa ratio, interfere with the AFM-spin-fluctuation-based Cooper pairing mechanism. In Ch. 5, we expanded the analysis to include both the hole- and electron-doped BaFe$_2$As$_2$ compounds. We found, similarly, that superconductivity either had a lower $T_c$ or was extinguished altogether, when the susceptibility for FM fluctuations was large relative to the susceptibility for AFM fluctuations. Therefore, our results show that a competition between FM and AFM fluctuations is a common feature in the Fe-based superconductors, and that this competition plays a role in determining the $T_c$. Secondly, the potential relevance of nematic fluctuations for superconductivity was addressed in Ch. 8 on the FeSe$_{1-x}$S$_x$ system. There, we found that quantum critical nematic fluctuations do not enhance $T_c$, and that, in fact, the doping ($x$) dependence of $T_c$ is nicely explained by the AFM fluctuations alone. Therefore, nematic fluctuations appear to be irrelevant for superconductivity. These two results, that FM correlations compete with AFM fluctuations to suppress $T_c$ and that nematic fluctuations are irrelevant to superconductivity, answer our motivating question and represent significant progress in the field of iron-based superconductivity.
In Ch. 6 on KFe$_2$As$_2$, there were several motivating questions. Before our research, there was known to be a non-monotonic $T_c$ as a function of pressure, with the slope changing at a critical pressure $p^*$. It was suggested that $p^*$ was a transition between superconducting states with different gap structures or even different gap symmetries. Furthermore, this material was shown to have strong electronic correlations and displayed behavior reminiscent of a coherence/incoherence crossover at a temperature $T^*$, suggesting that this material may be understood as a $d$-electron heavy-fermion superconductor. That a material with such strong AFM spin fluctuations had such a low $T_c$ was also a mystery. In Ch. 5, we confirmed the strong AFM fluctuations by NMR, but also found competing strong FM fluctuations in KFe$_2$As$_2$, which could explain the low $T_c$ value. Under pressure in Ch. 6, we found that the $T^*$ increased with increasing pressure. This is exactly what would be expected in the model of KFe$_2$As$_2$ as a $d$-electron heavy-fermion superconductor, since pressure increases the overlap and hybridization between the localized $d_{xy}$ orbitals and the other itinerant bands. Thus our results lend strong additional support to this $d$-electron heavy-fermion picture. Unfortunately, while we did observe the non-monotonic behavior of $T_c$, we did not detect any obvious change of superconducting gap structure above $p^*$. We did, however, observe two-component spin-lattice relaxation in the superconducting state, which suggests a real-space variation of the gap. The nature of the change of the superconducting state at $p^*$ thus remains an open question for future investigations.

In Ch. 7 we addressed our question on the origin of nematic order in iron-based superconductors. In the 122 materials, the nematic phase follows the stripe AFM phase across the phase diagram, suggesting a magnetic origin for nematicity. However, the observation of a nematic phase which appears to compete with the AFM phase in FeSe under pressure has posed a significant obstacle to a unified understanding of the nematic phase in iron-based superconductors. Using NMR, we observed a short-range local nematic order in FeSe under pressure well above the bulk nematic ordering temperature. Furthermore, we found that this short-range nematic order does not compete with AFM fluctuations. In fact, our results suggest that AFM fluctuations are always accompanied by local nematic order. While these results still do not explain the decrease of the bulk nematic
ordered phase with increasing pressure, our results add to a body of evidence suggesting cooperative behavior between nematicity and antiferromagnetism in FeSe, which could provide the basis for a unified understanding of the nematic phase.

Finally, I would like to close by emphasizing that this thesis has demonstrated the advantages of the NMR technique in providing detailed, local information on the properties of materials. We saw, for example, how NMR could be used to measure the polarization direction of both FM and AFM fluctuations (Fig. 5.3). In each project, we saw how the NMR shift can measure the intrinsic magnetic susceptibility $\chi$ even in the presence of paramagnetic impurities, which dominate bulk $\chi$ measurements at low temperatures. Furthermore, due to the local nature of the NMR technique, we could resolve the existence of twinned domains in the nematic phase (Fig. 7.1), which are averaged over in bulk measurements. We could even observe local twinned domains in the tetragonal, paramagnetic phase of FeSe. All of these microscopic insights can be achieved with relatively straightforward experimental equipment, without the need for a nuclear reactor or synchrotron light source.


[45] https://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/nmr1.htm


[70] 1/T₁ at each T was determined by fitting the nuclear magnetization M versus time t using the exponential functions 1−M(t)/M(∞) = 0.1e−t/T₁ +0.9e−6t/T₁ for 75As and 1−M(t)/M(∞) = 0.012e−t/T₁ +0.068e−6t/T₁ +0.206e−15t/T₁ +0.714e−28t/T₁ for 59Co, where M(t) is the nuclear magnetization at time t after saturation and M(∞) is the equilibrium nuclear magnetization at t → ∞.


[106] For the point at $x = 26\%$, we used the data from Ref. [51] with $K_{0,c} = 0.15\%$, and approximated $1/T_{1,||} T \sim (1/T_{1} T)_{H||ab}$ as $(1/T_{1} T)_{H||c}$ data were not available.


[171] See Supplemental Material (§7.6 of this thesis) for the experimental details, the temperature dependence of Knight shift and FWHM at ambient pressure, the temperature and pressure dependence of the coefficient of determination for the single-peak fit, the temperature dependence of NMR spectral splitting with $\theta \sim 25^\circ$ and $0^\circ$ under various pressures, the temperature dependence of $1/T_1/T$, under different pressure, and ac-susceptibility measurements, which includes Refs. [136; 55; 137; 57].


[182] E. Bertel and A. Menzel, Symmetry 2016, 8(6), 45; doi:10.3390/sym8060045


See Supplemental Material (§8.6 of this thesis) for the sample growth and characterization, the experimental details, the scaling analysis of $1/T_1 T$ and $K_{\text{spin}}^2$, the contour plot of $(1/T_1 T)_{\text{AFM}}$ and $K - \chi$ plot analysis.


Here, $(1/T_1 T)_{\|ab}$ is averaged over any $ab$ plane anisotropy due to nematicity [198].


For obtaining self-consistent charge density, we employed muffin-tin radii $R_{MT} = 2.0$ a.u. for Fe and Se, respectively, and $R_{MT}k_{\text{max}} = 8.0$ and which set the maximum $k$ value in the expansion of plane waves. The Se atom position was relaxed until the force on the Se atom was less than 0.1 mRy/a.u. Calculations were iterated, with 4800 $k$-points for whole Brillouin zone, to reach the total energy convergence criterion that was 0.01 mRy/cell. For the Fermi surface calculations, we choose we chose $k_z = 0.0(2\pi/c)$ plane and divide $-2\pi/a \leq k_x, k_x \leq 2\pi/a$ region by 200*220 mesh that resulted in 40401 k-points.


[213] Peter Hirschfeld, Lecture Notes, available at


APPENDIX A. FORM FACTOR CALCULATION FOR KORRINGA RATIO ANALYSIS

In the application of the Korringa ratio to the iron pnictides, the question arises as to the role of the hyperfine form factor, which can, in principle, filter out the AFM fluctuations at the As site. This filtering effect could affect the balance of FM vs. AFM fluctuations as measured by the Korringa ratio [85].

Here, we show how to directly calculate the appropriate form factors for the PM state of the iron pnictides according to the theory of Ref. [201]. We make the assumption that the external applied field is much larger than the hyperfine field, which is certainly true in the PM state. We further assume that the dynamic susceptibility tensor $\chi^{\alpha\beta}(q,\omega_0)$ is diagonal in the PM state. Under these assumptions, the spin-lattice relaxation rate in an external field $h_{\text{ext}}$ is given by

$$\frac{1}{T_1(h_{\text{ext}})} = \lim_{\omega_0 \to 0} \frac{\gamma^2 N k_B T}{2N k_B T} \sum_{\alpha,q} \mathcal{F}_{\alpha}^{h_{\text{ext}}}(q) \frac{\text{Im}[\chi^{\alpha\alpha}(q,\omega_0)]}{\hbar \omega_0},$$

where $\alpha = (a, b, c)$ sums over the crystallographic axes. The general expression for the form factor is

$$\mathcal{F}_{\alpha}^{h_{\text{ext}}}(q) = \sum_{\gamma,\delta} [R_{\text{hext}}^{x\gamma} R_{\text{hext}}^{y\delta} + (x \leftrightarrow y)] A_{q}^{\gamma\alpha} A_{-q}^{\delta\alpha},$$

where $R_{\text{hext}}$ is a matrix which rotates a vector from the crystallographic $(a, b, c)$ coordinate system to a coordinate system $(x, y, z)$ whose $z$-axis is aligned with the total magnetic field at the nuclear site. For details we refer the reader to Ref. [201]. When $h_{\text{ext}} || c$, the two coordinate systems coincide so that

$$R_{h_{\text{ext}} || c} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$
For \( \mathbf{h}_{\text{ext}} \parallel a \), the appropriate matrix is
\[
R_{\mathbf{h}_{\text{ext}} \parallel a} = \begin{pmatrix}
0 & 0 & 1 \\
0 & 1 & 0 \\
-1 & 0 & 0
\end{pmatrix}.
\] (A.4)

For the case of the As site in the iron pnictides, the matrix \( \mathbf{A}_q \) in Eq. A.2 is given by [201]
\[
\mathbf{A}_q = 4 \begin{pmatrix}
A^{aa}c_a c_b & -A^{ab} c_a s_b & i A^{ac} c_a c_b \\
-A^{ba} c_a s_b & A^{bb} c_a c_b & i A^{bc} c_a s_b \\
i A^{ca} c_a s_b & i A^{cb} c_a c_b & A^{cc} c_a c_b
\end{pmatrix},
\] (A.5)

where \( A^{\alpha\beta} \) are the components of the hyperfine coupling tensor and
\[
c_a = \cos \frac{q_a a_0}{2} \quad \quad c_b = \cos \frac{q_b b_0}{2} \\
s_a = \sin \frac{q_a a_0}{2} \quad \quad s_b = \sin \frac{q_b b_0}{2}.
\]
Here \( a_0 \) and \( b_0 \) are lattice constants. Of course, \( a_0 = b_0 \) in the PM state. Combining Eqs. A.2-A.5, we obtain
\[
F_{\mathbf{h}_{\text{ext}} \parallel a} (\mathbf{q}) = 16 (A^{ca} c_a c_b)^2 + 16 (A^{ab} c_a s_b)^2
\] (A.6)
\[
F_{\mathbf{h}_{\text{ext}} \parallel b} (\mathbf{q}) = 16 (A^{cb} c_a c_b)^2 + 16 (A^{bc} c_a s_b)^2
\] (A.7)
\[
F_{\mathbf{h}_{\text{ext}} \parallel c} (\mathbf{q}) = 16 (A^{cc} c_a c_b)^2 + 16 (A^{bc} c_a s_b)^2
\] (A.8)

and
\[
F_{\mathbf{h}_{\text{ext}} \parallel a} (\mathbf{q}) = 16 (A^{aa} c_a c_b)^2 + 16 (A^{ab} c_a s_b)^2
\] (A.9)
\[
F_{\mathbf{h}_{\text{ext}} \parallel b} (\mathbf{q}) = 16 (A^{bb} c_a c_b)^2 + 16 (A^{ab} c_a s_b)^2
\] (A.10)
\[
F_{\mathbf{h}_{\text{ext}} \parallel c} (\mathbf{q}) = 16 (A^{cc} c_a c_b)^2 + 16 (A^{bc} c_a s_b)^2
\] (A.11)

To calculate \( 1/T_1 \) from Eq. A.1, we assume for simplicity that \( \chi^{\alpha\beta}(\mathbf{q}, \omega_0) \) is non-zero only near the wavevectors \( \mathbf{q} = 0, \mathbf{q} = \mathbf{Q}_a \equiv (\pi/a_0, 0) \) and \( \mathbf{q} = \mathbf{Q}_b \equiv (0, \pi/b_0) \). By tetragonal symmetry we have \( a \leftrightarrow b \). In particular, \( \mathbf{Q}_a = \mathbf{Q}_b \equiv \mathbf{Q} \) and \( \text{Im}[\chi^{aa}(\mathbf{q}, \omega_0)] = \text{Im}[\chi^{bb}(\mathbf{q}, \omega_0)] = \chi''_{ab}(\mathbf{q}, \omega_0) \). We also now write \( \text{Im}[\chi^{cc}(\mathbf{q}, \omega_0)] \equiv \chi''_{c}(\mathbf{q}, \omega_0) \). We thus obtain
\[
\frac{1}{T_1 (\mathbf{h}_{\text{ext}} \parallel c)} = \lim_{\omega_0 \to 0} \frac{8 \gamma^2}{N k_B T} \left[ 2 (A^{aa})^2 \chi''_{ab}(\mathbf{0}, \omega_0) \frac{h}{\hbar \omega_0} + 2 (A^{ac})^2 \chi''_{ac}(\mathbf{Q}, \omega_0) \frac{h}{\hbar \omega_0} \right]
\] (A.12)
and

\[
\frac{1}{T_1(h_{\text{ext}}\|a)} = \lim_{\omega_0 \to 0} \frac{8\gamma_N}{N} k_B T \left[ 2(A^{\alpha\alpha})^2 \frac{\chi''_{ab}(Q,\omega_0)}{\hbar\omega_0} + (A^{\alpha\alpha})^2 \frac{\chi''_{ab}(0,\omega_0)}{\hbar\omega_0} \right. \\
+ \left. (A^{cc})^2 \frac{\chi''_c(0,\omega_0)}{\hbar\omega_0} + (A^{ac})^2 \frac{\chi''_c(Q,\omega_0)}{\hbar\omega_0} \right]. \tag{A.13}
\]

We have summed over two AFM wavevectors \( Q = (\pi/a_0,0) \) and \( Q = (0,\pi/a_0) \), which have the same value of \( \chi''(Q,\omega_0) \) in the PM state. Note that this differs from our published paper [102], where we incorrectly included the wavevectors \( Q = (-\pi/a_0,0) \) and \( Q = (0,-\pi/a_0) \) in the sum. These wavevectors are related by reciprocal lattice vectors to \( Q = (\pi/a_0,0) \) and \( Q = (0,\pi/a_0) \) and so shouldn’t be included in a sum over the first Brillouin zone. Notice that, for both field directions, AFM fluctuations at \( q = Q \) are completely filtered out if \( A^{ac} = 0 \), as pointed out in Ref. [16]. However, in the iron pnictides \( A^{ac} \neq 0 \) [38], and therefore AFM fluctuations are not filtered out. From Eqs. A.12 and A.13 we can easily calculate \( 1/T_{1,\|} = 2/T_1(h_{\text{ext}}\|a) - 1/T_1(h_{\text{ext}}\|c) \) and \( 1/T_{1,\perp} = 1/T_1(h_{\text{ext}}\|c) \)

\[
\frac{1}{T_{1,\perp}} = \lim_{\omega_0 \to 0} \frac{16\gamma_N}{N} k_B T \left[ (A^{\alpha\alpha})^2 \frac{\chi''_{ab}(0,\omega_0)}{\hbar\omega_0} + (A^{ac})^2 \frac{\chi''_c(Q,\omega_0)}{\hbar\omega_0} \right] \tag{A.14}
\]

\[
\frac{1}{T_{1,\|}} = \lim_{\omega_0 \to 0} \frac{16\gamma_N}{N} k_B T \left[ 2(A^{\alpha\alpha})^2 \frac{\chi''_{ab}(Q,\omega_0)}{\hbar\omega_0} + (A^{ac})^2 \frac{\chi''_c(0,\omega_0)}{\hbar\omega_0} \right]. \tag{A.15}
\]

Notice that the fluctuations probed by \( 1/T_{1,\|} \) and \( 1/T_{1,\perp} \) are consistent with the qualitative arguments used in Chapter 5.

For the case of BaFe\(_2\)As\(_2\), Ref. [38] gives \( A^{\alpha\alpha} = 0.66 \) \( T/\mu_B \), \( A^{cc} = 0.47 \) \( T/\mu_B \) and \( A^{ac} = 0.43 \) \( T/\mu_B \). \( A^{\alpha\alpha} \) and \( A^{cc} \) are determined by Knight shift measurements and \( A^{ac} \) is found by comparing the measured internal field in the AFM state to the value of the ordered moment obtained by neutron scattering. Therefore, we find that

\[
\frac{1}{T_{1,\perp}} \sim \left[ \left( 0.370 \frac{T^2}{\mu_B^2} \right) \frac{\chi''_{ab}(0,\omega_0)}{\hbar\omega_0} + \left( 0.221 \frac{T^2}{\mu_B^2} \right) \frac{\chi''_c(0,\omega_0)}{\hbar\omega_0} \right]. \tag{A.16}
\]

\[
\frac{1}{T_{1,\|}} \sim \left[ \left( 0.436 \frac{T^2}{\mu_B^2} \right) \frac{\chi''_{ab}(0,\omega_0)}{\hbar\omega_0} + \left( 0.185 \frac{T^2}{\mu_B^2} \right) \frac{\chi''_c(Q,\omega_0)}{\hbar\omega_0} \right]. \tag{A.17}
\]
For $\alpha_\perp$, it is clear that the form factor favors the FM fluctuations by a factor of 2.36. Thus, this analysis neatly explains why $\alpha_\perp$ seems to be more sensitive to FM fluctuations than $\alpha_\parallel$. (Recall, in Chapter 5, we always observed $\alpha_\perp < \alpha_\parallel$.) Furthermore, since we observed $\alpha_\perp \approx 0.3$ (favoring FM fluctuations by a factor of 3.33) at high temperature in the BaFe$_2$As$_2$ system, this suggests that $\chi''_{ab}(0, \omega_0) \approx \chi''_c(Q, \omega_0)$ at high temperature in this system. That is, the susceptibility for $ab$-plane polarized FM fluctuations is similar to the susceptibility for $c$-axis polarized stripe-type AFM fluctuations.

In the case of CaFe$_2$As$_2$, Ref. [211] gives $A^{aa} = 1.8 T/\mu_B$, $A^{cc} = 1.2 T/\mu_B$ and $A^{ca} = A^{ac} = 0.82 T/\mu_B$. Therefore, we find that

$$\frac{1}{T_{1,\perp}} \sim \left[ \left( \frac{3.24 T^2}{\mu_B^2} \right) \chi''_{ab}(0, \omega_0) \frac{h}{\hbar \omega_0} + \left( \frac{0.67 T^2}{\mu_B^2} \right) \chi''_c(Q, \omega_0) \frac{h}{\hbar \omega_0} \right]$$  (A.18)

$$\frac{1}{T_{1,\parallel}} \sim \left[ \left( \frac{1.34 T^2}{\mu_B^2} \right) \chi''_{ab}(Q, \omega_0) \frac{h}{\hbar \omega_0} + \left( \frac{1.44 T^2}{\mu_B^2} \right) \chi''_c(0, \omega_0) \frac{h}{\hbar \omega_0} \right]$$  (A.19)

For $\alpha_\perp$, it is clear that the form factor favors the FM fluctuations by a factor of 4.84. Since we observed $\alpha_\perp \approx 0.2$ (favoring FM fluctuations by a factor of 5) at high temperature in the CaFe$_2$As$_2$ system [102], this suggests that $\chi''_{ab}(0, \omega_0) \approx \chi''_c(Q, \omega_0)$ at high temperature in this system also.
APPENDIX B. CALCULATION OF $1/T_1$ IN THE SUPERCONDUCTING STATE

B.1 Introduction

The NMR/NQR spin lattice relaxation rate in the superconducting state is a sensitive probe of the reduction of the density of states (DOS) at the Fermi energy due to the superconducting energy gap. In general, $1/T_1$ in the SC state is given by [50]

$$\frac{1}{T_1} \sim \int_0^\infty \left[ N_s^2(E) + M_s^2(E) \right] f(E)(1 - f(E))dE,$$

where $N_s(E)$ is the DOS and $f(E)$ is the Fermi distribution function. $M_s(E)$ is the anomalous DOS arising from Cooper pair coherence. Within the BCS theory, $N_s(E)$ and $M_s(E)$ are given by

$$N_s(E) = \begin{cases} \frac{|E|}{\sqrt{E^2 - \Delta^2}} & |E| > \Delta \\ 0 & |E| < \Delta \end{cases} \tag{B.2}$$

$$M_s(E) = \begin{cases} \frac{\Delta}{\sqrt{E^2 - \Delta^2}} & |E| > \Delta \\ 0 & |E| < \Delta \end{cases} \tag{B.3}$$

Note that these expressions are singular at $E = \Delta$. This divergence is regulated by assuming a mild anisotropy of the gap magnitude $\Delta$ in reciprocal space [50; 212]. The variation of $\Delta$ over the Fermi surface is parameterized by replacing $\Delta$ by $\Delta(1 + a)$ and integrating over a distribution $P(a)$ with mean value $\langle a \rangle = 0$.

Thus, we have

$$N_s(E) = \text{Re} \int \frac{|E|P(a)da}{\sqrt{E^2 - (\Delta(1 + a))^2}} \tag{B.4}$$

$$M_s(E) = \text{Re} \int \frac{\Delta(1 + a)P(a)da}{\sqrt{E^2 - (\Delta(1 + a))^2}} \tag{B.5}$$
Here, the Fermi energy is defined as zero ($E_F \equiv 0$). The integrals in Eqs. B.4 and B.5 have been integrated numerically using $\Delta = 2$ and $\sigma_a = \sqrt{\langle a^2 \rangle} = 0.05$ for a Gaussian distribution $P(a)$ (illustrated in Fig. B.2).

These DOS functions, evaluated numerically, are illustrated in Fig. B.1.

To obtain analytical results for $N_s(E)$ and $M_s(E)$ one can use a simpler form of $P(a)$

$$P_n(a) = \begin{cases} 
0 & \text{a < } -1/n \\
 n^2a + n & -1/n < a < 0 \\
 -n^2a + n & 0 < a < 1/n \\
 0 & a > 1/n 
\end{cases}. \quad (B.6)$$

This is illustrated in Fig. B.2. The parameter $n$ determines the width of the distribution, with $P_n(a)$ tending to a delta function in the limit $n \to \infty$. The integrals in Eqs. B.4 and B.5 can then be evaluated. Here, I simply quote my result.

$$N_s(E, n, \Delta) = n^2|E| [I_1(|E|, n, \Delta) - I_2(|E|, n, \Delta)] + n|E|I_3(|E|, n, \Delta) \quad (B.7)$$

$$M_s(E, n, \Delta) = n\Delta [(1 + n)I_1(|E|, n, \Delta) + (1 - n)I_2(|E|, n, \Delta) + I_3(|E|, n, \Delta)$$

$$-nI_4(|E|, n, \Delta) + nI_5(|E|, n, \Delta)] \quad (B.8)$$
Figure B.2 Gaussian and simplified (Eq. B.6) broadening functions. For the Gaussian, \( \sigma_a = 0.05 \) and we plot \( P_{10}(a) \) for the simplified form.

where

\[
I_1(e,n,\Delta) = \begin{cases} 
0 & e < \Delta \left(1 - \frac{1}{n}\right) \\
g_2 + \sin^{-1} \left( \frac{\Delta \left(1 - \frac{1}{n}\right)}{e} \right) - \frac{\pi}{2} & \Delta \left(1 - \frac{1}{n}\right) < e < \Delta \\
-g_3 + g_2 - \sin^{-1} \left( \frac{\Delta \left(1 - \frac{1}{n}\right)}{e} \right) + \sin^{-1} \left( \frac{\Delta \left(1 + \frac{1}{n}\right)}{e} \right) & e > \Delta 
\end{cases} \tag{B.9}
\]

\[
I_2(e,n,\Delta) = \begin{cases} 
0 & e < \Delta \\
g_3 + \sin^{-1} \left( \frac{\Delta \left(1 + \frac{1}{n}\right)}{e} \right) - \frac{\pi}{2} & \Delta < e < \Delta \left(\frac{1}{n} + 1\right) \\
g_3 - g_4 + \sin^{-1} \left( \frac{\Delta \left(1 + \frac{1}{n}\right)}{e} \right) - \sin^{-1} \left( \frac{\Delta \left(1 - \frac{1}{n}\right)}{e} \right) & e > \Delta \left(\frac{1}{n} + 1\right) 
\end{cases} \tag{B.10}
\]

\[
I_3(e,n,\Delta) = \begin{cases} 
0 & e \leq \Delta \left(1 - \frac{1}{n}\right) \\
\frac{\frac{\pi}{2} - \sin^{-1} \left( \frac{\Delta \left(1 - \frac{1}{n}\right)}{e} \right)}{\Delta} & \Delta \left(1 - \frac{1}{n}\right) \leq e \leq \Delta \left(\frac{1}{n} + 1\right) \\
\sin^{-1} \left( \frac{\Delta \left(1 + \frac{1}{n}\right)}{e} \right) - \sin^{-1} \left( \frac{\Delta \left(1 - \frac{1}{n}\right)}{e} \right) & e \geq \Delta \left(\frac{1}{n} + 1\right) 
\end{cases} \tag{B.11}
\]
Figure B.3  Superconducting density of states functions \( N_s(E) \) (left) and \( M_s(E) \) (right). Here, the Fermi energy is defined as zero \( (E_F \equiv 0) \). The integrals in Eqs. B.4 and B.5 have been integrated analytically using \( \Delta = 2 \) and \( n = 10 \) for \( P(a) \) given by Eq. B.6.

\[
I_4(e, n, \Delta) = \begin{cases} 
0 & e < \Delta \\
\frac{\frac{3}{2}g_1 - \frac{3}{2}g_3 - \frac{1}{2}g_1 \sin^{-1}\left(\frac{\Delta}{e}\right)}{\Delta} - \frac{3}{2}g_1 - \frac{1}{2}g_1 \sin^{-1}\left(\frac{\Delta}{e}\right) + (\frac{3}{2} - \frac{3}{2}g_1 - 1)g_4 + \frac{1}{2}g_1 \sin^{-1}\left(\frac{\Delta + 1}{e}\right)}{\Delta} & \Delta < e < \Delta \left(\frac{1}{n} + 1\right) \\
& e > \Delta \left(\frac{1}{n} + 1\right)
\end{cases}
\]

\[
I_5(e, n, \Delta) = \begin{cases} 
0 & e < \Delta \left(1 - \frac{1}{n}\right) \\
\frac{\frac{3}{2}g_1 + \frac{1}{2}g_1 \sin^{-1}\left(\frac{\Delta}{e}\right) + (\frac{3}{2} - \frac{3}{2}g_1 + 1)(-g_2) - \frac{1}{2}g_1 \sin^{-1}\left(\frac{\Delta + 1}{e}\right)}{\Delta} & \Delta \left(1 - \frac{1}{n}\right) < e < \Delta \\
& e > \Delta
\end{cases}
\]

where \( g_1 = \left(\frac{e^2}{\Delta^2} + 2\right) \), \( g_2 = \sqrt{\frac{e^2}{\Delta^2} - \left(1 - \frac{1}{n}\right)^2} \), \( g_3 = \sqrt{\frac{e^2}{\Delta^2} - 1} \) and \( g_4 = \sqrt{\frac{e^2}{\Delta^2} - \left(\frac{1}{n} + 1\right)^2} \). The results of these analytical expressions for \( N_s(E) \) and \( M_s(E) \) are shown in Fig. B.3 for \( n = 10 \).
Figure B.4  Superconducting gap as a function of temperature for Aluminum ($T_c = 1.2$ K). The value of the maximum gap shown is the best fit value of $\Delta_0 = 0.165$ meV, for which $2\Delta_0 = 3.2k_BT_c$, which differs slightly from the BCS prediction [50; 212].

### B.2 Application to Aluminum

We can now use the above expressions to calculate the temperature dependence of $1/T_1$ in superconducting Aluminum ($T_c \approx 1.2$ K). The expression is (see B.1)

$$\frac{1}{T_1} = A \int_0^\infty \left[ N_s(E, n, \Delta(T)) + M_s(E, n, \Delta(T)) \right] \frac{e^{\frac{E}{k_BT}}}{(e^{\frac{E}{k_BT}} + 1)^2} dE,$$  \hspace{1cm} (B.14)

where $N_s$ and $M_s$ are given by Eqs. B.7, B.8 and $k_B = 0.08617$ meV/K is the Boltzmann constant. For the temperature dependence of the gap, we use a simple approximate form [213]

$$\Delta(T) = \begin{cases} 
0 & T > T_c \\
\Delta_0 \tanh \left( \frac{\pi}{\Delta_0 k_BT_c} \sqrt{\frac{2}{3}\left(1.426\frac{T_c}{T}\right)^2 - 1} \right) & T < T_c 
\end{cases}.$$

(B.15)

The temperature dependence of $\Delta(T)$ is illustrated in Fig. B.4. In the BCS theory $\Delta_0 = 1.764k_BT_c$. There is also a discontinuous jump in the specific heat across $T_c$, given by $\Delta C_v/\gamma_nT_c = 1.426$, where $\gamma_n$ is the normal state Sommerfeld coefficient [214]. The integral in Eq. B.14 is evaluated numerically from the analytical expressions for $N_s$ and $M_s$. 


Figure B.5  Temperature dependence of $1/T_1$ in the superconducting state of Aluminum. The experimental data points are from [212]. The parameters in Eq. B.14 are $A = 35$, $n = 10$, $T_c = 1.2$ K and $\Delta_0 = 0.165$ meV. The integral is evaluated numerically from analytical expressions for $N_s$ and $M_s$ (Eqs. B.7, B.8).

The calculated temperature dependence of $1/T_1$ is shown in Fig. B.5. For Aluminum, the best fit is obtained with the gap anisotropy parameter $n = 10$ and the proportionality constant $A = 35$, which is a material-dependent measure of the normal-state DOS. There is a peak just below $T_c$, known as the Hebel-Slichter coherence peak [215]. The height of the peak cannot be reproduced without the $M_s(E)$ “coherence” term. I performed a similar calculation for the Hebel-Slichter peak observed in CaPd$_2$As$_2$ [203].

B.3 Application to KFe$_2$As$_2$

The compound KFe$_2$As$_2$ may have a nodal superconducting gap structure [110], in contrast to the full-gap BCS model discussed in the previous section. To model a nodal gap structure, let us assume a $d$-wave type symmetry such that the gap in $k$-space is given by $\Delta_k = \Delta \cos(2\phi)$, where $\phi$ is the polar angle in $k$-space. In this case, the density of states is given by [216]

$$N_s(E) = \int \frac{d\Omega}{4\pi} \frac{E}{\sqrt{E^2 - \Delta_k^2}} = \int_0^{2\pi} \frac{E d\phi}{2\pi \sqrt{E^2 - \Delta^2 \cos^2(2\phi)}}.$$  \hspace{1cm} (B.16)
This integral can be evaluated to obtain

\[
N_s(E, \Delta) = \begin{cases} 
   E \left( K\left( \frac{\Delta^2}{E^2} \right) + \frac{K\left( \frac{E^2}{\Delta^2 - 1} \right)}{\sqrt{1 - \frac{E^2}{\Delta^2}}} \right) \pi \Delta, & E \leq \Delta, \\
   K\left( \frac{\Delta^2}{E^2} \right) + \frac{K\left( \frac{E^2}{\Delta^2 - 1} \right)}{\sqrt{1 - \frac{E^2}{\Delta^2}}} \pi, & E > \Delta
\end{cases}
\]  

(B.17)

where \( K(m) \) is the complete elliptic integral of the first kind. The result is shown in Fig. B.6. Note the clear difference between this and the full gap structure of Fig. B.1.

The compound KFe\(_2\)As\(_2\) shows no coherence peak below \( T_c \). Therefore, to model the behavior of \( 1/T_1 \), we simply neglect the BCS coherence term \( M_s(E) \). KFe\(_2\)As\(_2\) also has different values of the gap \( \Delta \) on different Fermi surface sheets. In this case, the expression for \( 1/T_1 \) is instead

\[
\frac{1}{T_1} = A \sum_{i=1,2} f_i^2 \int_0^\infty N_{s,i}^2(E, \Delta_i(T)) \frac{e^{E/k_BT}}{e^{E/k_BT} + 1} dE,
\]  

(B.18)
Figure B.7  Left: Total two-nodal gap density of states in a model for KFe$_2$As$_2$. Right: Temperature dependence of $1/T_1$ assuming the density of states on the left. Data from Ref. [110]. The parameters in Eq. B.18 are $A = 140$, $\Delta_1 = 0.602$ meV, $\Delta_2 = 0.07$ meV, $f_1 = 0.45$, $f_2 = 0.55$ and $T_c = 3.5$ K.

where $N_s(E, \Delta)$ is given by Eq. B.17 and $f_i$ is the fraction of the total density of states attributed to gap $\Delta_i$ ($f_1 + f_2 = 1$). The integral can again be evaluated numerically to extract the temperature dependence of $1/T_1$, as shown in Fig. B.7. For comparison, I have also evaluated Eq. B.18 using the analytical full-gap density of states (Eq. B.7) with $n = 5$ and all other parameters the same. This is shown in Fig. B.8.

Since there are two gaps, it is interesting to see the temperature dependence of each gap individually. This is shown in Fig. B.9.
Figure B.8  Left: Total two-full gap (broadening parameter $n = 5$ in Eq. B.7) density of states in a model for KFe$_2$As$_2$. Right: Temperature dependence of $1/T_1$ assuming the density of states on the left. The other parameters are the same as in Fig. B.7.

Figure B.9  Left: A single nodal gap with $\Delta_1 = 0.602$ meV ($f_1 = 1$, $f_2 = 0$, $A = 70$). Right: A single nodal gap with $\Delta_2 = 0.07$ meV ($f_1 = 0$, $f_2 = 1$, $A = 70$).
APPENDIX C.  FeSe ADDITIONAL RESULTS

In this Appendix, we briefly provide additional evidence that the broadening of the NMR spectrum above $T_s$ in FeSe under pressure is due to local nematic order, as discussed in Ch. 7.

In Fig. 7.1, the NMR spectrum is a single, broad peak for 2 GPa. Yet in Fig. 7.3, we report a non-zero splitting of the spectrum $\Delta K$ at 2 GPa. How do we know that the spectrum at 2 GPa consists of unresolved split peaks? One way to see this is to continue the single-peak fit below $T_s$ (even though two resolved peaks are present), and examine the behavior of the FWHM over the entire temperature range. This is shown in Fig. C.1. In this figure, the splitting of the NMR spectrum below $T_s$ shows up simply as additional broadening of the spectrum. This method, therefore, treats splitting and broadening on equal footing. One can see the clear resemblance to Fig. 7.3. Also shown in Fig. C.1 is the same quantity measured with the crystal rotated by $\theta = 25^\circ$ away from the tetragonal [110] direction within the $ab$ plane, as we did in Fig. 7.2. One can clearly see that the FWHM of the spectrum at 2 GPa is reduced by a similar factor as the rest. To confirm this, Fig. C.1 shows the same data with the vertical axes for $\theta = 0^\circ$ and $\theta = 25^\circ$ scaled by a constant factor.

The important point is that the FWHM of the single peak observed at 2 GPa in Fig. 7.1, scales precisely with the measurable splitting $\Delta K$ for the other pressures, as the crystal is rotated. This clearly shows that the broadening of the spectrum above $T_s$ has the same origin as the splitting below $T_s$, as stated in Ch. 7.
Figure C.1  The FWHM of a single-Lorentzian fit to the NMR spectrum with $H_{\|}[110]$ tetragonal (filled symbols) and with the crystal rotated by $\theta = 25^\circ$ away from $H_{\|}[110]$ tetragonal within the $ab$ plane. The arrow denotes $T_{\text{FWHM}}^*$, which is essentially pressure independent.

Figure C.2  Same as Fig. C.1, but with the vertical axes for $\theta = 0^\circ$ and $\theta = 25^\circ$ scaled by a constant factor (1.78).