RICE UNIVERSITY

Neutron scattering studies of doped iron pnictides

by

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A THESISSubmitted
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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Houston, Texas
January, 2019
ABSTRACT

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Unraveling the mechanism of unconventional superconductivity is one of the long-sought crown jewels in condensed matter physics. Outstanding among many of the challenges is the critical importance of electron-electron interactions, which gives rise to new emergent collective electronic orders, including magnetism, electronic nematic order, and superconductivity. These degrees of freedom are closely intertwined in iron-based superconductors. The interplay between these orders, can be unraveled by studying their co-evolution across phase diagrams, which nature conveniently grants us access through chemical substitution. Such an understanding provides the foundation for a description that unifies these different orders as different flavors of the same electrons, and sets the stage for future applications of these fascination materials.

Within this thesis I present several neutron scattering works on prototypical iron-based superconductors, derived from BaFe$_2$As$_2$ and NaFeAs. Neutron scattering directly probes the magnetic correlations of atoms, and it also allows for the measurement of the structural properties that directly couple to the electronic nematic order. Complemented by physical property measurements that directly probe superconductivity, this enables us to carry out a comprehensive survey of how these entangled orders behave across the temperature and doping phase diagram.

In Ni doped NaFeAs, we found both nematic and magnetic orders compete with
superconductivity, demonstrating an intricate balance between the different orders that results from the fact they are different manifestations of the same electrons. At high temperature or high doping-levels, where these orders were assumed to be absent, using high-resolution neutron diffraction and neutron Larmor diffraction techniques we uncovered local orthorhombic distortions, indicating electronic nematic order persists on a local length scale, over a much large region of the phase diagram than previous thought. Our observation of these unexpected local orthorhombic distortions demonstrate fluctuations of the electronic nematic order that are maximized near a putative quantum critical point, when coupled with random strain fields, result in locally pinned electronic nematic states, from which global superconductivity precipitates.

In a similar vein, locally-broken fourfold rotational symmetry is also observed in heavily Cu-doped Ba(Fe\(_{1-x}\)Cu\(_x\))\(_2\)As\(_2\). Combining transport, magnetic susceptibility, elastic and inelastic neutron scattering measurements, we identified for the first time the existence of short-range magnetic order over a large doping range beyond the putative quantum critical point. This discovery reveals while the system on average is tetragonal and exhibit four-fold rotational symmetry, small patches can exhibit locally broken fourfold symmetry, giving rise to magnetic order. Our findings point to an inherent tendency towards the lowering of crystallographic symmetry, on a local scale if not globally, providing the backdrop from which superconductivity emerges.

Our neutron scattering results on partially detwinned NaFe\(_{0.985}\)Co\(_{0.015}\)As show that neutron spin resonance in this system only appears at the antiferromagnetic wave vector. Combined with electronic band analysis, our results indicate that the neutron spin resonances in NaFe\(_{0.985}\)Co\(_{0.015}\)As arise mostly from quasiparticle excitations between the hole and electron Fermi surfaces with the \(d_{yz}\) orbital character. Our analysis suggests that intraorbital quasiparticle scattering of the \(d_{yz}-d_{yz}\) orbitals are important for superconductivity.

The combination of these works provides a significant advance in the understand-
ing of the interplay between electronic nematic order, magnetism and unconventional superconductivity in iron-based superconductors, underscores the physics at the local scale which is critical for potential applications, and motivates future studies to examine the intricate interplay of complex orders at the local scale.
Acknowledgments

Firstly I would like to express my sincere gratitude to my advisor Dr. Pengcheng Dai for his patience, support and trust during my PhD journey. His hardworking and passionate attitudes towards science problems always inspire me.

The Dai group has been a source of friendships and collaborations. I would like to thank former group members who taught me many lessons in both science and life, Dr. Chenglin Zhang, Dr. Xingye Lu, Dr. Scott Carr, Dr. Yu Song, Dr. Yu Li and Dr. Haoran Man. I would like to acknowledge current group members, David Tam, Rui Zhang, Dr. Ding Hu, Dr. Bin Gao, Tong Chen, Lebing Chen and Yaofeng Xie. The thesis would not have been possible without their continuous support. I am thankful to all undergraduate students that I have had the pleasure to work with or alongside of, Chao Zhou, Zongyuan Zhang, Mengke Liu, Zhuang Xu, Xiaokun Teng, Haoyu Liu, and Hao Li. I am grateful to visiting scholars in our lab, with whom I had many valuable discussions and collaborations, Jiangang Guo, Chongde Cao, Li Zhang and Jae-Ho Chung.

I would like to thank all the neutron scattering instrument scientists I have worked with in this thesis work, from whom I learned not only ways to perform neutron scattering experiments but rigorous and enthusiastic attitudes as well, Dr. Kuo-Feng Tseng, Dr. Thomas Keller, Dr. Leland Harriger, Dr. Songxue Chi, Dr. Wei Tian, Dr. Huibo Cao, Dr. Russell Ewing, Dr. Jitae Park and Dr. Alexandre Ivanov. I would like to thank my theory collaborators, Dr. Andriy Nevidomskyy, Dr. Rong Yu and Dr. Zhiping Yin.

I would like to thank my committee members for providing guidance and advice in the completion of my degree, Dr. Pengcheng Dai, Dr. Emilia Morosan, Dr. Junichiro Kono, Dr. Randall Hulet and Dr. Eugene Levy.

Lastly, I would like to thank my family and friends for all their love and support.
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Chapter 1

Neutron Scattering Techniques

In this chapter, I first introduce basic neutron scattering formalisms and discuss experimentally commonly used results and approximations. Then, I introduce two types of neutron scattering instruments which are relevant for the present thesis work. More detailed formalisms and instrument introductions can be found in several books [1, 2, 3]. Commonly seen neutron scattering background signals are discussed in appendix.

1.1 General Introduction to Neutron Scattering

Neutron is a subatomic particle with no charge and spin $\frac{1}{2}$. Since neutron has zero net charge and its electric dipole moment is either zero or too small to be measured by the most sensitive modern techniques, the interaction between neutron and electron cloud in matter is negligible and neutron can penetrate deeply into the target.

Neutrons interact with atoms via nuclear forces and with magnetic fields from unpaired electrons via magnetic dipole interactions. The neutrons used for scattering experiments are thermal neutrons produced by a reactor or an accelerator source. The wavelength of such neutrons is of the same order of magnitude as the interatomic distances in solids. Thus thermal neutrons offer an ideal probe for determining atomic structure and magnetic structure of crystals. Moreover, the energy of thermal neutrons is of the same order of magnitude as that of many excitations in condensed
matter (phonon, magnon, crystalline electric fields, etc.), which makes neutron as one of the best methods to study these excitations.

We denote $\mathbf{k}_i$ and $\mathbf{k}_f$ as incident and scattered neutron wavevectors and $E_i$ and $E_f$ as corresponding neutron energies. The momentum and energy transfer from neutron to the target follows equation (1.1) and (1.2) with $m$ as neutron mass.

$$\hbar \mathbf{Q} = \hbar (\mathbf{k}_i - \mathbf{k}_f)$$  \hspace{1cm} (1.1)

$$E = \hbar \omega = \frac{\hbar^2}{2m}(k_i^2 - k_f^2)$$  \hspace{1cm} (1.2)

In neutron scattering experiments, we manipulate the wavevectors and energies of incident and scattered neutrons and probe the neutron scattering cross-sections of the object at specific momentum and energy transfer.

### 1.2 Nuclear Elastic and Inelastic Scattering

The partial differential cross-sections for nuclear scattering is given by (1.3).

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i} \frac{1}{2\pi\hbar} \sum_{j,j'} b_j b_{j'} \int_{-\infty}^{\infty} \langle e^{-i\mathbf{Q} \cdot \hat{R}_j(0)} e^{i\mathbf{Q} \cdot \hat{R}_j(t)} \rangle e^{-i\omega t} dt$$  \hspace{1cm} (1.3)

$k_f$ and $k_i$ are the magnitude of scattered and incident neutron wavevectors $\mathbf{k}_f$ and $\mathbf{k}_i$. $b_j$ is the neutron scattering length for the atomic nucleus $j$. $\hat{R}_j(t)$ is time-dependent Heisenberg operator and describes the position of the atomic nucleus $j$ at time $t$.

In elastic nuclear scattering where $\hbar \omega = 0$ and $k_f = k_i$, (1.4) and (1.6) can be derived from (1.3) to describe the coherent and incoherent elastic neutron cross-section.

$$(\frac{d\sigma}{d\Omega})_{coh} = N_0 \frac{(2\pi)^3}{v_0} e^{-2W(Q)} \sum_{\tau} |S_{\tau}|^2 \delta(Q - \tau)$$  \hspace{1cm} (1.4)
where $N_0$ denotes the unit cell number of the system and $v_0$ is the unit cell volume in real space. $e^{-2W(Q)}$ is the Debye-Waller factor, which describes the mean-squared displacements of the atoms from their equilibrium positions. The Debye-Waller factor is close to unity at low temperatures. $S_\tau$ is the so-called structure factor, and it is determined by atomic nucleus neutron scattering length and relative positions of atoms within one unit cell following (1.5).

$$S_\tau = \sum_d b_d e^{i\tau \cdot d}$$ (1.5)

Elastic neutron scattering provides a handy way to determine the crystal structure. By examining the momentum transfer $Q$ at which Bragg reflections occur and analyzing the intensities of the Bragg reflections, one can determine the structure factor $S_\tau$ and further get the information on the locations of the atoms within the unit cell.

$$\left(\frac{d\sigma}{d\Omega}\right)_{inc} = N(<b^2> - <b>^2)$$ (1.6)

$N$ is the total atom number of the system. Incoherent scattering arises from the random distribution of the deviations of the scattering lengths from their mean value. More specifically, it arises from (i) nucleus-neutron system having different combined spin, (ii) multiple isotopes of the same element existing in the scattering system. The incoherent elastic scattering is isotropic and yields a constant background.

Coherent one-phonon neutron scattering cross-section can also be derived from (1.1) and be described with formula (1.7).
\[
\frac{d^2\sigma}{d\Omega d\omega} = \frac{4\pi^3}{v_0} \cdot \frac{k_f}{k_i} \sum_{s,q} \frac{1}{\omega_s(q)} \left| \sum_d \frac{b_d}{\sqrt{M_d}} e^{-W_d(Q)} e^{iQ \cdot d} (Q \cdot e_{d,s}(q)) \right|^2 \\
\times \left[ (n_s(q) + 1)\delta(\omega - \omega_s(q)) \sum_\tau \delta(Q - q - \tau) \\
+ n_s(q)\delta(\omega + \omega_s(q)) \sum_\tau \delta(Q + q - \tau) \right]
\]  
\text{(1.7)}

where

\[
n_s(\omega) = (e^{\frac{\hbar \omega_s(q)}{k_B T}} - 1)^{-1}
\]  
\text{(1.8)}

$M_d$ is the atomic mass and $\omega_s(q)$ and $e_{d,s}(q)$ are the eigenvalue and eigenvector for the phonon mode with polarization index $s$ of atom $d$.

$n((\omega_s(q) + 1)$ term and $n(\omega_s(q))$ term correspond to the neutron energy loss (phonon emission) and neutron energy gain (phonon absorption) separately. The cross-section of neutron energy loss side is larger than that of neutron energy gain side, and most of neutron experiments measure at the neutron loss side of the spectrum to get data with better statistics.

$Q \cdot e_{d,s}(q)$ suggests that only phonon mode with polarization along $Q$ contributes to measured neutron intensities. In experiments, we can utilize this property and the symmetry of the crystal to selectively measure the phonon modes with different polarizations (e.g. longitudinal or transverse).

### 1.3 Magnetic Elastic and Inelastic Scattering

The cross-sections of magnetic scattering are analogies of nuclear scattering cross-section formula. The general spin-only scattering master formula takes following formula.
**Figure 1.1:** Magnetic form factor for Fe$^{2+}$ ion. The wavevector dependence of Fe$^{2+}$ magnetic form factor is calculated based on analytical approximations. The detail formalisms and coefficients can be found on Institut Laue-Langevin website [4].

The wavevector dependence of Fe$^{2+}$ magnetic form factor is calculated based on analytical approximations. The detail formalisms and coefficients can be found on Institut Laue-Langevin website [4].

\[
\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i} \frac{1}{2\pi\hbar} (\gamma r_0)^2 F^2(Q) e^{-2W(Q)} \sum_{\alpha,\beta} (\delta_{\alpha,\beta} - \frac{Q_\alpha Q_\beta}{Q^2}) \times \sum_{j,j'} \int_{-\infty}^{\infty} e^{iQ(R_j-R_{j'})} \langle \hat{S}_j^\alpha(0)\hat{S}_{j'}^\beta(t) \rangle e^{-i\omega t} dt
\]

(1.9)

\[\gamma\] is the gyromagnetic ratio with the value of 1.913 and \(r_0\) is known as the classical radius of the electron with the value of \(2.818 \times 10^{-15}\) m. \(S_j^\alpha\) is the projection of the spin operator along \(\alpha\)-axis (\(\alpha = x, y, z\)).

\(F(Q)\) is the dimensionless magnetic form factor defined as the Fourier transform of the normalized spin density of a single atom, and it ranges from 0 to 1. \(F(Q)\) usually falls off with increasing the magnitude of the scattering vector \(Q\), and that’s why most magnetic neutron studies force on low \(Q\) regime. Moreover, this property helps to distinguish whether newly discovered signals have magnetic origins. Figure 1.1 shows the form factor of an Fe$^{2+}$ atom.

The term \(\left(\delta_{\alpha,\beta} - \frac{Q_\alpha Q_\beta}{Q^2}\right)\) is so-called polarization factor, and only magnetic moments
or spin fluctuations perpendicular to \( Q \) contributes to the measured intensities. This property allows to determine the moment directions of magnetic ordered materials or to distinguish spin fluctuation polarizations. This property can lead to non-monotonic change of magnetic signal intensities with \( Q \).

Elastic neutron scattering cross-section has formula (1.10).

\[
\frac{d\sigma}{d\Omega} = (\gamma r_0)^2 F^2(Q) e^{-2W(Q)} \sum_{\alpha,\beta} (\delta_{\alpha,\beta} - \frac{Q_\alpha Q_\beta}{Q^2}) \sum_l e^{iQ \cdot l} \langle \hat{S}_\alpha^0 \rangle \langle \hat{S}_\beta^l \rangle
\]  

(1.10)

For a magnet contained only one type of magnetic atom with collinear magnetic order, equation (1.10) can be further reduced to a simpler form (1.11).

\[
\frac{d\sigma}{d\Omega} = N_m \frac{(2\pi)^3}{v_0 m} (\gamma r_0)^2 e^{-2W(Q)} \sum_{\tau_m} |S_m(\tau_m)|^2 < 1 - \left( \frac{\tau_m \cdot e}{\tau_m} \right)^2 > \delta(Q - \tau_m)
\]  

(1.11)

Similar to equation (1.4), \( N_m \) is the number of the magnetic unit cells and \( v_0 m \) is the magnetic unit cell volume in real space. \( S_m(\tau_m) \) is the magnetic structure factor. We denote \( z \)-direction as the spin direction in cartesian system, and \( < S^z > \) stands for the spin size. \( \sigma_d \) can be +1 or -1.

\[
S_m(\tau_m) = < S^z > F(\tau_m) \sum_d \sigma_d e^{i\tau_m \cdot d}
\]  

(1.12)

Once the nuclear and magnetic structure of target material is known, we can utilize equation (1.4) and (1.11) to calculate \( < S^z > \) and derive the ordered moment \( \mu = g\mu_B < S^z > \). We will discuss the details of magnetic ordered moment normalization via nuclear peak intensity in Chapter 3.

We introduce magnetic scattering function (1.13) and rewrite (1.9) into (1.14).
\[ S^{\alpha\beta}(Q, \omega) = \frac{1}{2\pi \hbar} \sum_{j,j'} \int_{-\infty}^{\infty} e^{iQ \cdot (R_j - R_{j'})} < \hat{S}_j^{\alpha}(0) \hat{S}_{j'}^{\beta}(t) > e^{-i\omega t} dt \] (1.13)

\[ \frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i} (\gamma r_0)^2 F^2(Q) e^{-2W(Q)} \sum_{\alpha,\beta} (\delta_{\alpha,\beta} - \frac{Q_{\alpha} Q_{\beta}}{Q^2}) S^{\alpha\beta}(Q, \omega) \] (1.14)

Thus, neutron scattering measures the Fourier transform of the spin-spin correlation function in space and time. Utilizing the fluctuation-dissipation theorem (1.15), the cross-section of inelastic magnetic neutron scattering relates to dynamic spin susceptibility directly.

\[ S^{\alpha\beta}(Q, \omega) = \frac{N\hbar}{\pi} (1 - e^{-\frac{k}{\gamma r_0}})^{-1} \text{Im} \chi^{\alpha\beta}(Q, \omega) \] (1.15)

### 1.4 Neutron Scattering Instruments

The kinematic condition equations (1.1), (1.2) in neutron scattering process are shown schematically in figure 1.3. The basic idea of neutron scattering experiments is to control or measure \( k_i \) and \( k_f \) precisely. The capability of inelastic neutron scattering techniques compared to other commonly used investigate methods is summarized in figure 1.2. For measurements of nuclear or magnetic excitations with \( E \lesssim 100 \text{meV} \), neutron scattering is the most suitable technique to use.

Neutron scattering measurements in this thesis are carried out on three-axis/triple-axis spectrometer (TAS) spectrometer and time-of-flight instrument (TOF). The former is commonly installed at nuclear reactor sources, while the latter can be performed at either a nuclear reactor or a spallation source.
Figure 1.2: **Schematic of kinematic condition in neutron scattering experiments.** Moment and energy of neutrons are conserved during the whole scattering process, and \( Q \) is the momentum transfer with the sample.

1.4.1 Three-axis spectrometer

The top view of the TAS is shown in figure 1.4. As the name suggested, there are three independent rotation axes (monochromater, sample and analyzer) on the instrument. Monochromator and analyzer are built with crystals with known lattice spacing \( d \), and Bragg’s law \( n\lambda = 2d\sin \theta \) is used to select neutrons with certain wavevector and energy. Monochromator and analyzer of modern TAS are commonly vertically curved to focus the neutrons on the sample. And they typically have the capability to curve horizontally to focus more neutrons on the sample by trading off resolution. The plane spanned by \( k_i \) and \( k_f \) is called scattering plane. TAS can measure scattering function at any point in momentum and energy space accessible to the spectrometer on the scattering plane. Common scan types include constant-\( Q \) scan, constant-energy scan and temperature scan.

Other common components of TAS include neutron guide, collimator, filters and slits. By using these components properly, one can achieve excellent energy and momentum resolutions. One should be cautious about the background signals in TAS experiments. Since TAS measures one point in momentum and energy space at
Figure 1.3: Energy and length for neutron scattering techniques compared to other investigate methods. Figure taken from https://www.mlz-garching.de/englisch/neutron-research/experimental-methods/inelastic-scattering.html. The light yellow region shows the energy and length coverage of inelastic neutron scattering.

a time, it can be very hard to tell backgrounds from real signals in some experiments.

Though TAS was invented more than sixty years ago, it is still the most versatile instrument for inelastic neutron scattering. Different sample environment (low temperature cryostat, high field magnet, pressure cell) and experiment setups (polarized neutron) can be integrated seamlessly with TAS. Newly developed TAS tends to have multiple detectors to increase the measurement efficiency. For example, Multi Axis Crystal Spectrometer (MACS) at the NIST center for neutron scattering (NCNR)
Figure 1.4 : **Schematic of three-axis spectrometer** Monochromater, sample and analyzer are three rotation axes, and orange arrows mark the neutron propagating direction.

have 20 independent detector channels.

### 1.4.2 Time-of-Flight Instrument

Time-of-flight technique is a general method for probing the kinetic energy (magnitude of wavevector) of a traveling neutron by measuring the time it takes him to fly between fixed points whose distance is known. In scattering experiment, neutrons travels with velocity around several hundred meters per second. Either $k_i$ or $k_f$ can be determined with time-of-flight technique. Figure 1.5 shows the layout and phase space diagram of direct geometry TOF neutron instrument where $k_i$ is selected by Fermi choppers and $k_f$ is measured with time-of-flight technique [1].
TOF instruments usually equipped with huge position-sensitive detector banks to cover a large area in the momentum and energy space. The energy and momentum resolutions are complex functions of the chopper frequency, incident neutron energy, the distance between sample and detector, etc.

While TOF measures the scattering function in a wide range of momentum and energy space simultaneously, it should be noted that $Q$ and $E$ in measured signals cannot be completely decoupled without changing sample setup. In Cartesian coordinate representation, scattering function can be written as $S(Q, E) = S(Q_x, Q_y, Q_z, E)$. Three of these four variables ($Q_x, Q_y, Q_z$ and $E$) can be individually chosen. The fourth variable is constrained by kinematic conditions, eq. 1.1 and 1.2. If the measured signals have weak $L$ modulation (e.g. most magnetic excitations in unconventional superconductors are quasi-2D), a common experiment setup is $k_i \parallel c$ and one can completely map out the magnetic excitations in ab plane. For 3-D signals, one needs to collect a series of measurements with different sample setups (e.g. by rotating sample) to reconstruct $S(Q_x, Q_y, Q_z, E)$. 
Figure 1.5: Schematic of Time-of-Flight Instrument. (a) instrument schema and (b) phase space diagrams of direct time-of-flight techniques. The velocity of incident neutron $v_i$ is selected by Fermi Chopper, and the time when neutron pass Fermi Chopper is recorded as $T_0$. The arrival time of neutrons at the sample $T_S$ can be calculated precisely. After the scattering, position-sensitive detector records the neutron arrival time $T_D$. Then the velocity of scattered neutron can be calculated as $v_f = D/(T_D - T_S)$ where $D$ is the distance between sample and detector.
Chapter 2

Introduction

In this chapter, a brief introduction to iron pnictide compounds is given, including phase diagram, crystal and magnetic structure. We also discuss electronic nematic phase in iron pnictide systems to present a general background for later chapters.

2.1 General introduction to iron based superconductors

The origin of superconductivity in conventional superconductors is electron-phonon coupled electron pairs (Cooper pairs), and conventional superconductivity is described by Bardeen-Cooper-Schrieffer (BCS) theory and its extensions. In contrast, superconductivity which does not conform to BCS theory is called unconventional superconductivity. The first unconventional superconductor is heavy fermion compound CeCu$_2$Si$_2$ with superconducting transition temperature $T_c \approx 0.5$K [5] in 1979. Following the discoveries of unconventional superconductivity in heavy fermion materials, several copper based compounds (cuprates) and iron-based compounds (iron pnictides and iron chalcogenide) are also found to be superconductor. YBa$_2$Cu$_3$O$_{6+x}$ with $T_c \approx 90$K (1987) [6] is the first superconductor whose transition temperature is above the boiling point of liquid nitrogen (77K). The discovery of high $T_c$ in cuprates starts the age of intensive research of high-temperature superconductivity, and the highest temperature superconductor at ambient pressure is HgBa$_2$Ca$_2$Cu$_3$O$_x$ with $T_c \approx 138$K [7]. Iron based superconductors are discovered in 2008 [8], and the rich physical proper-
ties of this system provide a perfect playground to study the origin of unconventional superconductivity and attract great research focuses since then. Studying the origin of unconventional superconductivity is not only an interesting physics topic, but a giant leap towards room-temperature superconductors as well.

2.1.1 Phase diagram

Superconductivity in copper-based, iron-based and heavy fermion superconductors are often derived from their antiferromagnetic parent compounds by doping, pressure and other tuning parameters. Figure 2.1 shows the general phase diagram of unconventional superconductors. The proximity to magnetically ordered phase and the persistence of strong magnetic fluctuations in paramagnetic states suggest that magnetism plays a key role in mediating superconductivity in unconventional superconductors [9, 10].

Figure 2.1: Schematic of phase diagram for unconventional superconductors. $\eta$ stands for the tuning parameters, including electron/hole doping, isovalent substitution, pressure, etc.
Figure 2.2 shows the phase diagram of electron and hole-doped BaFe$_2$As$_2$. At room temperature, BaFe$_2$As$_2$ is paramagnetic (PM) with tetragonal lattice structure. Upon doping with Ni at Fe site or K at Ba site, PM to antiferromagnetic (AFM) transition temperature $T_N$ is suppressed and superconductivity (SC) emerges. SC coexists with AFM order in the underdoped regions in both electron and hole doped samples. Close to optimal superconducting region, the system exhibits more complex behaviors. Commensurate long-range magnetic order is replaced with incommensurate short-range magnetic order in electron doped side, while a new magnetic phase with different magnetic structure appears in hole doped side (not shown in figure 2.1). The tetragonal to orthorhombic structure transition $T_S$ coincides with $T_N$ in BaFe$_2$As$_2$, and $T_S$ separates from $T_N$ with electron doping. The region between $T_S$ and $T_N$ is electronic nematic phase (section 2.2). The phase diagram of NaFeAs is very similar to the electron doped side of BaFe$_2$As$_2$ (figure 5.1). Hole doping via chemical substitution cannot be achieved in NaFeAs.

In terms of doping, the whole phase diagram can be split into: parent compound, underdoped, near-optimal doped, optimal doped, overdoped and heavily overdoped regions. In terms of temperature, the phase diagram can be split into: high-temperature tetragonal ($T \geq T_S$), nematic ($T_N \leq T \leq T_S$), non-superconducting ordered ($T_c \leq T \leq T_N$) and superconducting regimes ($T \leq T_c$). Phase diagram serves as a road map for detailed studies.

### 2.1.2 Crystal and magnetic structure

Owing to large single crystal sample sizes and simple crystal structures, BaFe$_2$As$_2$ (Ba122) and NaFeAs (Na111) are two most widely studied iron based superconducting systems. In this thesis, we discuss our research results on Ni doped NaFeAs (chapter
Figure 2.2: Phase diagram of electron and hole-doped BaFe$_2$As$_2$. The figure is from [11, 9]. $T_S$, $T_N$ and $T_c$ are the transition temperature for structure, magnetic and superconducting separately. Paramagnetic (PM), antiferromagnetic (AFM) and superconducting (SC) regions are marked in the figure. Tet and Ort stands for tetragonal and orthorhombic structure separately. IC-AFM is incommensurate short range magnetic order.

3), Cu doped BaFe$_2$As$_2$ (chapter 4) and Co doped NaFeAs (chapter 5). We introduce the crystal and magnetic structure of BaFe$_2$As$_2$ and NaFeAs here. Figure 2.3 shows the crystal structure for magnetic ordered BaFe$_2$As$_2$ and NaFeAs in orthorhombic chemical cell presentation (figure 2.3 plots two NaFeAs unit cells along c). a, b, c are lattice parameters, and ordered moment orientations are marked with black arrows. In orthorhombic notation, $a \approx b \approx 5.56$ Å, and $c \approx 13.0$ Å in BaFe$_2$As$_2$, and $a \approx b \approx 5.73$ Å, and $c \approx 6.96$ Å in NaFeAs. Iron pnictides are layer compounds and Fe-As layers are the key building blocks. Within one Fe-As layer, Fe ions and As ions are bounded tightly with covalent bonds, and superconductivity is believed to happen in Fe-As layers. Compared with BaFe$_2$As$_2$ which has two Fe-As layers in each orthorhombic unit cell, there is only one layer of Fe-As in each NaFeAs orthorhombic unit cell. Because of this, the magnetic unit cell of NaFeAs doubles the orthorhombic
unit cell along c-axis. The magnetic ordering wave vector is $Q_{\text{Orth}} = (1,0,1)$ in BaFe$_2$As$_2$ and $Q_{\text{Orth}} = (1,0,0.5)$ in NaFeAs in orthorhombic structural notation.

![Figure 2.3: Crystal structures for BaFe$_2$As$_2$ and NaFeAs.](image)

Another commonly used notation is tetragonal chemical unit cell notation. Figure 2.4 shows the schematic of orthorhombic and tetragonal chemical unit cell and corresponding Brillouin zones. The in-plane axes of tetragonal unit cell aligns 45 degree from nearest Fe-Fe direction, and the tetragonal axes are $1/\sqrt{2}$ times the orthorhombic axes. Thus the in-plane Brillouin zone area of tetragonal unit cell is twice as big as that of orthorhombic unit cell. The in-plane component of magnetic ordering wave vector is $Q_{\text{Tet}} = (0.5,0.5)$ in tetragonal chemical unit cell notation.

As shown in figure 2.3, As ions and Fe ions don’t strictly lay in the same plane.
Figure 2.4: Schematic of orthorhombic and tetragonal chemical unit cell in iron pnictides. Orthorhombic chemical unit cell (a) and corresponding Brillouin zone (c). Tetragonal chemical unit cell (b) and corresponding Brillouin zone (d). The in plane component of magnetic order wave vector is $Q_{\text{Orth}} = (1,0)$ in orthorhombic notation and $Q_{\text{Tet}} = (0.5,0.5)$ in tetragonal notation.
The vertical distance between As ion and the Fe plane is defined as the iron pnictogen height [10]. It is argued that electronic correlations in iron pnictides is very sensitive to the iron pnictogen height [12, 13]. Thus a careful characterization of the iron pnictogen height is crucial to understand the physical properties in iron pnictides [12, 13, 14].

2.2 Nematic phase in iron based superconductors

Nematic phase was first used in liquid crystals. In a nematic phase, rod-shaped organic molecules have long-range directional order where molecular long axes roughly parallel, and these molecules don’t have positional order [figure 2.5(c)]. Liquid crystal in nematic phase breaks rotational symmetry but preserves translational symmetry [figure 2.5(c)]. On the contrary, isotropic liquid preserves both rotational and translational symmetry (figure 2.5(a)), and crystalline solid has these two symmetries broken [figure 2.5(e)]. The nematic phase in liquid crystal describes the intermediate state where one type of symmetry is broken (rotational symmetry in liquid crystal) and another type of symmetry is preserved (translational symmetry in liquid crystal).

In iron pnictide, the electronic system exhibits discrete four-fold ($C_4$) lattice rotational symmetry and $O(3)$ spin rotational symmetry at high temperature [figure 2.5(b)]. On lowering the temperature, these two symmetries are broken in two steps: the lattice rotational symmetry is broken from $C_4$ to $C_2$ at $T_S$ [figure 2.5(d)] and $O(3)$ symmetry is broken at $T_N$ [figure 2.5(f)]. Electric nematic phase in iron pnictide is an analogy of that in liquid crystal. It refers to paramagnetic orthorhombic phase ($T_N < T < T_S$) where the discrete lattice rotational symmetry is broken and time-reversal symmetry is preserved [15].

Nematic order breaks the discrete lattice rotational symmetry by making the $x$ and
y directions in the iron plane non-equivalent [15]. This tetragonal-to-orthorhombic transition is not a regular phonon-driven structural transition [16, 17, 18]. The lattice distortion instability is too small to induce the large anisotropies in electronic properties [16, 17, 18]. Instead, the nematic order originates from the symmetry breaking of electronic degree of freedom, and the orthorhombic distortion is induced from the lattice coupling with that. It is unclear which electronic degree of freedom is the driver, and the potential candidates are spin order and charge/orbital order. In spin order scenario, spin fluctuations are considered as the driving force for nematic transition. Spin susceptibilities along \( a \) and \( b \) axis become different [15]. On the other hand, in orbital/charge order picture, iron \( d_{xz} \) and \( d_{yz} \) orbitals become inequivalent in energy at nematic transition and the occupations \( n_{xz} \) and \( n_{yz} \) of the \( d_{xz} \) and \( d_{yz} \) orbitals become different [15]. The spin-driven picture is supported by several neutron scattering experiments [18, 19], and angle-resolved photoemission spectroscopy (ARPES) measurements [20, 21] give evidences for the orbital/charge scenario. Since spin, orbital and lattice degree of freedoms are always strongly coupled together, all three types of order are present no matter which drives the nematic instability [15].

Nematic order in iron pnictide attracts great research attentions because nematic fluctuations are proposed to enhance superconductivity [22]. The structural, magnetic and superconducting phase transitions and their couplings to each other are usually modeled with phenomenologically Ginzburg-Landau (GL) approach. For example, superconductivity coexists and competes with nematic order in electron underdoped BaFe\(_{1-x}\)Co\(_x\)As [23] and NaFe\(_{1-x}\)Ni\(_x\)As (chapter 3) [24]. The effective free energy can be written in terms of only the superconducting order parameter \( \Delta \) and the orthorhombicity \( \delta \equiv (a - b)/(a + b) \) [24].
Figure 2.5: Schematic of nematic phase in liquid crystal and iron pnictide. In isotropic liquid, the system has both rotational and translational symmetry (a). The rotation symmetry is broken, while translation symmetry is preserved in liquid crystal state (c). Both symmetries are broken in crystalline solid (e). The nematic phase (paramagnetic orthorhombic state) in iron pnictide is shown in (d), while paramagnetic tetragonal state is shown in (b) and antiferromagnetic orthorhombic state is shown in (f).
\[ F[\Delta, \delta] = \frac{C}{2} \delta^2 + \frac{D}{4} \delta^4 - \frac{\alpha}{2} |\Delta|^2 + \frac{\beta}{4} |\Delta|^4 + \gamma |\Delta|^2 \delta^2 \] (2.1)

where the last term describes the competition between nematicity and superconductivity.

In hole-doped \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) (figure 2.2) and isovalent-doped \( \text{BaFe}_2\text{As}_{2-x}\text{P}_x \) system, structural and magnetic transitions are simultaneous [25, 26], while electron-doped \( \text{BaFe}_{2-x}\text{Ni}_x\text{As}_2 \) (figure 2.2) exhibits separate \( T_S \) and \( T_N \) [11]. Moreover, \( \text{NaFeAs} \) exhibits \( T_S \approx 58\text{K} \) and \( T_N \approx 45\text{K} \) [27], and the large separation between the \( T_S \) and \( T_N \) provides a unique opportunity to study the nematic phase without dopant.
Chapter 3

Phase Diagram and Lattice Distortions in NaFe\(_{1-x}Ni_x\)As

In this chapter, we use neutron scattering to probe magnetic and nematic orders throughout the phase diagram of NaFe\(_{1-x}Ni_x\)As, finding that while both static antiferromagnetic and nematic orders compete with superconductivity, the onset temperatures for these two orders remain well-separated approaching the putative quantum critical points. We uncover local orthorhombic distortions that persist well above the tetragonal-to-orthorhombic structural transition temperature \(T_s\) in underdoped samples and extend well into the overdoped regime that exhibits neither magnetic nor structural phase transitions. This work has been published in Nature Communication [24].

3.1 Introduction

As discussed in section 2.2, nematic transition describes the \(C_4 \rightarrow C_2\) symmetry-breaking and it is typically associated with the structural transition at \(T_s\). However, there are numerous reports of its observation well above \(T_s\) and in overdoped compounds [28, 29, 30, 31, 32, 33, 34]. These observations are either reflective of an intrinsic rotational-symmetry-broken phase above \(T_s\), which can occur in the bulk [28, 29, 30] or on the surface of the sample [31], or simply result from a large nematic susceptibility [32, 33, 34, 35]. In the first case, there is a small but non-zero nematic order parameter throughout the material above \(T_s\), although no additional symmetry-
breaking occurs below $T_s$ despite the sharp increase of the nematic order parameter. For the latter scenario, only local orthorhombic distortions can be present and the system remains tetragonal on average. One way to differentiate the two scenarios is to directly and quantitatively probe the distribution of the inter-planar atomic spacings ($d$-spacings) and its temperature dependence.

Ideally, when the system becomes orthorhombic, two different in-plane $d$-spacings corresponding to different in-plane lattice parameters can be resolved; on the other hand, when there are only local orthorhombic distortions, the $d$-spacing distribution only broadens while the average structure remains tetragonal [figure 3.1]. However, experimentally it can be very difficult to distinguish the two scenarios when $\delta$ is too small for a splitting to be resolved, then a broadening is also seen even when the system goes through a tetragonal-to-orthorhombic phase transition. In such cases, it is more instructive to examine the temperature dependence of the experimentally obtained broadening, characterized either by $\delta$ or by the width of the $d$-spacing distribution, $\Delta d/d$ [figure 3.1]. For a phase transition, the broadening should exhibit a clear order-parameter-like onset; for local orthorhombic distortions in an average tetragonal structure, the broadening instead tracks the nematic susceptibility, which exhibits a Curie-Weiss temperature dependence [36] [figure 3.1].

In electron-doped Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$, BaFe$_{2-x}$Ni$_x$As$_2$, and NaFe$_{1-x}$Co$_x$As, long-range magnetic order becomes short-range and incommensurate along the in-plane transverse direction near optimal superconductivity [37, 38, 39, 40, 41]. The short-range magnetic order displays characteristics of a cluster spin glass [42, 43], possibly due to disorder effects of dopants. Spin-glass-like magnetic order is also observed in BaFe$_2$(As$_{1-x}$P$_x$)$_2$ and Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$, although magnetic order remains commensurate [26, 39, 44]. Given the strong magnetoelastic coupling in the iron pnictides
[15, 45], it is unclear how such changes in AF order affect the nematic order.

Figure 3.1: Schematic of Long-range Nematic Order and Local Nematic Distortion. Schematic of how the \(d\)-spacing distribution changes from a tetragonal state at high temperatures to an orthorhombic state through a phase transition [characterized by \(\delta = (a - b)/(a + b)\)] or a state with local orthorhombic distortions (characterized by broadening of the \(d\)-spacing distribution \(\Delta d/d\)) that on average remains tetragonal. For the orthorhombic state, when the splitting \(\delta\) is too small to be resolved experimentally, a broadening is also observed (red dashed line). In such cases, the two situations can nonetheless be differentiated by examining the temperature dependence of \(\delta\) or \(\Delta d/d\).

Single crystals of NaFe\(_{1-x}\)Ni\(_x\)As with \(x=0.004, 0.008, 0.010, 0.012, 0.013, 0.015\) and 0.017 were prepared by the self-flux method [46]. The temperature and doping dependence of the in-plane electrical resistivity \(\rho(T)\) were measured using the
standard four-probe method, the results of superconducting samples are normalized to $\rho(200 \text{ K})$ and summarized in figure 3.2. The superconducting transitions for all measured samples are sharp. The kinks associated with the structural transition at $T_s$ can be clearly identified in underdoped samples (figure 3.2 (a)-(d)), similar to NaFe$_{1-x}$Cu$_x$As [47]. These kinks are progressively suppressed with increasing Ni concentration.

Our neutron results are reported using the orthorhombic structural unit cell with lattice parameters $a \approx b \approx 5.56 \text{ Å}$ and $c \approx 7.05 \text{ Å}$ for NaFeAs [27, 48]. The momentum transfer $\mathbf{Q} = H\mathbf{a}^* + K\mathbf{b}^* + L\mathbf{c}^*$ is denoted as $\mathbf{Q} = (H, K, L)$ in reciprocal lattice units (r.l.u.) with $\mathbf{a}^* = \hat{a}2\pi/a$, $\mathbf{b}^* = \hat{b}2\pi/b$ and $\mathbf{c}^* = \hat{c}2\pi/c$. In this notation, magnetic Bragg peaks are at $\mathbf{Q} = (1, 0, L)$ with $L = 0.5, 1.5, 2.5, \cdots$. Samples were mostly aligned in the $[1, 0, 0] \times [0, 0, 1]$ scattering plane, which allows scans of magnetic peaks along $H$ and $L$; the $x = 0.012$ sample was also studied in the $[1, 0, 1.5] \times [0, 1, 0]$ plane. We have carried out neutron diffraction, neutron Larmor diffraction, and inelastic neutron scattering experiments on NaFe$_{1-x}$Ni$_x$As.

3.2 Magnetic order in NaFe$_{1-x}$Ni$_x$As system

Elastic neutron experiments were carried out on the Spin Polarized Inelastic Neutron Spectrometer (SPINS) at the NIST Center for Neutron Research (NCNR), United States and the HB-1A triple-axis spectrometer at the High-Flux-Isotope Reactor (HFIR), Oak Ridge National Laboratory (ORNL), United States. We used pyrolytic graphite [PG(002)] monochromators and analyzers in these measurements. At HB-1A, the monochromator is vertically focused with fixed incident neutron energy $E_i = 14.6 \text{ meV}$ and the analyzer is flat. At SPINS, the monochromator is vertically focused and the analyzer is flat with fixed scattered neutron energy $E_f = 5 \text{ meV}$. 
Figure 3.2: Temperature dependence of in-plane resistivity for NaFe$_{1-x}$Ni$_x$As single crystals. The insert in (d) shows a zoom-in to highlight the weak kink associated with structural transition $T_s$ in the $x = 0.013$ sample.
A PG filter was used at HB-1A and a Be filter was used at SPINS to avoid contamination from higher-order neutrons. Collimations of 40'-40'-sample-40'-80' and guide-40'-sample-40'-open were used on HB-1A and SPINS, respectively.

### 3.2.1 Ordered magnetic moment calculation

The partial differential cross-section of coherent elastic nuclear and magnetic scattering (with collinear magnetic order) are giving by equations (1.4) and (1.11). The total scattering cross-section is defined as following:

\[
\sigma_{\text{tot}} = \int_{\text{all directions}} \left(\frac{d\sigma}{d\Omega}\right) d\Omega \tag{3.1}
\]

When performing the rocking scan measurements in TAS experiment, the integrated number of scattered neutrons per unit time in the Bragg peak \( P(\tau) \) can be connected with scattering cross sections with formula (3.2) and (3.3).

\[
P_{\text{nuclear}}(\tau) = \Phi N_0 \left(\frac{2\pi}{v_0}\right)^3 e^{-2W(\tau)} |S_\tau|^2 / (k^3 \sin(S_{\text{nuclear}}^2)) \tag{3.2}
\]

\[
P_{\text{magnetic}}(\tau_m) = \Phi N_m \frac{(2\pi)^3}{v_{0m}} \left(\gamma r_0\right)^2 e^{-2W(\tau_m)} |S_m(\tau_m)|^2 < 1 - \left(\frac{\tau_m \cdot e}{\tau_m}\right)^2 > / (k^3 \sin(S_{\text{mag}}^2)) \tag{3.3}
\]

where \( \Phi \) is the flux of the incident neutrons, \( k \) is the wavevector magnitude of incident neutrons, \( S_{\text{nuclear}}^2 \) and \( S_{\text{mag}}^2 \) are the scattering angles (2\( \theta \)) for nuclear and magnetic Bragg peaks (figure 1.2).

For known nuclear and magnetic structure, nuclear structure factor, magnetic form factor and polarization factor can all be calculated. Since most studies on magnetic ordering are carried out at low temperature, Debye-Waller factor can be treated as
unity. If all measurements are performed in the same experiment setup ($\Phi$ and $k$ keep the same), the magnetic structure factor $S_m(\tau_m)$ can be obtained directly from the intensity ratio between magnetic Bragg peak and nuclear Bragg peak.

$$\frac{P_{\text{magnetic}}(\tau_m)}{P_{\text{nuclear}}(\tau)} = \frac{1}{4}(\gamma r_0)^2 \frac{|S_m(\tau_m)|^2 < 1 - (\frac{\tau_m \cdot 0}{\tau_m})^2 >}{|S_\tau|^2} \frac{1/sin(S^2_{\text{mag}})}{1/sin(S^2_{\text{nuclear}})}$$  \hspace{1cm} (3.4)

In iron pnictide systems, an additional $1/2$ is required to describe the twinning effect. Thus, we have the following formula.

$$\frac{P_{\text{magnetic}}(\tau_m)}{P_{\text{nuclear}}(\tau)} = \frac{1}{4}(\gamma r_0)^2 \frac{|S_m(\tau_m)|^2 < 1 - (\frac{\tau_m \cdot 0}{\tau_m})^2 >}{|S_\tau|^2} \frac{1/sin(S^2_{\text{mag}})}{1/sin(S^2_{\text{nuclear}})}$$  \hspace{1cm} (3.5)

Utilizing equation (1.12), one can extract the spin size $S^z$ from $S_m(\tau_m)$. And the ordered moment can be calculated by $\mu = g\mu_B < S^z >$. Please note that Laudé $g$-factor shouldn’t be omitted even if the magnetic moment is reported in the unit of $\mu_B$.

For systems with weak magnetic signals, one should use weak nuclear peaks for such calculations to minimize the errors. In iron pnictides, a commonly used nuclear peak is $Q = (2, 0, 0)$ in orthorhombic notation.

### 3.2.2 Experiment Details and Results

Magnetic order parameters of NaFe$_{1-x}$Ni$_x$As with $x=0.004, 0.010, 0.012, 0.015$ samples are measured at AF wavevector $Q = (1, 0, 1.5)$. No magnetic order is observed for $x = 0.015$. While the magnetic order parameter for the $x = 0.004$ sample resembles that of NaFeAs [figure 3.3(a) and (b)], magnetic order becomes strongly suppressed upon entering the superconducting state for $x = 0.010$ [figure 3.3(c)], similar to other iron pnictides [49, 50]. For the $x = 0.012$ sample, magnetic order onsets at $T_N \approx 19$ K.
and becomes strongly suppressed upon entering the superconducting state below $T_c$ and re-enters into the paramagnetic state without any long-range order below $T_r \approx 10$ K [figure 3.3(d)].

Figure 3.3: Doping-dependence of the magnetic order parameter for NaFe$_{1-x}$Ni$_x$As. Magnetic order parameters measured at $Q = (1,0,1.5)$ for NaFe$_{1-x}$Ni$_x$As with (a) $x = 0$, (b) $x = 0.004$, (c) $x = 0.010$ and (d) $x = 0.012$. No magnetic order is observed for $x = 0.015$. Data in (a) are from Ref. [41]. All vertical error bars in the figure represent statistical errors of 1 s.d.

To ensure that $T_i$ for NaFe$_{1-x}$Ni$_x$As ($x = 0.012$) is well inside the superconducting state, we measure its magnetic susceptibility as a function of temperature. As shown in figure 3.4, the sample displays a sharp superconducting transition at $T_c \approx 17$ K, with a width $\Delta T_c \approx 2$ K. $T_i$ is well inside the superconducting state, unaffected by the width of the superconducting transition.
Figure 3.4: Temperature dependence of the magnetic susceptibility for NaFe$_{1-x}$Ni$_x$As ($x=0.012$). $T_c$ and $T_r$ marked by arrows are superconducting transition temperature and temperature when static antiferromagnetic order is suppressed, respectively.

This reentry behavior is similar to that of nearly-optimal-doped Ba(Fe$_{0.941}$Co$_{0.059}$)$_2$As$_2$ [51], although AF order in Ba(Fe$_{0.941}$Co$_{0.059}$)$_2$As$_2$ is short-range and incommensurate [37]. To confirm that the magnetic order in our $x=0.012$ sample is long-range and commensurate, we carried out scans along the $[H,0,1.5]$, $[1,K,1.5]$ and $[1,0,L]$ directions in $[1,0,1.5] \times [0,1,0]$ and $[1,0,0] \times [0,0,1]$ scattering planes [figure 3.5(a)], with results summarized in figure 3.5(b)-(d). As can be seen, magnetic order remains long-range along all three high-symmetry directions (with spin-spin correlation lengths exceeding 100 Å) for the $x=0.012$ sample near optimal superconductivity, before disappearing near $x=0.015$. These wave-vector scans also confirm the complete disappearance of long-range magnetic order below $T_r$. For comparison, we note that magnetism in electron-doped Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ ($\sim6\%$) [37], BaFe$_{2-x}$Ni$_x$As$_2$ ($\sim5\%$) [40], and NaFe$_{1-x}$Co$_x$As ($\sim2.3\%$) [41] exhibits cluster spin glass and incommensurate magnetic order near optimal superconductivity likely related to impurity effects [42, 39]. The absence of such behavior in NaFe$_{1-x}$Ni$_x$As is likely a result of signifi-
cantly lower dopant concentration in NaFe$_{1-x}$Ni$_x$As (~1.3%) near optimal doping.

![Neutron scattering geometry and constant energy scan for NaFe$_{1-x}$Ni$_x$As x = 0.012.](image)

The magnetic moments of NaFe$_{1-x}$Ni$_x$As with $x = 0, 0.004, 0.010, 0.012$ are normalized with equation (3.5). Rocking scans at magnetic Bragg peak $Q = (1, 0, 1.5)$ and nuclear Bragg peak $Q = (2, 0, 0)$ for NaFe$_{1-x}$Ni$_x$As $x = 0.010$ are shown in figure 3.6. Assuming the peaks having Gaussian line shape, we can extract peak height and width with equation (3.6) or width and area under the peak with (3.7). The extracted full-width-at-half-maximum (FWHM) of the nuclear Bragg peak $Q = (2, 0, 0)$ in NaFe$_{1-x}$Ni$_x$As $x = 0.010$ is $0.536 \pm 0.017$ degree. The finite width in rocking scan comes from sample mosaicity and instrument resolution, and we can use that to
evaluate the correlation length of magnetic order. The FWHM of magnetic Bragg peak $Q = (1,0,1.5)$ with value $0.542 \pm 0.015$ at $T = 15K$ confirms the long-range nature of our magnetic Bragg peaks.

$$f = a + b \times x + h \times \exp(-4 \ln(2) \frac{x - x_0}{w})$$ (3.6)

$$f = a + b \times x + 2 \left( \frac{\ln(2)}{\pi} \right)^{\frac{1}{2}} \frac{\text{area}}{w} \times \exp(-4 \ln(2) \frac{x - x_0}{w})$$ (3.7)

where $a$ and $b$ described the linear background, $h$ represents the peak height, $w$ is the FWHM and $\text{area}$ is the area under the peak.

The normalized magnetic moments of NaFe$_{1-x}$Ni$_x$As with $x = 0$, 0.004, 0.010, 0.012 are summarized in table 3.1. In reference, the moment of parent compound NaFeAs is reported as $M = 0.17 \pm 0.034 \mu_B/\text{Fe}$. The value is smaller than what we calculate here. One possible reason is that reference [41] ignored the Laudé Factor in the calculation.
Table 3.1: Magnetic moment for NaFe$_{1-x}$Ni$_x$As. Magnetic moment for $x = 0$ is calculated from raw data in [41].

<table>
<thead>
<tr>
<th>x</th>
<th>Temperature (K)</th>
<th>Moment ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5</td>
<td>0.323 ± 0.067</td>
</tr>
<tr>
<td>0.004</td>
<td>5</td>
<td>0.273 ± 0.057</td>
</tr>
<tr>
<td>0.010</td>
<td>2.6</td>
<td>0.061 ± 0.014</td>
</tr>
<tr>
<td>0.010</td>
<td>15</td>
<td>0.113 ± 0.022</td>
</tr>
<tr>
<td>0.012</td>
<td>15</td>
<td>0.052 ± 0.012</td>
</tr>
</tbody>
</table>

3.3 Neutron spin resonance in NaFe$_{1-x}$Ni$_x$As with $x = 0.012$

To further determine if superconductivity is affected by the vanishing AF order below $T_c$, we carried out inelastic neutron scattering experiments to study the neutron spin resonance related to the superconducting superfluid density [9, 11] in NaFe$_{1-x}$Ni$_x$As with $x = 0.012$.

Our inelastic neutron scattering experiment was carried out on the HB-3 triple-axis spectrometer at HFIR, ORNL, United States. Vertically-focused pyrolytic graphite [PG(002)] monochromator and analyzer with fixed scattered neutron energy $E_f = 14.7$ meV were used. A PG filter was used to avoid higher-order neutron contaminations. The collimation used was 48'-40'-sample-40'-120'.

Figure 3.7 shows temperature dependence of the energy scans at $Q = (1, 0, 0.5)$. The temperature difference plots below and above $T_c$ at 1.5 K and 9 K are essentially identical [figure 3.7(b)], revealing a clear resonance at $E_r = 7$ meV similar to optimally doped NaFe$_{1-x}$Co$_x$As [52]. Figure 3.7(c) shows wave vector dependence of the resonance at different temperatures, and confirms the results of figure 3.7(a) and 3.7(b). Temperature dependence of the resonance is shown in figure 3.7(d), over-
plotted with temperature dependence of the AF order parameter. The intensity of the resonance increases smoothly below $T_c$ and $T_r$, displaying no response when AF order is completely suppressed below $T_r$. These results demonstrate the coexistence of robust superconductivity without AF order in NaFe$_{1-x}$Ni$_x$As with $x = 0.012$ below $T_r$.

![Image of graphs showing inelastic neutron scattering measurements for NaFe$_{1-x}$Ni$_x$As ($x = 0.012$).](image)

Figure 3.7: **Inelastic neutron scattering measurements for NaFe$_{1-x}$Ni$_x$As ($x = 0.012$)** (a) Energy scans at $Q = (1,0,0.5)$ for NaFe$_{1-x}$Ni$_x$As with $x = 0.012$ at $T = 1.5$, 9 and 35 K. (b) Energy scans at $T = 1.5$ and 9 K in (a) after subtracting the scan at 35 K. (c) Constant-energy scan along $[H,0,0.5]$ with $E = 7$ meV at $T = 1.5$, 9 and 35 K. (d) Temperature dependence of magnetic excitations at $E = 7$ meV and $Q = (1,0,0.5)$ in NaFe$_{1-x}$Ni$_x$As with $x = 0.012$. The magnetic order parameters from figure 3.3(d) is over-plotted for comparison. All vertical error bars in the figure represent statistical errors of 1 s.d.
3.4 Orthorhombic lattice distortion

Having established the evolution of AF order and its interplay with superconductivity in NaFe$_{1-x}$Ni$_x$As, we examined the Ni-doping evolution of the nematic order in NaFe$_{1-x}$Ni$_x$As. To precisely determine the evolution of the orthorhombic distortion, we used high-resolution neutron diffraction and neutron Larmor diffraction to investigate the temperature evolution of the orthorhombic lattice distortion.

3.4.1 Lattice distortion measurement with high-resolution neutron diffraction

Elastic longitudinal scans at structure peak positions in TAS experiments are commonly used to extract the lattice parameters. Since these measurements are carried out by changing $\theta$ and $2\theta$ simultaneously, these scans are also called $\theta - 2\theta$ scans (figure 3.8(b)). Ideally, for a system with one set of lattice parameters, the $\theta - 2\theta$ scan should be a $\delta$-function at the Bragg angle $\theta_4$ where the Bragg condition is met (figure 3.8(a)). In real experiment, measured peak usually exhibits Gaussian line-shape due to the finite instrument resolution, sample mosaicity and intrinsic lattice parameter distribution (figure 3.8(c)). This scenario applies to the tetragonal phase in iron pnictides. When the system becomes orthorhombic, different in-plane lattice parameters emerge and the $\theta - 2\theta$ scan should have the shape shown in figure 3.8(d) and (e). In system with large orthorhombicity $\delta$, splitting can be resolved (figure 3.8(e)), while only peak broadening can be observed in system with small $\delta$ (figure 3.8(d)).

Since the peak width in tetragonal state comes from finite instrument resolution, sample mosaicity and lattice parameter distribution from multiple origins (e.g. impurities), it will not change with temperature. We can extract the orthorhombicity
in orthorhombic phase by fitting the longitudinal scans using two Gaussians with fixed widths obtained from above $T_s$.

If the centers of the two Gaussian peaks are $A_4 - \delta$ and $A_4 + \delta$ in the longitudinal scan. According to the Bragg Law, we have equation (3.8) and (3.9).

\[
\frac{2\pi}{a} = Q_a = 2k \sin \frac{A_4 - \Delta}{2} \tag{3.8}
\]

\[
\frac{2\pi}{b} = Q_b = 2k \sin \frac{A_4 + \Delta}{2} \tag{3.9}
\]

Divide both side of the equations, we have

\[
\frac{a}{b} = \frac{\sin (A_4 - \Delta)/2}{\sin (A_4 + \Delta)/2} = \frac{1 + \tan (\Delta/2) \cot (A_4/2)}{1 - \tan (\Delta/2) \cot (A_4/2)} \tag{3.10}
\]

As a result we can derive $\delta$ with fitted $\Delta$ and $A_4$ with equation (3.11).

\[
\delta = \frac{\tan \Delta/2}{\tan A_4/2} \tag{3.11}
\]

3.4.2 Lattice distortion measurement with neutron Larmor diffraction

Neutron Larmor diffraction (NLD) is a high resolution diffraction based on the Larmor precession of polarized neutron, and it has the capacity of measuring lattice spacing $d$ with $\Delta d/d \approx 10^{-5}$ relative resolution.

The basic principle of NLD is shown in figure 3.9. NLD spectrometer has two arms with a constant magnetic field $B$, and the magnetic field is negligible outside the arms. The spin direction of polarized neutron and guide field direction are shown in the figure 3.9. The neutron spin precesses inside the field with the Larmor frequency
Figure 3.8: **Schematic of lattice distortion measurement with high-resolution neutron diffraction**  
(a) Ideally the longitudinal scan should be a $\delta$-function at the angle $A_4$ where the Bragg condition is met.  
(b) Schematic for longitudinal scan in reciprocal space.  
(c) Longitudinal scan for single lattice parameter with peak center at $A_4$ in real experiment. The finite peak width comes from the instrument resolution and intrinsic lattice parameter distribution.  
(d) and (e) show the longitudinal scans for lattice with two sets of lattice parameters. In iron pnictide, peak splitting (e) can be resolved with sample of large orthorhombicity $\delta$, while only peak broadening (d) can be observed when $\delta$ is small.
\( \omega_{\text{Lar}} = \gamma B \), where \( \gamma \) is the gyromagnetic ratio with the value of 2.916 kHz/Gauss.

The precession angle of polarized neutron with velocity \( v_1 \) in the first arm (\( L_1 \)) is

\[
\Phi_1 = \omega_{\text{Lar}} t = \gamma |B| L_1 / v_1 \quad (3.12)
\]

Figure 3.9: Schematic of neutron Larmor diffraction Assume the neutron The magnetic guide field \( B \) is marked on the figure. \( L_1 \) and \( L_2 \) are the effective field lengths before and after the sample.

In NLD, neutron scatters elastically with the sample, so the velocity of scattered neutron \( v_2 = v_1 \). Assuming \( L_2 = L_1 = L \), the total neutron precession phase is

\( \phi_{\text{tot}} = 2\omega_{\text{Lar}} L / v \). Utilizing the Bragg law \( |Q| = |G| = 2k \sin \theta_B \), |\( G | = 2\pi/d \) and \( v = \hbar k/m_n \), the total precession phase can be written as

\[
\phi_{\text{tot}} = \frac{2m_n \gamma BL \sin \theta_B}{\pi \hbar} d \quad (3.13)
\]

Different from high resolution neutron diffraction introduced in section 3.4.1, NLD does not depend on the accurate measurement of the Bragg angles. As a result, the instrument resolution is independent of neutron beam collimation and monochromaticity.

Polarization of the scattered neutrons \( P \) is measured as a function of the total
Larmor precession phase $\phi_{\text{tot}}$. By analyzing measured $P(\phi_{\text{tot}})$, information about the sample’s $d$-spacing distribution can be obtained.

For an ideal crystal with $d$-spacing described by a $\delta$-function, $P$ is independent of $\phi_{\text{tot}}$ with $P(\phi_{\text{tot}}) = P_0$. $P_0$ accounts for the non-ideal polarization of the neutrons and can be corrected for by Ge crystal calibration measurements. In real materials due to internal strain, sample inhomogeneity or in the case of iron pnictides, a twinned orthorhombic phase, the $d$-spacing should instead be described by a distribution $f(\epsilon)$, with $\epsilon = \delta d/d$. $\delta d$ is the deviation from the average $d$-spacing $d$. $P(\phi_{\text{tot}})$ is then described by

$$P(\phi_{\text{tot}}) = P_0 \int_{-\infty}^{\infty} f(\epsilon) \cos(\phi_{\text{tot}} \epsilon) d\epsilon.$$  \hspace{1cm} (3.14)

Thus, $P(\phi_{\text{tot}})$ can be regarded as the Fourier transform of the lattice $d$-spacing distribution $f(\epsilon)$. By measuring $P(\phi_{\text{tot}})$, it is possible to resolve features with a resolution better than $10^{-5}$ in terms of $\epsilon$, limited by the range of accessible $\phi_{\text{tot}}$.

The distribution of $d$-spacing $f(\epsilon)$ is commonly described as a Gaussian function with full-width-at-half-maximum (FWHM) $\epsilon_{\text{FWHM}}$, also denoted as $\Delta d/d$ in the rest of the paper. Equation 3.14 then becomes

$$P(\phi_{\text{tot}}) = P_0 \exp\left(- \frac{\epsilon_{\text{FWHM}}^2}{16 \ln 2} \phi_{\text{tot}}^2 \right).$$  \hspace{1cm} (3.15)

In iron pnictides with a non-zero nematic order parameter, due to twinning, $f(\epsilon)$ becomes the sum of two Gaussian functions. Assuming the two Gaussian peaks have identical FWHM $\epsilon_{\text{FWHM}}$, Eq. 3.15 becomes

$$P(\phi_{\text{tot}}) = P_0 \exp\left(- \frac{\epsilon_{\text{FWHM}}^2}{16 \ln 2} \phi_{\text{tot}}^2 \right) \times \sqrt{r^2 + (1 - r)^2 + 2r(1 - r) \cos(\phi_{\text{tot}} \Delta \epsilon)},$$  \hspace{1cm} (3.16)

where $r$ and $(1 - r)$ denotes the relative populations of the two lattice $d$-spacings $a$ and $b$, and $\Delta \epsilon = 2(a - b)/(a + b) = 2\delta [53]$. Therefore, the nematic order parameter can be extracted by fitting $P(\phi_{\text{tot}})$ using Eq. 3.16.
More details can be found in following references [54, 55, 56].

3.4.3 Experiment details and results

To measure the structural distortion in NaFe$_{1-x}$Ni$_x$As ($x = 0.012$) at SPINS, we changed the collimation to guide-20'-sample-20'-open to improve the resolution and removed the Be filter. Our measurement was carried out nominally around a weak nuclear Bragg peak $Q = (2, 0, 0)$, but the measured intensity at this position mostly come from higher-order neutrons [$Q = (4, 0, 0)$ for $\lambda/2$ neutrons and $Q = (6, 0, 0)$ for $\lambda/3$ neutrons]. While we do not resolve two split peaks in the orthorhombic state, clear broadening can be observed. Typical scans along the $[H, 0, 0]$ direction centered at $Q = (2, 0, 0)$ are shown in figure 3.10. $\delta$ in figure 3.10(b) is obtained by assuming $\delta = 0$ at $T = 50$ K and fitting broadening at lower temperatures as two split peaks with fixed widths of the peak at $T = 50$ K. The extracted temperature of orthorhombicity $\delta$ is shown in figure 3.11(b).

![Figure 3.10: Structural measurements for NaFe$_{1-x}$Ni$_x$As ($x = 0.012$) using SPINS (a) Scans of the structural Bragg peak $Q = (2, 0, 0)$ along the $H$ direction for NaFe$_{1-x}$Ni$_x$As with $x = 0.012$ are compared between 15 K and 50 K. Similarly, a comparison between 3 K and 50 K is shown in (b).]
Our neutron Larmor diffraction measurements were carried out at the three axes spin-echo spectrometer (TRISP) at Forschungs-Neutronenquelle Heinz Maier-Leibnitz (MLZ), Garching, Germany. Neutrons are polarized by a super-mirror bender, and higher-order neutrons are eliminated using a velocity selector. We used double-focused PG(002) monochromator and horizontal-focused Heusler (Cu$_2$MnAl) analyzer in these measurements. Incident and scattered neutron energies are fixed at $E_i = E_f = 15.67$ meV ($k_i = k_f = 2.750$ Å$^{-1}$).

At TRISP, the uniform DC magnetic fields with sharp field boundaries is achieved by neutron resonance spin echo technique, and four radio-frequency spin flip coils are installed in each arm.

Neutron Larmor diffraction measurements of $P\phi_{tot}$ at $Q = (4, 0, 0)$ for NaFe$_{1-x}$Ni$_x$As ($x = 0.013$) at different temperatures (5K - 50K) are shown in figure 3.11. The solid lines are fit to equation 3.16.

When $\delta$ is too small to be directly resolved by Larmor diffraction, $P(\phi_{tot})$ can be well described by either Eq. 3.15 or Eq. 3.16. In such cases, we have two ways to interpret the data:

- extract $\Delta d/d$ directly from Eq. 3.15. Ge normalization is very important to get correct value of $\Delta d/d$.
- extract $\delta$ by assuming at $T = 50$ K, $\delta = 0$ and extract $\epsilon_{\text{FWHM}}$, then fit to Eq. 3.16 by fixing $\epsilon_{\text{FWHM}}$ to this value.

A key feature of equation 3.16 is an oscillation in $P(\phi_{tot})$, which can be seen in raw data in figure 3.11(d)-(i), in these cases the measurement provides definitive evidence of an orthorhombic state. For other panels in figure 3.11, due to limited range of $\phi_{tot}$, $P(\phi_{tot})$ can be equally well-described by equation 3.15, for such data we cannot
differentiate between a true splitting and a broadening from measurement done at a single temperature.

Figure 3.11: Neutron Larmor diffraction measurements of $P\phi_{tot}$ at $Q = (4, 0, 0)$ for $\text{NaFe}_{1-x}\text{Ni}_x\text{As}$ ($x = 0.013$) at different temperatures. Solid lines are fit to equation 3.16.
For NaFe$_{1-x}$Ni$_x$As with $x \leq 0.013$, we can see clear orthorhombic lattice distortion below $T_s$, also confirmed by anomalies in the temperature dependence of electrical resistivity measurements (figure 3.2). Figures 3.12 show temperature and Ni-doping dependence of the orthorhombic distortion $\delta$. For NaFe$_{1-x}$Ni$_x$As with $x \leq 0.013$ at temperatures above $T_s$, and for $x \geq 0.015$ at all temperatures, the system is on average tetragonal and should in principle have $\delta = 0$. Surprisingly, we see clear temperature-dependent $\delta$. Moreover, while $\delta$ below $T_s$ behaves as expected for an order parameter associated with a phase transition, $\delta$ in temperature regimes with an average tetragonal structure exhibits a Curie-Weiss temperature dependence, suggesting it arises from local orthorhombic distortions. In all cases, we find that $\delta$ decreases dramatically below $T_c$, indicating that orthorhombic distortion, whether long-range or local, competes with superconductivity. The competition between superconductivity and long-range nematic order is similar to Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [23].

We emphasize that the local orthorhombic distortions we uncovered in the tetragonal phase of NaFe$_{1-x}$Ni$_x$As are distinct from the phase separation into superconducting tetragonal and antiferromagnetic orthorhombic regions found in Ca(Fe$_{1-x}$Co$_x$)$_2$As$_2$ under biaxial strain [57, 58]. In the latter compound, the quantum phase transition between the superconducting tetragonal and AF orthorhombic phases is first-order, and the resulting phase separation into these two phases with different in-plane lattice parameters allows the material to respond to biaxial strain in a continuous fashion; this would occur even if there were no quenched disorder. In NaFe$_{1-x}$Ni$_x$As, the quantum phase transition is second order and therefore an analogous phase separation does not occur. Instead, the local orthorhombic distortions we observe in NaFe$_{1-x}$Ni$_x$As likely result from the large nematic susceptibility near optimal superconductivity, pinned by quenched disorder.
Figure 3.12: Neutron diffraction and neutron Larmor diffraction studies of Ni-doping dependence of the orthorhombic distortion in NaFe$_{1-x}$Ni$_x$As. Temperature dependence of the orthorhombic distortion $\delta$ for NaFe$_{1-x}$Ni$_x$As with (a) $x = 0.01$, (b) $x = 0.012$, (c) $x = 0.013$, (d) $x = 0.015$, (e) $x = 0.017$, and (f) $x = 0.02$. Data in (b) are obtained from high-resolution neutron diffraction, whereas all the other panels are obtained from neutron Larmor diffraction measurements. Solid lines are guides-to-the-eye. $\delta$ is obtained by assuming it is 0 at $T = 50$ K and broadening at lower temperatures are fit with two split peaks with widths of the single peak at $T = 50$ K. Open symbols correspond to measurements where a splitting is definitively observed, and solid symbols represent measurements that only resolve a broadening due to experimental limitations. All vertical error bars in the figure represent least-square fits to the raw data with errors of 1 s.d.
Given that the orthorhombic distortion with Curie-Weiss temperature dependence arises from local orthorhombic distortions, an alternative way to characterize such distortion is broadening of $d$-spacing distribution width $\Delta d/d$. In figure 3.13(a)-(d), we show $\Delta d/d$ obtained from our neutron Larmor diffraction results for NaFe$_{1-x}$Ni$_x$As. Given the local orthorhombic distortions arise from quenched disorder coupled with a large nematic susceptibility near a nematic QCP, it should track temperature dependence of the nematic susceptibility, since the quenched disorder should depend weakly on temperature. Therefore, we have fitted $\Delta d/d$ in figure 3.13(a)-(d) with the Curie-Weiss form $\Delta d/d \propto 1/(T - T^*)$ and extracted the Weiss temperature $T^*$ as a function of doping, as shown in figure 3.13(e). Our $\Delta d/d$ results are well described by the Curie-Weiss form with $T^*$ changing from positive in underdoped to negative in overdoped regime [figure 3.13(e)], suggesting a nematic QCP near optimal superconductivity. These results are reminiscent of temperature and doping dependence of the nematic susceptibility from elastoresistance [59] and shear modulus measurements [60], thus suggesting that temperature dependence of $\Delta d/d$ is a direct measure of the nematic susceptibility without the need to apply external stress.

### 3.5 Overall phase diagram and discussion

Figure 3.14(a) summarizes all measurement results above and shows the overall phase diagram determined from our experiments, with $T_s$, $T_N$, and $T_c$ marked. Although for optimal-doped and overdoped regimes the samples on average exhibit a tetragonal structure at all temperatures, there are local orthorhombic distortions resulting in broadening of $d$-spacing distribution that can be characterized by $\delta$ or $\Delta d/d$. The orthorhombic distortion $\delta$ is plotted in a pseudo-color scheme as a function of temperature and doping near optimal doping in figure 3.14(a). Figure 3.14(b) shows the
Figure 3.13: Curie-Weiss fit to temperature dependence of $\Delta d/d$ as a function of $x$ for NaFe$_{1-x}$Ni$_x$As. Temperature dependence of $\Delta d/d$ and Curie-Weiss fit to the data for (a) $x = 0.01$. (b) $x = 0.015$. (c) $x = 0.017$. (d) $x = 0.02$. Clear reduction below $T_c$ is seen for all tetragonal samples. (e) Ni-doping dependence of Weiss temperature $T^*$, showing a change of sign around $x = 0.015$, suggesting the presence of a nematic QCP. Data points in (a)-(d) with $T < 50$ K are obtained from the same neutron Larmor diffraction data used to extract $\delta$ in figure 3.12. All vertical error bars in the figure represent least-square fits to the raw data with errors of 1 s.d.
Ni-doping dependence of the ordered magnetic moment and $\delta$ at $T = 5$ K, and $T = T_c$ for superconducting samples. With increasing Ni-doping $x$, the AF ordered moment and $T_N$ decrease monotonically, and no magnetic order is detected in the $x = 0.015$ sample [figure 3.14(b)].

In NaFe$_{1-x}$Ni$_x$As, the orthorhombic distortion and the structural phase transition temperature are $\delta \approx 1.7 \times 10^{-3}$ and $T_s \approx 58$ K for $x = 0$ [48, 41]; for $x = 0.012$ they become $\delta \approx 7 \times 10^{-4}$ and $T_s \approx 33$ K. We find no evidence for a structural phase transition for samples with $x \geq 0.015$, thus suggesting the presence of a putative nematic QCP at $x = x_c$, where $x_c \gtrsim 0.015$. These results are consistent with recent Muon spin rotation and relaxation study of magnetic phase diagram of NaFe$_{1-x}$Ni$_x$As [61]. They are also consistent the with Ni-doping dependence of $T^*$ determined from Curie-Weiss fits to temperature dependence of the $\Delta d/d$, which changes from positive to negative near $x \approx 0.015$ [figure 3.13(e)]. Since our neutron Larmor diffraction measurements were carried out using polarized neutron beam produced by an Heusler monochromator, which has an energy resolution of about $\Delta E \approx 1.0$ meV [62, 55], the local orthorhombic distortions captured in our measurements are either static or fluctuating slower than a time scale of $\tau \sim h/2\Delta E \sim 0.3$ ps, where $h$ is the reduced Planck constant [63, 64]. One possible origin of such slow fluctuations may be in-plane transverse acoustic phonons that exhibit significant softening in the paramagnetic tetragonal phase when approaching a nematic instability [65]. Future neutron scattering experiments with energy resolutions much better than $\Delta E \approx 1$ meV are desirable to separate the static and slowly fluctuating contributions and elucidate the relationship between the observed local orthorhombic distortion and in-plane transverse acoustic phonon anomaly. Our results also indicate that the nematic QCP would occur at a $x$ value that is distinctively larger than that of the magnetic QCP.
Figure 3.14: The phase diagram of NaFe$_{1-x}$Ni$_x$As determined from neutron scattering measurements. (a) The phase diagram of NaFe$_{1-x}$Ni$_x$As. $T_s$, $T_N$ and $T_c$ are the transition temperatures for the tetragonal-to-orthorhombic structural phase transition, the AF phase transition and the superconducting transition. The vertical errors represent our estimated temperature uncertainties of $T_s$, $T_N$, and $T_c$. The point for $x = 0$ is obtained from Ref. [41]. (b) The Ni-doping dependence of the ordered magnetic moment and orthorhombic distortion $\delta$ at $T = 5$ K, and $T = T_c$ for superconducting samples. The error bars in (a) are estimated errors from fits to order parameters and transition temperatures.
absence of superconductivity. In the phase diagram of iron pnictides with decoupled $T_s$ and $T_N$, due to the competition between superconductivity with both nematic and magnetic orders, magnetic order forms a hump peaked at $T_c$ near optimal doping [figure 3.14(a)], and the structural phase transition disappears in a similar fashion at a larger $x$.

Theoretically, a determinantal quantum Monte Carlo study of a two-dimensional sign-problem-free lattice model reveals an Ising nematic QCP in a metal at finite fermion density [66]. In the nematic phase, the discrete lattice rotational symmetry is spontaneously broken from four fold to two fold, and there are also nematic quantum critical fluctuations above the nematic ordering temperature. Within the numerical accuracy of the determinantal quantum Monte Carlo study, the uniform nematic susceptibility above the nematic ordering temperature has a Curie-Weiss temperature dependence, signaling an asymptotic quantum critical scaling regime consistent with our observation [66]. Alternatively, the observed Curie-Weiss temperature dependent behavior of the nematic susceptibility can be understood from spin-driven nematic order theory, where magnetic fluctuations associated with the static AF order induce formation of the nematic state [67]. In this picture, the effect of lattice strain coupled to the nematic order parameter produces a mean-field Curie-Weiss like behavior, arising from the nemato-elastic coupling which has direction-dependent terms in the propagator for nematic fluctuations. The Curie-Weiss temperature dependent nematic susceptibility should occur in the entire phase diagram where there is a significant softening of the elastic modulus [67]. This means that Curie-Weiss temperature dependence of the local orthorhombic distortions we observe is a signature of nemato-elastic coupling, which does not suppress the magnetic fluctuations that cause the nematic order, but transforms the Ising-nematic transition into a mean-field
transition [67].

Our discovery of local orthorhombic distortions exhibiting with Curie-Weiss temperature dependence across the phase diagram of NaFe$_{1-x}$Ni$_x$As results from the proliferation of nematic fluctuations and large nematic susceptibility near the nematic QCP. Quenched disorder that are always present in such doped materials act to pin the otherwise fluctuating local nematic domains, resulting in static (or quasi-static) local orthorhombic distortions that can lead to rotational-symmetry-breaking observation seen with multiple probes [28, 31, 29, 32, 33, 30, 34]. We have definitively observed local nematic distortions in NaFe$_{1-x}$Ni$_x$As that are static or quasi-static, in contrast to local distortions seen in Sr$_{1-x}$Na$_x$Fe$_2$As$_2$ using pair distribution function analysis that contain significantly more dynamic contributions [68], and which would not cause rotational-symmetry-breaking seen by static probes. Our observation of local nematic distortions highlights the presence of nematic fluctuations near the nematic QCP, which can play an important role in enhancing superconductivity of iron pnictides [69, 70, 22, 71], while the intense Ising-nematic spin correlations near the nematic QCP may be the dominant pairing interaction [72, 73, 74].

In this chapter, we use high-resolution neutron diffraction and neutron Larmor diffraction to map out the phase diagram of NaFe$_{1-x}$Ni$_x$As [75], focusing on the interplay between magnetic order, nematic order, and superconductivity near optimal superconductivity. Unlike most other iron pnictide systems, we find $T_N$ in NaFe$_{1-x}$Ni$_x$As to be continuously suppressed towards $T_N \approx T_c$ near optimal doping, while the order remains long-range and commensurate. This allows us to demonstrate that $T_s$ and $T_N$ in NaFe$_{1-x}$Ni$_x$As remain well-separated near optimal superconductivity, indicating distinct quantum critical points associated with nematic and AF orders similar to quantum criticality in electron-doped Ba$_2$Fe$_{2-x}$Ni$_x$As$_2$ [76]. Utiliz-
ing the high resolution provided by neutron Larmor diffraction [62, 55], we probed the nematic order parameter in underdoped NaFe$_{1-x}$Ni$_x$As below $T_s$ and surprisingly, uncovered local orthorhombic distortions well above $T_s$ and in overdoped samples without a structural phase transition. Although the average structure is tetragonal in these regimes, broadening of the d-spacing distribution is unambiguously observed. Such local orthorhombic distortions were hinted at in previous high-resolution neutron powder diffraction measurements on electron-overdoped NaFe$_{0.975}$Co$_{0.025}$As, where a small broadening of Bragg peaks at low temperature was observed [75]. Regardless of whether orthorhombic distortions are long-range due to a structural phase transition or local in nature, resulting from a large nematic susceptibility, we find that they become suppressed inside the superconducting state similar to AF order. Our results therefore elucidate the interplay between AF order, nematicity, and superconductivity in NaFe$_{1-x}$Ni$_x$As; at the same time, our observation of local orthorhombic distortions with a Curie-Weiss temperature dependence across the phase diagram accounts for rotational symmetry-breaking seen in nominally tetragonal iron pnictides. In addition, our measurements demonstrate that neutron Larmor diffraction can be used to determine the nematic susceptibility of free-standing iron pnictides without the need to apply external stress or strain. These results should stimulate future high-resolution neutron/X-ray diffraction work to study orthorhombic lattice distortion and its temperature dependence in the nominally tetragonal phase of iron-based superconductors.
Chapter 4

Short-range Magnetic Ordered Phase in Heavily Overdoped Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$

In this chapter, we investigate Cu-doped Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ with transport, magnetic susceptibility, and elastic neutron scattering [77] and time-of-flight neutron scattering measurements (unpublished). In the heavily Cu-doped regime where long-range stripe-type antiferromagnetic order in BaFe$_2$As$_2$ is suppressed, Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ (0.145 ≤ $x$ ≤ 0.553) samples exhibit spin-glass-like behavior in magnetic susceptibility and insulating-like temperature dependence in electrical transport. Using elastic neutron scattering, we find stripe-type short-range magnetic order in the spin-glass region identified by susceptibility measurements. The persistence of short-range magnetic order over a large doping range in Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ likely arises from local arrangements of Fe and Cu that favor magnetic order, with Cu acting as vacancies relieving magnetic frustration and degeneracy. Time-of-flight spectroscopy on Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ with $x$=0.316 reveals one-dimensional broad spin excitations. These results indicate locally broken four-fold rotational symmetry, suggesting that stripe-type magnetism is ubiquitous in iron pnictides.

4.1 Introduction

Superconductivity in iron pnictides such as BaFe$_2$As$_2$ and NaFeAs can be induced by substituting Fe with transition metals such as Co and Ni, which also suppresses the magnetic and structural phase transitions [78, 9, 79]. In the overdoped regime where
both the magnetic and structural transitions are suppressed, the system maintains average fourfold rotational symmetry without long-range magnetic order, although inelastic neutron scattering revealed substantial stripe-type fluctuations even in non-superconducting overdoped BaFe$_{1.7}$Ni$_{0.3}$As$_2$ [11]. For BaFe$_{2-x}$TM$_x$As$_2$ ($TM = \text{Co, Ni, Cu}$), while Co- and Ni-doping result in superconducting domes with optimal $T_c \sim 20 \text{ K}$, optimal $T_c \sim 2 \text{ K}$ or no superconductivity is observed in $A$Fe$_{2-x}$Cu$_x$As$_2$ ($A = \text{Ba, Sr}$) [80, 44, 81]. This contrast points to the inadequacy of a simple rigid band picture [82, 83, 84] and highlights differences between dopants [85, 39].

Compared to $A$Fe$_{2-x}$Cu$_x$As$_2$, superconductivity with optimal $T_c = 11.5 \text{ K}$ is observed in NaFe$_{1-x}$Cu$_x$As [47, 41]. With increasing Cu concentration ($x \gtrsim 10\%$), insulating-like transport and short-range magnetic order develop, evolving towards an insulator with long-range magnetic order and Fe-Cu ordering near $x \approx 50\%$ [86]. Evolution from metallic to insulating/semiconducting transport is also observed in Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ ($x \geq 0.145$), Sr(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ ($x \geq 0.06$) [81], Fe$_{1.01-x}$Cu$_x$Se ($x \geq 0.03$) [87, 88], and Fe$_{1+\delta-x}$Cu$_x$Te ($x \geq 0.06$) [89, 90]. The insulating transport in NaFe$_{1-x}$Cu$_x$As is a result of electron correlations [86, 91] facilitated by ordering of Fe and Cu into quasi-1D chains [86]. In contrast, disorder is suggested to be responsible for the insulating transport in Fe$_{1-x}$Cu$_x$Se [92].

In NaFe$_{1-x}$Cu$_x$As with short-range magnetic order, temperature-dependence of the magnetic order parameter is broad indicative of spin-glass (SG) behavior, commonly observed in doped strongly-correlated materials [93]. SG behavior seen in magnetization measurements is also reported for other heavily Cu-doped iron pnictides [47, 81] and chalcogenides [87, 88, 87, 90], pointing to the possible presence of short-range magnetic order. Importantly, in both $A$Fe$_{1-x}$Cu$_x$As$_2$ and NaFe$_{1-x}$Cu$_x$As where SG behavior is observed, doped Cu are in nonmagnetic $3d^{10}$ configuration
[81, 86] and therefore any SG or short-range magnetic order must be due to Fe. While the long-range magnetic and Fe-Cu orders in the ideal NaFe$_{0.5}$Cu$_{0.5}$As compound lacks four-fold rotational symmetry, there is so far no evidence of magnetic order or four-fold symmetry breaking in other iron pnictides and chalcogenides in the non-superconducting heavily overdoped regime.

Single crystal of Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ samples were prepared using the same self-flux method as for BaFe$_{2-x}$Ni$_x$As [94]. The Cu substitution levels reported in this paper were determined by inductively coupled plasma atomic-emission spectroscopy (ICP). Samples with nominal Cu concentrations of 10, 20, 30, 50 and 70% were prepared, resulting in actual Cu concentrations of $x = 14.5$, 25.4, 31.6, 44.7 and 55.3%.

Magnetic susceptibility measurements were carried out using a commercial superconducting quantum interference device magnetometer from Quantum Design, measurements were taken on warming with applied field $\mu_0 H = 1$T perpendicular to the c-axis. In-plane electrical resistivity measurements were carried out using the standard four-probe method on a commercial physical property measurement system from Quantum Design. Magnetic susceptibility results for Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ single crystals ($x = 0.316, 0.447$ and 0.553) with zero-field-cooling (ZFC) and field-cooling (FC) are shown in figure 4.1. The separation between ZFC and FC susceptibilities occurring at low temperatures indicates SG-like behavior, similar to other heavily Cu-doped iron pnictides and chalcogenides [47, 81, 89, 88, 87, 90].

The temperature dependence of the in-plane resistivity for Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ single crystals is shown in figure 4.2(a), and resistivity normalized to its room temperature value ($\rho/\rho_{300K}$) is shown in figure 4.2(b). The evolution from metallic to insulating-like transport with increasing Cu substitution is similar to Sr(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ [81]. Despite the insulating-like temperature dependence, the largest measured resis-
Figure 4.1: Magnetic susceptibility measurement for Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ with ZFC (open marks) and FC (solid marks).

...tivity for all samples is of the order $m\Omega \cdot \text{cm}$, smaller than resistivity in NaFe$_{1-x}$Cu$_x$As with $x \approx 50\%$ by three orders of magnitude [86].

Figure 4.2: (a) Temperature dependence of the in-plane electrical resistivity for Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ single crystals. (b) Temperature dependence of the resistivity normalized to its room temperature value.
4.2 Elastic Neutron Scattering Details

Elastic neutron scattering experiments were carried out using the SPINS triple-axis spectrometer (TAS) \((x = 0.145, 0.254, 0.316, 0.447, 0.553)\) at the NIST Center for Neutron Research, and the HB-1A TAS \((x = 0.553)\) at the High Flux Isotope Reactor, Oak Ridge National Laboratory. We used pyrolytic graphite \([\text{PG}(002)]\) monochromators and analyzers in all experiments. At SPINS, the monochromator is vertically focused and the analyzer is flat with fixed \(E_f = 3.7\) meV. At HB-1A, the monochromator is vertically focused with fixed incident neutron energy \(E_i = 14.6\) meV and the analyzer is flat. Be filter and PG filter were used at SPINS and HB-1A to avoid contamination from higher-order neutrons. The collimations of guide-40'-sample-40'-open and 40'-40'-sample-40'-80' were used at SPINS and HB-1A, respectively. Single-crystal neutron diffraction experiment on a \(x = 0.316\) sample was carried out using the four-circle diffractometer HB-3A at the High Flux Isotope Reactor, Oak Ridge National Laboratory. The data was measured at 5 K with a neutron wavelength of 1.003 Å from a bent Si(331) monochromator using an Anger camera detector.

While \(\text{Ba(Fe}_{1-x}\text{Cu}_x)_{2}\text{As}_2\) is tetragonal for \(x \gtrsim 0.05\) \([44]\), our results are reported using the orthorhombic structural unit cell of \(\text{BaFe}_{2}\text{As}_2\) \((a \approx b \approx 5.6\) Å and \(c \approx 12.9\) Å) \([95]\). The momentum transfer \(\mathbf{Q} = H\mathbf{a}^* + K\mathbf{b}^* + L\mathbf{c}^*\) is denoted as \(\mathbf{Q} = (H, K, L)\) in reciprocal lattice units (r.l.u.), where \(H, K, L\) are Miller indices and \(\mathbf{a}^* = \hat{a}2\pi/a, \mathbf{b}^* = \hat{b}2\pi/b\) and \(\mathbf{c}^* = \hat{c}2\pi/c\). In this notation, magnetic Bragg peaks in the parent compound \(\text{BaFe}_{2}\text{As}_2\) appears at \(\mathbf{Q} = (1, 0, L)\) with \(L = 1, 3, 5, \cdots\). Samples were aligned in the \([H, 0, 0] \times [0, 0, L]\) scattering plane, which allows scans along \(H\) and \(L\) centered at \(\mathbf{Q} = (1, 0, L)\). To carry out scans of the magnetic peak along \(K\) at \(\mathbf{Q} = (1, 0, 1)\), the \(x = 0.553\) sample was also studied in the \([H, 0, H] \times [0, K, 0]\) scattering plane [figure 4.3].
Figure 4.3: **Schematic of scattering plane.** Schematic of $[H, 0, L]$ and $[H, K, H]$ scattering planes that allow scans centered at $Q = (1, 0, 1)$ along $H$, $L$ and $K$ directions.

Elastic neutron scattering scans along $H$ and $L$ centered at $Q = (1, 0, 1)$ are summarized in figure 4.4(a) and (b) for Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ ($x = 0.145, 0.254, 0.316, 0.447, 0.553$). These results are measured in the $[H, 0, L]$ scattering plane using identical configurations on SPINS and backgrounds obtained at high temperatures have been subtracted. The relative intensities have been normalized by sample mass to allow for a direct comparison between different dopings. In the $x = 0.145$ sample, a weak peak centered at $Q = (1, 0, 1)$ can be readily seen. Increasing the Cu concentration to $x = 0.254$, magnetic order becomes significantly stronger. Upon further increasing Cu doping, the magnetic peaks become broader along both directions. Notably in the $x = 0.553$ sample, short-range magnetic order becomes almost independent of $L$, forming a rod of diffuse scattering in reciprocal space.

To extract the doping evolution of spin-spin correlation lengths, we fit the data in figure 4.4(a) and 4.4(b) using a lattice sum of Lorentzian peaks multiplied by the
Figure 4.4: (a) High-temperature-background-subtracted elastic scans of \( \mathbf{Q} = [1, 0, 1] \) along the \( H \) direction for \( \text{Ba(Fe}_{1-x}\text{Cu}_x\text{)}_2\text{As}_2 \) with \( x = 0.553, 0.447, 0.316, 0.254 \) and 0.145. Corresponding scans along \( L \) direction are shown in (b). Solid lines are fits with the lattice sum of Lorentzian peaks multiplied by the magnetic form factor. The results for different dopings are normalized by sample mass. (c) and (d) show spin-spin correlation lengths as a function of doping along \( H \) and \( L \). (f) Integrated magnetic intensity in the \([H, 0, L]\) plane as a function of doping, obtained from fitting results in (a) and (b). The error bars in (a) and (b) represent statistical error (1 s.d.). The error bars in (c), (d) and (f) are from least square fits (1 s.d.).
magnetic form factor

\[ I = F^2(Q) \sum_{x_c} \frac{h(\frac{Q}{2})^2}{(x - x_c)^2 + (\frac{Q}{2})^2} \]  

(4.1)

where \( F(Q) \) is the dimensionless magnetic form factor, \( x \) is either \( H \) or \( L \), \( h \) is the Lorentzian peak height, and \( \Gamma \) is the full width at half maximum (FWHM) for the Lorentzian peak. The summation is over \( x_c = \ldots, -5, -3, -1, 1, 3, 5, \ldots \), corresponding to magnetic Bragg peak positions in BaFe\(_2\)As\(_2\) along \( H \) and \( L \). Magnetic correlation lengths in units of Å\(^{-1}\) is obtained through \( \xi_H = \frac{a}{\pi \Gamma_H} \) along \( H \) and \( \xi_L = \frac{c}{\pi \Gamma_L} \) along \( L \) [96].

The resulting doping dependence of spin-spin correlation lengths along \( H \) and \( L \) are respectively shown in Fig. 4.4(c) and Fig. 4.4(d). Due to weak magnetic intensity, the correlation lengths for the \( x=0.145 \) sample cannot be reliably obtained. \( \xi_H > \xi_L \) is found for all measured samples, similar to short-range magnetic order in NaFe\(_{1-x}\)Cu\(_x\)As [86]. Increasing Cu concentration leads to a decrease of correlation lengths along both \( H \) and \( L \), in stark contrast to NaFe\(_{1-x}\)Cu\(_x\)As where correlation lengths increase monotonically with increasing Cu-doping [86]. This difference is likely due to Fe and Cu order in NaFe\(_{1-x}\)Cu\(_x\)As but not in Ba(Fe\(_{1-x}\)Cu\(_x\))\(_2\)As\(_2\).

Assuming the spin-spin correlation function in the \([H, 0, L]\) plane can be described by multiplying the correlation function along \([H, 0, 1]\) and \([1, 0, L]\) [obtained from fits in figure 4.4(a) and 4.4(b)], the integrated intensity of diffuse scattering in the \([H, 0, L]\) plane can be obtained. Two-dimensional (2D) plots of spin-spin correlation function in the \([H, 0, L]\) plane obtained this way are shown in figure 4.4(e) for \( x = 0.316 \) and \( x = 0.553 \) samples, and doping dependence of the integrated intensity in \([H, 0, L]\) plane is shown in figure 4.4(f). The integrated magnetic signal increases with Cu-doping, suggesting an enhanced magnetic moment on Fe due to hole doping of Cu similar to NaFe\(_{1-x}\)Cu\(_x\)As [86]. This conclusion also holds when \( \xi_K \) is taken into
consideration to obtain the integrated volume of diffuse scattering, assuming $\xi_K$ either evolves in a similar fashion as $\xi_H$ and $\xi_L$ with doping or depends weakly on doping. The increase of integrated diffuse scattering is likely a result of the hole-doping effect of Cu, which has $3d^{10}$ configuration in the heavily doped regime of iron pnictides [81, 86, 97].

The temperature dependence of magnetic intensity at $Q = (1, 0, 1)$ for different dopings is summarized in figure 4.5, with figure 4.5(a)-(e) obtained on SPINS with an energy resolution $\Delta E \approx 0.1$ meV and figure 4.5(f) measured on HB-1A with $\Delta E \approx 1$ meV. A clear but broad onset of magnetic intensities is observed in all cases, and the broad onset is consistent with SG-like behavior revealed by susceptibility measurements in figure 4.1. One feature of glassy magnetism is that the measured onset temperature of magnetic intensity depends on energy resolution [98, 43, 99]. To see if this is the case in $\text{Ba(Fe}_{1-x}\text{Cu}_x\text{)}_2\text{As}_2$, we compare measured temperature dependence on the same $x = 0.553$ sample using different instrument energy resolutions, as shown in figure 4.5(e) and (f). With the coarser energy resolution on HB-1A, an onset temperature of $T_N \approx 150$ K is obtained [figure 4.1(f)] compared to $T_N \approx 70$ K obtained with finer resolution [figure 4.1(f)], confirming the glassy nature of magnetism. While we only studied the $x = 0.553$ sample with different energy resolutions, we anticipate such a resolution-dependent onset temperature should be observed for all samples with $0.145 \leq x \leq 0.553$. The effect of energy resolution on the onset temperature in $\text{Ba(Fe}_{1-x}\text{Cu}_x\text{)}_2\text{As}_2$ is much more significant than what is seen in the cluster spin-glass phase of $\text{BaFe}_{2-x}\text{Ni}_x\text{As}_2$ [43], but comparable to Cu-Mn spin-glass alloys [99].

While the finding of short-range stripe-type AF order suggests the breaking of fourfold rotational symmetry, it is not conclusive evidence. For example, the double-$Q$ magnetic order that retains fourfold rotational symmetry in hole-doped iron pnictides
Figure 4.5: Order parameters in Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ Temperature dependence of magnetic intensity measured on SPINS at $Q = (1, 0, 1)$ for Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ with (a) $x = 0.145$, (b) $x = 0.254$, (c) $x = 0.316$, (d) $x = 0.447$ and (e) $x = 0.553$. (f) Temperature dependence for the $x = 0.553$ sample measured on HB-1A.
also results in magnetic peaks at the same ordering vector [100, 101, 102, 103]. A unique way to determine if there is breaking of rotational symmetry for short-range order is to examine the directional dependence of the spin-spin correlation lengths, as done for charge order in cuprates [104].

To compare the in-plane spin-spin correlation lengths, we carried out scans along $H$, $K$ and $L$ directions centered at $Q = (1, 0, 1)$ for the $x = 0.553$ sample. The measurements are done by mounting the sample in the $[H, 0, L]$ and $[H, K, H]$ scattering planes [figure 4.3], and are carried out using HB-1A. The results are summarized in figure 4.6 and fit using a lattice sum of Lorentzian peaks described above with backgrounds measured at $T = 200$ K subtracted from the data. For the in-plane longitudinal direction $H$ [figure 4.6(a)], magnetic signal is broad but relatively well-defined, resulting in a correlation length of $\xi_H \approx 11$ Å, in agreement with similar measurement on SPINS [figure 4.4(a)]. For the in-plane transverse direction $K$ [figure 4.6(b)], the signal is considerably broader resulting in $\xi_K \approx 2$ Å. We note this large difference of in-plane correlation lengths is intrinsic and unlikely to arise from strain. There is almost no modulation of intensity along $L$ as shown in figure 4.6(c), with the intensity gradually decreasing for increasing momentum transfer following the magnetic form factor, suggesting the magnetic moments are aligned in-plane perpendicular to the ordering vector, similar to heavily-doped NaFe$_{1-x}$Cu$_x$As [86].

To compare with NaFe$_{1-x}$Cu$_x$As system directly, we perform identical measurements on NaFe$_{0.61}$Cu$_{0.39}$As at HB-1A. The results are summarized in figure 4.7, and solid lines are fits with the lattice sum of Lorentzian peaks multiplied by the magnetic form factor (equation (4.1)).

Figure 4.8 summarizes the overall phase diagram of Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$. The stripe-type AF order in BaFe$_2$As$_2$ is suppressed at $x \approx 5\%$ [44]. For samples with $x \gtrsim$
Figure 4.6: Elastic scans along $H$, $K$, and $L$ in Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ with $x = 0.553$. High-temperature-background-subtracted elastic scans along (a) $H$, (b) $K$ and (c) $L$ directions for the $x = 0.553$ sample measured on HB-1A. Solid lines are fits with the lattice sum of Lorentzian peaks multiplied by the magnetic form factor. The error bars represent statistical error (1 s.d.).
0.1, we detected the presence of short-range magnetic order occurring at the stripe-type ordering vector, with the onset temperatures determined from elastic neutron order parameter measurements on SPINS [4.5(b)-(f)].

4.3 Inelastic Neutron Scattering Details

Having mapped out the phase diagram of heavily overdoped Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$, it is interesting to map out the entire magnetic spectrum of these compounds and compare that with magnetic excitations of BaFe$_2$As$_2$ and heavily overdoped NaFe$_{1-x}$Cu$_x$As. We synthesized and co-aligned 11.26 grams of Ba(Fe$_{0.68}$Cu$_{0.316}$)$_2$As$_2$. We carried out INS experiments using the MAPS chopper spectrometer at the Rutherford-Appleton Laboratory. The TOF experiments used incident neutrons parallel to the c axis ($k_i \parallel c$) with incident energies $E_i = 80$, 250, and 450 meV with corresponding Fermi chopper frequencies $\omega = 250$, 350, 600 Hz, respectively. Similar to section 4.2, we report our results with orthorhombic notation where $a = b = 5.699$ and $c = 12.72$.

Before examining the experiment results, I introduce the data analysis procedure in TOF experiments with $k_i \parallel c$. As discussed in section 1.4.2, energy $E$ of mag-
Figure 4.8: The phase diagram of Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$. The phase diagram of Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$. The region with $x \lesssim 0.1$ is obtained from reference [44]. The onset temperature of short-range magnetic order on the overdoped side are measured with an energy resolution $\Delta E \approx 0.1$ meV using SPINS. Error bars are estimated uncertainties of the onset temperature of short-range magnetic order.
getic excitations is coupled with $L$ in such experiment configuration, and data are commonly presented in 2-dimensional slices in $[H, K]$ plane by binning $L$ and $E$. Typical background subtraction consists masking signals, fitting background, subtracting background, symmetrizing data, smoothing output figure and cutting subtracted data. Data analysis procedures are demonstrated with data collected at 10K at $E = [30, 50]$ meV with $E_i = 250$ meV in $\text{Ba(Fe}_{0.684}\text{Cu}_{0.316})_2\text{As}_2$.

- **Masking signals** We can roughly estimate magnetic signal areas in the raw data (figure 4.9(a)), and mask these areas manually. Figure 4.9(b) presents the data after masking, and we assume that all remain points are pure background. Since the signals at high energies are usually much broader than those at low energies, signal masks are commonly larger on analyzing high energy data sets.

- **Fitting background** We assume the background signals (figure 4.9(b)) is radially symmetric. We integrate all these data points as a function of $|Q|$ (figure 4.9(c)), and we fit these points with a polynomial function. The polynomial order is manually chosen. We usually use high order ($n = 2, 3, 4, 5, 6$) polynomial for low energy background, and flat line ($n = 0$) for high energy background. The blue line in figure 4.9 shows $n = 6$ order polynomial fitting.

- **Subtracting background** The fitting background model is applied to raw data (figure 4.9(a)), and we can get subtracted data set (figure 4.9(d)).

- **Symmetrizing data (Optional)** To improve the data statistics, we can utilize the underlying sample symmetry and fold data from same origin together. In $\text{Ba(Fe}_{1-x}\text{Cu}_x)_2\text{As}_2$, measured data has four-fold symmetry, i.e. magnetic signals at $(1,0)$, $(-1,0)$, $(0,1)$ and $(0,-1)$ have the same origin. In figure 4.9(e), we fold data along diagonal lines, and the data in black margins are unique.

- **Smoothing figure (Optional)** We convolve a $3 \times 3$ weighted matrix with
analysis data once to reduce the noise. (figure 4.9(f)).

- **Cutting subtracted data** One dimensional cut on subtracted data are commonly performed to make sure the background subtraction is neither over- nor under-fitted. Figure 4.9(g) and (h) shows the longitudinal and transverse cuts of the magnetic signals separately. And these two cuts are marked with orange and brown lines in figure 4.9(e).

Background subtracted magnetic excitations are summarized in figure 4.10. Similar to the magnetic order in this system, magnetic excitations are highly anisotropic in $[H,K]$ plane, and the correlation length along longitudinal direction is longer than that along transverse direction in all measured energies (figure 4.10). Magnetic signals broaden in both directions with increasing energy. On increasing energy to $E = 60\pm 10$ meV, spin excitations begin to fill entire Brillouin zone along transverse direction (figure 4.10(e)). Moreover, magnetic excitations eventually become completely flat along transverse direction on $E = 110\pm 10$ meV (figure 4.10(h)).

To understand how spin excitations evolve with energy, we make a series of cuts on images of spin excitations in figure 4.10 along the longitudinal $[H, 0]$ direction (orange line in figure 4.9(e)) and the transverse $[1, K]$ direction (brown line in figure 4.9(e)). The cuts are summarized in figure 4.11. The peak along longitudinal and transverse direction can be described with Gaussian function (equation (4.2)) and sum of Gaussian peaks (equation (4.3)) separately.

\[
I = h \exp \left( -4 \log(2) \left( \frac{x - x_c}{\Gamma} \right)^2 \right) \tag{4.2}
\]

\[
I = h \sum_{x_c} \exp \left( -4 \log(2) \left( \frac{x - x_c}{\Gamma} \right)^2 \right) \tag{4.3}
\]
Figure 4.9: TOF data analysis demonstration (a) Raw data collected at 10K at $E = [30, 50]$ meV with $E_i = 250$ meV in Ba(Fe$_{0.684}$Cu$_{0.316}$)$_2$As$_2$. (b) Masked data. (c) Background intensity as a function of $|Q|$ and polynomial fitting ($n = 6$) is marked in the figure (blue line). (d) Background subtracted data from (a) with fitting model in (c). (e) Data are folded along diagonal lines. Data within black margins are unique. (f) shows smoothed figure by convolving a $3 \times 3$ matrix once with (e). (g) and (h) shows the longitudinal and transverse cuts of the magnetic signals separately. The cut directions are marked with orange and brown lines separately in (e). Red lines are fittings discussed in main text.
Figure 4.10: Constant-energy slices of magnetic excitations in Ba(Fe$_{0.684}$Cu$_{0.316}$)$_2$As$_2$. Data is obtained by measuring with $k_i||c$, and data within the energy ranges $E = 7.5 \pm 2.5$, $15 \pm 5$, $25 \pm 5$, $40 \pm 10$, $50 \pm 10$, $80 \pm 10$, $100 \pm 10$ and $110 \pm 10$ are binned shown in (a) through(h). The data have been folded along diagonal lines and only data within black margins are unique. The intensities are normalized to absolute units of mbarn-steradian$^{-1}$·meV$^{-1}$·f.u.$^{-1}$. The purple box in (a) shows the integrate area for dynamic susceptibility measurements.
where \( h \) is the Gaussian peak height and \( \Gamma \) is the full width at half maximum for Gaussian peak. The summation in equation (4.3) is over \( x_c = \ldots, -4, -2, 0, 2, 4, \ldots \), corresponding to peak centers of magnetic scattering along transverse directions. The fittings are shown as solid lines in figure 4.11.

The fit Gaussian peak widths from figure 4.11 are summarized in figure 4.12. The cuts confirm that magnetic signals in this system along both directions become broader with increasing energy, and no peak splitting is observed in all measured energies.

Local dynamic spin susceptibility can be calculated from background subtracted data (figure 4.10(e)) with method described in [9, 105]. We integrate background subtracted intensities in one Brillouin zone (purple box in figure 4.10(a)). Assuming the magnetic excitation is isotropic, we have

\[
\frac{d^2\sigma}{d\Omega dE} = \frac{2(\gamma r_0)^2 k_f}{\pi g^2 \mu_B^2 k_i} |F(Q)|^2 \frac{\chi''(q, \omega)}{1 - \exp(-\hbar\omega/kT)}
\]  

(4.4)

where \( \gamma = 1.913 \), \( r_0 = 2.828 \times 10^{-15} \text{m} \), \( k_i \) and \( k_f \) are the incident and scattered neutron wave vectors, and \( |F(Q)|^2 \) is the isotropic magnetic form factor for a Fe\(^{2+}\) orbital. In practice, original data are normalized to an absolute scale (mbarn-steradian\(^{-1}\).meV\(^{-1}\).f.u.\(^{-1}\)) by comparing the count rate with that from vanadium standard measurement. The factor \( \frac{k_f}{k_i} \) is also reduced in standard normalization process at the MAPS spectrometer.

Energy dependence of the measured local dynamic spin susceptibility for Ba(Fe\(_{0.684}\)Cu\(_{0.316}\))\(_2\)As\(_2\) is plotted in figure 4.13(a). To compare with the local dynamic spin susceptibility in parent compound BaFe\(_2\)As\(_2\), we use the same script to recalculate that from raw data collected in [106], and our calculated results is consistent with reference [106]. Our collaborator performs a combined density functional theory (DFT) and dynamical
Figure 4.11: **Longitudinal and transverse cuts of magnetic excitations in Ba(Fe$_{0.684}$Cu$_{0.316}$)$_2$As$_2$.** Cuts on images of spin excitations in figure 4.10 along the longitudinal $[H, 0]$ direction (orange dashed line in figure 4.9(e)) and the transverse $[1, K]$ direction (brown dashed line in figure 4.9(e)). Cuts for the energy ranges $E = 7.5 \pm 2.5, 15 \pm 5, 25 \pm 5, 40 \pm 10, 50 \pm 10, 80 \pm 10, 100 \pm 10$ and $110 \pm 10$ are shown in (a) through (p). Transverse cuts are shown in left panels, and solids lines are fits to sum of Gaussian peaks. Longitudinal cuts are shown in right panels, and solid lines are fits to Gaussian peak.
Figure 4.12: Fitted peak width of magnetic excitation peaks along longitudinal and traverse direction in Ba(Fe$_{0.7}$Cu$_{0.3}$)$_2$As$_2$. The points are obtained from fits shown in figure 4.11, with error bars are from least square fits (1 s.d.).

4.4 Discussion

We first exam the results in magnetic elastic measurements. One of the key differences between Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ and NaFe$_{1-x}$Cu$_x$As is that Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ can potentially form As-As covalent bonding along $c$-axis, which is impossible in the case of NaFe$_{1-x}$Cu$_x$As [86]. With increasing Cu-doping, the As-As distance decreases and Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ eventually forms a non-magnetic $sp$ metal with significantly reduced $c$-axis lattice parameter when Fe is entirely replaced by Cu [107]. For the doping range studied in this work, while the $c$-axis lattice parameter reduces with increasing $x$, extrapolating to $x = 1$ using data for $x \lesssim 0.5$ results in a much larger
Figure 4.13: Energy dependence of local dynamic spin susceptibility for \( \text{Ba(Fe}_{0.684}\text{Cu}_{0.316})_{2}\text{As}_{2} \) and \( \text{BaFe}_{2}\text{As}_{2} \). (a) \( \text{BaFe}_{2}\text{As}_{2} \) points are recalculated from raw data in reference \([106]\) with the method described in main text. The calculated result of \( \text{BaFe}_{2}\text{As}_{2} \) is consistent with published results in \([106]\). Horizontal errorbar stands for the energy bin range, and vertical errorbar is statistical error (1 s.d.). (b) DFT+DMFT calculation results for dynamic spin susceptibility in \( \text{Ba(Fe}_{0.684}\text{Cu}_{0.316})_{2}\text{As}_{2} \) and \( \text{BaFe}_{2}\text{As}_{2} \).

c-axis lattice parameter than what is found in \( \text{BaCu}_{2}\text{As}_{2} \) \([107]\), as shown in figure 4.14(a).

Similar to reference \([107]\), we calculate interlayer and intralayer distances between arsenic layers, as defined in figure 4.16(a). \( \text{BaFe}_{2}\text{As}_{2} \) lattice parameters and atom relative position \( (z_{x}) \) at \( T = 5 \text{ K} \) are from ref. \([95]\) and \( \text{BaCu}_{2}\text{As}_{2} \) lattice parameters and \( z_{x} \) at \( T = 300 \text{ K} \) are from ref. \([107]\). \( z_{x} \) for \( x = 0.316 \) sample is refined from single crystal neutron diffraction at HB-3A at 5K. Since \( z_{x} \) for \( x = 0 \) and \( x = 0.316 \) are quite close, we believe that \( z_{x} \) doesn’t vary much and use \( z_{x} \) for \( x = 0.316 \) sample for all other heavily doped samples. The results are summarized in figure 4.15. The linear change of intralayer \( d_{\text{As–As}} \) is a result of ion radius difference of Fe and Cu ions, and the sudden change of interlayer \( d_{\text{As–As}} \) in \( \text{BaCu}_{2}\text{As}_{2} \) suggests the formation of As-As covalent bonding.
This suggests while there may be some degree of covalent bonding in our samples, full covalent bonding as in BaCu₂As₂ has not developed. This suggests similar to NaFe<sub>1-x</sub>Cu<sub>x</sub>As, Cu-doping in Ba(Fe<sub>1-x</sub>Cu<sub>x</sub>)₂As₂ also increases the valence of Fe, although possibly to a lesser degree. This can also be seen in the doping dependence of Ba(Fe<sub>1-x</sub>Cu<sub>x</sub>)₂As₂ unit cell volume in figure 4.14(b).

The highly anisotropic in-plane static correlation lengths ξ<sub>H</sub> and ξ<sub>K</sub> demonstrate that short-range magnetic order in Ba(Fe<sub>1-x</sub>Cu<sub>x</sub>)₂As₂ breaks four-fold rotational symmetry of the lattice. The order of correlation lengths in the x = 0.553 sample is ξ<sub>H</sub> > ξ<sub>K</sub> > ξ<sub>L</sub>, identical to short-range magnetic order in NaFe₀.₆₁Cu₀.₃₉As (figure 4.7), suggesting a similar origin of magnetic order in both systems. Magnetic order in NaFe<sub>1-x</sub>Cu<sub>x</sub>As becomes long-range when x ≈ 50% with Fe and Cu ordering into quasi-1D chains, resulting in super-lattice structural peaks persisting at room temperature [86]. In Ba(Fe<sub>1-x</sub>Cu<sub>x</sub>)₂As₂, we did not detect any super-lattice peaks for the x = 0.316 sample on HB-3A, suggesting Cu to be much more disordered. Fe-Cu or-
Figure 4.15: Doping dependence of arsenic layer distances in Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$. $z_x$ in BaFe$_2$As$_2$ at $T = 5$ K are from ref. [95] and $z_x$ in BaCu$_2$As$_2$ at $T = 300$ K are from ref. [107]. $z_x$ in $x = 0.316$ sample is refined from single crystal neutron diffraction at HB-3A at 5K. $z_x$ in all other heavily doped sample are assumed to be identical as that in $x=0.316$.

Figure 4.16: Crystal Structure of Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$. (a) Using the orthorhombic structural unit cell of BaFe$_2$As$_2$. Interlayer and intralayer As-layer distance is defined [107]. (b) Exchange couplings are defined for the Fe/Cu-plane on the right of the unit cell.
dering in NaFe\(_{1-x}\)Cu\(_x\)As reduces hopping between Fe ions [86], and its absence likely contributes to the much smaller resistivity in Ba(Fe\(_{1-x}\)Cu\(_x\))\(_2\)As\(_2\).

While there may be weak Fe-Cu ordering in Ba(Fe\(_{1-x}\)Cu\(_x\))\(_2\)As\(_2\) that is hard to pick up in diffraction measurements, it is likely short-range magnetic order can exist even when Cu and Fe are completely disordered. This is because in an disordered system there can be regions with local arrangements of Fe and Cu that are favorable for stabilizing magnetic order. In the \(J_1 - J_2\) description of magnetism in iron pnictides [108], the nearest-neighbor coupling \(J_1\) and next-nearest-neighbor coupling \(J_2\) [figure 4.16(b)] are frustrated, and lead to stripe-type AF order with two degenerate grounds states. Because Cu is non-magnetic and effectively act as vacancies in the heavily-doped regime, for certain arrangements of Fe and Cu [such as, but not limited to, Fe-Cu ordering in NaFe\(_{1-x}\)Cu\(_x\)As], the frustration can be relieved and the degeneracy removed, favoring a magnetically ordered state. But because Fe and Cu are overall mostly disordered, such favorable Fe and Cu configurations can only be realized over short length scales, resulting in glassy short-range magnetic order that we observe. The decrease of correlation lengths with increasing Cu concentration [figure 4.4(c) and (d)] is consistent with this picture.

Now, we discuss our inelastic results. Figure 4.17 summarizes the low energy and high energy magnetic excitations of BaFe\(_2\)As\(_2\) [106], NaFe\(_{0.5}\)Cu\(_{0.5}\)As [109] and Ba(Fe\(_{0.684}\)Cu\(_{0.316}\))\(_2\)As\(_2\). In most electron-doped iron pnictides such as NaFeAs, BaFe\(_2\)As\(_2\), SrFe\(_2\)As\(_2\), low energy magnetic excitations are transversely elongated (figure 4.17(a)). This effect can be interpreted with localized moment model, where the largest exchange coupling in this system is antiferromagnetic coupling \(J_{1a}\) [110]. A Dispersion of magnetic excitation along transverse direction can be clearly resolved in BaFe\(_2\)As\(_2\), while no peaks splitting (figure 4.11) is observed in constant-\(Q\) cuts in
Ba(Fe$_{0.684}$Cu$_{0.316}$)$_2$As$_2$ in all measured energies. This suggests that the magnetic signals in Ba(Fe$_{0.684}$Cu$_{0.316}$)$_2$As$_2$ and BaFe$_2$As$_2$ have different origins.

Low energy magnetic excitations in NaFe$_{0.5}$Cu$_{0.5}$As stem from magnetic Bragg peaks $Q = (1, 0, 0.5)$ and $(1, 1, 0)$, so both (1,0) and (1,1) exhibit magnetic excitation in figure 4.17(b). The excitations become less transversely-dependent with increasing energy, and they become completely flat along transverse direction at high energies. Moreover, clear dispersion can be resolved along longitudinal direction. These results can be interpreted with unique magnetic structure in NaFe$_{0.5}$Cu$_{0.5}$As where one dimensional Fe chains are well separated by non-magnetic Cu chains. The whole magnetic spectrum can be interpreted with local moment exchange coupling picture [109]. Given that magnetic order in Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ and NaFe$_{1-x}$Cu$_x$As have same origins, magnetic excitations in Ba(Fe$_{0.684}$Cu$_{0.316}$)$_2$As$_2$ can be understood similar to NaFe$_{1-x}$Cu$_x$As. We propose that the flat magnetic excitation along transverse direction also come from one dimensional Fe chain, and the absence of dispersion along longitudinal direction is a result of randomness of Fe, Cu ordering. Our magnetic excitation is a direct result of local breaking of four-fold rotational symmetry by short-range magnetic order.

Compare with BaFe$_2$As$_2$, the magnetic dynamic susceptibility in Ba(Fe$_{0.684}$Cu$_{0.316}$)$_2$As$_2$ has lower spin-wave bandwidth. The reduced spin-wave band width upon Cu doping is due to the increased electronic correlation strength of the conducting 3d electron upon Cu doping. Cu ion is close to 3d$^{10}$, which effectively drives Fe ion from 3d$^6$ towards 3d$^5$. This results in increased Fe 3d electronic correlation strength and reduced Fe 3d band width, which leads to reduced spin-wave band width. Moreover, the spin excitation intensity upon Cu doping is also reduced. This is a result of two factors. First, more than 30 percent Fe ions are replaced with Cu, and Cu is nonmag-
Figure 4.17: Comparison of inelastic magnetic scattering between BaFe$_2$As$_2$, NaFe$_{0.5}$Cu$_{0.5}$As and Ba(Fe$_{0.684}$Cu$_{0.316}$)$_2$As$_2$. BaFe$_2$As$_2$ schematic is drafted based on data in [106], and NaFe$_{0.5}$Cu$_{0.5}$As is based on [109].
netic. The overall spin excitation is reduced by 30 percent as only 70 percent of all lattice sites contributes to spin excitations. Second, since Cu doesn’t contribute to the Fermi surfaces and the electronic states around the Fermi level, Cu doping results in a reduction of the density of states (DOS) around Fermi level. This results in an additional reduction of the bare spin susceptibility $\chi_0$ and consequently the total spin susceptibility.

We have observed emergence of stripe-type short-range magnetic order due to the presence of effective vacancies in the system, different from the appearance of stripe-type long-range order in lightly-doped BaFe$_2$As$_2$ through an Ising-nematic state. The robustness of stripe-type magnetism suggests it is an inherent instability of the FeAs-plane and may be the driving force of physics in iron pnictides. Given similar susceptibility and transport behaviors seen in several other Cu-doped iron pnictide and chalcogenide systems [81, 89, 88, 87, 90], it is probable stripe-type short-range magnetic order is also present in those systems.

4.5 Conclusion

We investigate heavily overdoped Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ with electrical transport, magnetic susceptibility, elastic and inelastic neutron scattering measurements. Similar to other Cu-doped iron pnictides and chalcogenides, Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ shows insulating and SG behaviors in the heavily overdoped regime. Using elastic neutron scattering, we have found short-range magnetic order in Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ ($0.145 \leq x \leq 0.553$) over an extremely large doping range. Different in-plane correlation lengths of the short-range magnetic order point to locally broken four-fold rotational symmetry. Our time-of-flight inelastic neutron measurements map out the whole magnetic spectrum in Ba(Fe$_{0.684}$Cu$_{0.316}$)$_2$As$_2$, and find both spin-wave band width and spin excitation
intensities reducing with Cu doping. Our results suggest magnetic order/excitation in Ba(Fe$\text{1-x}^{\text{Cu}_{x}}$)$_{2}$As$_{2}$ have the same origins as that in NaFe$_{1-x}^{\text{Cu}_{x}}$As. Our finding suggests stripe-type magnetism to be a robust ground state in iron pnictides. Our discovery of short-range magnetic order in Ba(Fe$_{1-x}^{\text{Cu}_{x}}$)$_{2}$As$_{2}$ reveals an inherent instability towards stripe-type magnetic order and highlights the role of magnetic frustration in iron pnictides.
Chapter 5

Orbital selective neutron spin resonance in underdoped superconducting NaFe$_{0.985}$Co$_{0.015}$As

In this chapter, we use neutron scattering to study the electron-doped superconducting NaFe$_{0.985}$Co$_{0.015}$As ($T_c = 14$ K), which has co-existing static antiferromagnetic (AF) order ($T_N = 31$ K) and exhibits two neutron spin resonances ($E_{r1} \approx 3.5$ meV and $E_{r2} \approx 6$ meV) at the in-plane AF ordering wave vector $Q_{AF} = Q_1 = (1, 0)$ in reciprocal space. In the twinned state below the tetragonal-to-orthorhombic structural transition $T_s$, both resonance modes appear at $Q_1$ but cannot be distinguished from $Q_2 = (0, 1)$. By detwining the single crystal with uniaxial pressure along the orthorhombic $b$-axis, we find that both resonances appear only at $Q_1$ with vanishing intensity at $Q_2$. Since electronic bands of the orbital $d_{xz}$ and $d_{yz}$ characters split below $T_s$ with the $d_{xz}$ band sinking $\sim 10$ meV below the Fermi surface, our results indicate that the neutron spin resonances in NaFe$_{0.985}$Co$_{0.015}$As arise mostly from quasi-particle excitations between the hole and electron Fermi surfaces with the $d_{yz}$ orbital character.

5.1 Introduction

Understanding the role of magnetism in the electron pairing of unconventional superconductors such as copper oxides, iron pnictides, and heavy Fermions continues to be an important topic in modern condensed matter physics because superconductivity in these materials is derived from their long-range antiferromagnetic (AF) ordered
parent compounds [72, 111, 9, 112]. One of the key evidences suggesting that magnetism is involved in the electron pairing and superconductivity is the observation by inelastic neutron scattering (INS) of a neutron spin resonance in the superconducting state of various unconventional superconductors [113, 114, 115, 116, 117, 118, 119, 120, 52, 121, 122, 123]. The resonance is a collective magnetic excitation occurring below the superconducting transition temperature $T_c$ with a temperature-dependence similar to the superconducting order parameter, and is located at the AF ordering wave vector $Q_{AF}$ of their parent compound [113, 114, 115, 116, 117, 118, 119, 120, 52, 121, 122, 123]. Moreover, the energy of the resonance has been associated with $T_c$ or superconducting gap size $\Delta$ [124, 125].

In iron pnictide superconductors, the resonance is generally interpreted as a spin exciton arising from sign-reversed quasiparticle excitations between the hole (at $\Gamma$ point) and electron (at $X$ and $Y$ points) Fermi surfaces [figure 5.2(a)] [126, 127]. In reciprocal space, the $\Gamma - X$ and $\Gamma - Y$ Fermi surface nesting corresponds to wave vectors of $Q_1 = (1, 0)$ and $Q_2 = (0, 1)$, respectively [figure 5.2(b)]. If this is indeed the case, one would expect that significant modifications of the Fermi surfaces should affect the wave vector dependence and energy of the resonance [9].

In electron-doped superconducting NaFe$_{1-x}$Co$_x$As [figure 5.1] [75, 48, 128, 41], INS experiments have mapped out the Co-doping dependence of the resonance [119, 120, 52]. For underdoped NaFe$_{0.985}$Co$_{0.015}$As with $T_c = 14$ K and a tetragonal-to-orthorhombic structural transition below $T_s \approx 40$ K, where the static long-range AF order ($T_N = 31$ K) microscopically coexists with superconductivity [120, 129, 130, 131], superconductivity induces one dispersive sharp resonance near $E_{r1} = 3.5$ meV and a broad dispersionless mode at $E_{r2} = 6$ meV at a wave vector consistent with $Q_{AF} = Q_1 = (1, 0)$ but cannot be distinguished from $Q_2 = (0, 1)$ [120]. Although
nuclear magnetic resonance (NMR) measurements on NaFe$_{1-x}$Co$_x$As suggested the presence of a 8% volume fraction paramagnetic phase for $x < 0.0175$ samples that is doping independent [131], the bulk nature of neutron scattering does not allow us to separate this phase from the dominant AF phase. Upon further Co-doping to reach optimal superconductivity without static AF order, the double resonances in NaFe$_{1-x}$Co$_x$As become a single resonance [119, 120, 52]. Since the disappearance of the double resonances occurs at approximately the same doping level as the vanishing static AF order with increasing Co-doping [119, 120, 52], the presence of double resonances has been interpreted as due to the coexisting AF order and superconductivity [132, 133]. In this picture, one would expect that the resonance associated with the AF order to exclusively appear at $Q_{AF} = Q_1 = (1, 0)$ in a completely detwinned sample as the collinear AF order explicitly breaks the $C_4$ rotational symmetry of the orthorhombic lattice [see inset of figure 5.1], while the resonance associated with itinerant electrons and simple nested Fermi surfaces (without considering the inter- and intra- orbital scattering processes) should be present at both $Q_{AF} = Q_1$ and $Q = Q_2$ [figure 5.2(a)] [132, 133].

Alternatively, the presence of double resonances can arise from orbital-selective pairing-induced superconducting gap anisotropy [134]. From angle resolved photoemission spectroscopy (ARPES) experiments [20, 21, 135], it was found that the superconducting gap anisotropy appearing in the low Co-doping regime of NaFe$_{1-x}$Co$_x$As disappears in electron overdoped NaFe$_{0.955}$Co$_{0.045}$As [136, 137]. The double resonances at $Q_{AF} = Q_1$ in underdoped NaFe$_{1-x}$Co$_x$As can therefore be due to the presence of superconducting gap anisotropy in the underdoped regime [120]. Since AF order is not expected to affect the superconducting gap anisotropy, one would expect the presence of the double resonances at $Q_{AF} = Q_1$ and $Q = Q_2$ in a detwinned single crystal
Figure 5.1: The phase diagram of NaFe\(_{1-x}\)Co\(_x\)As. The arrow indicates the Co-doping concentration in our experiment. The inset shows positions of magnetic excitations in the [\(H, K\)] plane under uniaxial pressure along the \(b\)-axis.

Figure 5.2: Schematic of Fermi surface in NaFe\(_{0.985}\)Co\(_{0.015}\)As in the paramagnetic tetragonal state. (a) Different orbitals are characterized with different colors. The arrows mark nesting wave vectors \(Q_1 = (1,0)\) and \(Q_2 = (0,1)\). (b) Schematic \(d_{yz}\) and \(d_{xz}\) orbital bands in NaFe\(_{1-x}\)Co\(_x\)As above and below \(T_s\) as seen by ARPES [20, 21].
of NaFe$_{0.985}$Co$_{0.015}$As [134]. Therefore, by using uniaxial pressure to detwin the single crystal [138, 139, 140, 18], one can potentially determine the microscopic origin of the double resonances [141]. In previous INS experiment on partially detwinned NaFe$_{0.985}$Co$_{0.015}$As, it was reported that the double resonance are present with similar intensity at both $Q_{AF} = Q_1$ and $Q = Q_2$, thus suggesting that the double resonance originates from the anisotropic superconducting gap in the underdoped regime [141]. However, the detwinning ratio of studied compound was estimated from two separate experiments under possibly not identical pressure condition. In addition, due to the large background level at the elastic scattering channel originated from the pressure device in the experiment, the reported detwinning ratio in [141] is likely to be overestimated. Therefore, to conclusively determine the effect of detwinning and uniaxial pressure on the resonance, one needs to carry out INS experiments by comparing directly pressured and pressureless case using the same sample holder with the same spectrometer setup.

If we assume that low energy spin excitations in iron pnictides originate from quasi-particle excitations between hole and electron Fermi surfaces [figure 5.2(a)], the orbital characters of hole and electron Fermi surfaces should determine the nature of observed spin excitations at $Q_1$ and $Q_2$ [126, 127]. For example, INS experiments on LiFe$_{1-x}$Co$_x$As system reveal that transverse incommensurate spin excitations observed in superconducting LiFeAs [142, 143] change to commensurate spin excitations for nonsuperconducting LiFe$_{0.88}$Co$_{0.12}$As arising mostly from the hole-electron Fermi surface nesting of the $d_{xy}$ orbitals, thus suggesting that Fermi surface nesting conditions of the $d_{yz}$ and $d_{xz}$ orbitals are important for superconductivity [144]. In the case of NaFe$_{1-x}$Co$_x$As [75, 48, 41, 128], ARPES measurements on uniaxial pressure detwinned single crystals reveal the splitting of the $d_{xz}$ and $d_{yz}$ orbitals at temper-
atures below $T_s$ (although in case of large pressure, the splitting actually first takes place at temperatures above $T_s$), where the bands of dominant $d_{yz}$ orbital character shift up in $\Gamma - X$ direction ($Q_1$) and bands of dominant $d_{xz}$ orbital character sink below Fermi surface in $\Gamma - Y$ direction ($Q_2$) [Figure 5.2(b)] [20, 21]. This means that low-energy spin excitations at wave vectors $Q_1$ and $Q_2$ should behave differently in the low-temperature superconducting state. Since bands of dominant $d_{yz}$ orbital characters sink below Fermi surface below $T_s$, neutron spin resonance associated with quasiparticle excitations of hole-electron Fermi surface $\Gamma$ at $Q_2$ should be absent below $T_c$, while the resonance associated with $d_{yz}$ and $d_{xy}$ orbitals should appear below $T_c$ at $Q_1$ [figure 5.2(a) and (b)].

5.2 Experiment Details

To test if this is indeed the case, we carried out INS experiments on uniaxial detwinned NaFe$_{0.985}$Co$_{0.015}$As single crystal. Compared with earlier experiments on the same doping concentration [141], the new measurements have much better statistics and collected uniaxial pressured/pressureless data using the same experimental setup. We find the presence of double resonance at $Q_1$ and $Q_2$ with intensity ratio of the modes between $Q_1$ and $Q_2$ agreeing well with the detwinning ratio obtained using magnetic Bragg peaks at these two wave vectors. These results therefore indicate that superconductivity induced resonance arises from the nesting of hole-electron Fermi surfaces with dominant $d_{yz}$ orbital characters.

Our neutron scattering experiment was carried out on IN8-Thermal neutron three-axis spectrometer at Institut Laue-Langevin, Grenoble, France. We used horizontally and vertically focused pyrolytic graphite [PG(002)] monochromator and analyzer with fixed scattered (final) energy $E_f = 14.68$ meV. The high order harmonics from the
Figure 5.3: Detwin ratio of partially detwinned NaFe$_{0.985}$Co$_{0.015}$As determined from elastic measurements. Temperature differences of transverse scans at the (1,0,0.5) and (0,1,0.5) magnetic Bragg peak positions in NaFe$_{0.985}$Co$_{0.015}$As single crystal under uniaxial pressure of $\sim$10 MPa.

Figure 5.4: Temperature dependence of the antiferromagnetic peak intensity at $Q_1 = (1,0,0.5)$ under uniaxial pressure in NaFe$_{0.985}$Co$_{0.015}$As. Vertical dashed lines indicate $T_c = 14$ K, $T_N = 31$ K, and $T_s = 40$ K.
Figure 5.5: Energy scans at antiferromagnetic peak positions in partially detwinned sample and pressure released NaFe$_{0.985}$Co$_{0.015}$As sample. (a) Neutron spin resonance modes at $Q_1 = (1, 0, 0.5)$ and $Q_2 = (0, 1, 0.5)$ are obtained by taking temperature differences of the constant-$Q$ scans below and above $T_c$ in uniaxial pressure partially detwinned sample. (b) Neutron spin resonance modes in pressure released sample obtained using the same sample and the same sample holder with the same spectrometer setup as in (a). The similar intensity of the resonance at $Q_1$ and $Q_1$ indicate that the sample becomes nearly 100% twinned. (c) Sum of neutron spin resonance mode intensities at $Q_1$ and $Q_2$ in partially detwinned and pressure released sample separately. (d) The ratio between temperature difference of constant-$Q$ scans (below and above $T_c$) at $Q_1$ and $Q_2$ in partially detwinned sample. Points with large error bars around $E = 4.5$ meV are not shown. The open circle labels the detwinning ratio measured from the static AF order.
PG(002) monochromator are suppressed by an oriented PG-filter in the scattered beam. Using structural orthorhombic unit cell with lattice parameters $a \approx b \approx 5.5968\text{Å}$ and $c \approx 6.9561\text{Å}$ at $T = 1.5$ K, we denote the momentum transfer $Q = Ha^* + Kb^* + Lc^*$ as $Q = (H, K, L)$ in reciprocal lattice units (r.l.u.) with $a^* = \hat{a}2\pi/a$, $b^* = \hat{b}2\pi/b$ and $c^* = \hat{c}2\pi/c$. In the AF ordered state of a completely detwinned sample with uniaxial pressure applied along the $b$-axis direction, AF Bragg peaks occur at $Q = (1, 0, L)$ with $L = 0.5, 1.5, 2.5 \ldots$ and there are no magnetic peaks at $(0, 1, L)$ [48].

High-quality NaFe$_{0.985}$Co$_{0.015}$As single crystals are prepared by self-flux method [46], and we cut one large single crystal (~300 mg) into the rectangular shape along the $[1, 0, 0]$ and $[0, 1, 0]$ directions. The sample is mounted inside aluminum-based sample holder with a uniaxial pressure of $P \approx 10$ MPa along the $b$-axis direction (although it is rather difficult to precisely determine the magnitude of the actual uniaxial strain on the sample). Similar to previous neutron works [18], we align the sample in the $[1, 0, 0.5] \times [0, 1, 0.5]$ scattering plane. In such a scattering geometry, we are able to measure the static magnetic order and excitations at both $Q_1 = (1, 0, 0.5)$ and $Q_2 = (0, 1, 0.5)$.

Figure 5.3 shows background subtracted elastic transverse scans across $Q_1$ and $Q_2$. By comparing the intensities between these two positions, we estimate that the sample has a detwinning ratio $\eta = [I(1, 0) - I(0, 1)]/[I(1, 0) + I(0, 1)] \approx 62.4\%$. Temperature dependence of the magnetic order parameter measured at $Q_1$ reveals $T_N \approx 31$ K and a suppression of the static AF order below $T_c \approx 14$ K [figure 5.4]. Figure 5.5(a) shows temperature difference of the energy scans at $Q_1$ and $Q_2$ below and above $T_c$. Similar to the results in twinned sample [52], two neutron spin resonance modes are found at $E_{r_1} \approx 3.5$ meV and $E_{r_2} \approx 6$ meV, respectively, and a spin gap opens below $E = 3$
meV in the superconducting state. Moreover, intensities for both resonance modes are higher at the AF position $Q_1$ than at $Q_2$. This is different from our previous data obtained on PUMA [141], which is likely due to the improved detwinning ratio in the present study. To further confirm that such difference is induced by uniaxial strain, we released the uniaxial pressure and carried out same energy scans on the same sample under same experiment setup. Figure 5.5(b) shows temperature difference of the energy scans upon releasing the uniaxial pressure. As expected, the sample goes back to the twinned state, and there are no observable differences of the both resonance modes between $Q_1$ and $Q_2$.

Since our experiments are carried out using the same spectrometer setup on the same uniaxial pressure detwinned and twinned (pressure released) sample with the same sample holder, we are able to compare the effect of uniaxial pressure on the double resonances directly. Figure 5.5(c) shows the intensity sum of the double resonances at $Q_1$ and $Q_2$ in partially detwinned sample and twinned sample. We find that the resonance intensities are identical in these two cases, thus indicating that the intensity gain at $Q_1$ in detwinned sample comes from the intensity loss at $Q_2$. Figure 5.5(d) shows the ratio of resonance intensities between $Q_1$ and $Q_2$ in the partially detwinned sample. Since the intensity ratios for both resonance modes agree well with the detwinning ratio obtained using magnetic Bragg peaks [figure 5.3], we conclude that neutron spin resonance modes in this system only appear at $Q_1$ in a 100% detwinned sample.

Figure 5.6(a) shows background subtracted temperature dependence of the second resonance ($E_{r2} = 6.5$ meV) measured at $Q_1$ and $Q_2$ under uniaxial pressure. The intensity kink at $T_N$ and strong increase below $T_c$ at both wave vectors agree with previous INS results in twinned sample [52]. At temperatures well above $T_c$, 
Figure 5.6: (a) Temperature dependence of background subtracted spin excitations at $E_{r2} = 6.5$ meV at $Q_1$ and $Q_2$ in the partially detwinned sample. (b) The corresponding ratio of temperature dependence of spin excitations at $E_{r2} = 6.5$ meV between $Q_1$ and $Q_2$. $T_c$, $T_N$ and $T^* > T_s$ are labeled with dashed lines in (a) and (b).

$T_N$, and $T_s$, magnetic scattering at $Q_1$ and $Q_2$ are identical and independent of the applied uniaxial pressure. On cooling to 80 K ($> T_s$), we start to see higher magnetic scattering at $Q_1$, consistent with earlier work on other iron pnictide superconductors suggesting the presence of a spin nematic phase [18, 74]. The intensity ratio between $Q_1$ and $Q_2$ at $E_{r2} = 6.5$ meV is shown in figure 5.6(b). The clear spin excitation anisotropy above $T_S$ is likely due to the applied uniaxial pressure as discussed in references [145, 55]. As a function of decreasing temperature, the magnetic scattering anisotropy starts to build up below $T^*$, saturates at temperatures slightly below $T_N$, and shows no anomaly across $T_c$.

Figures 5.7(a) and (b) summarize the wave vector dependence of the double resonances in the partially detwinned sample at $Q_1$ and $Q_2$. The intensity ratios between $Q_1$ and $Q_2$ at both resonance energies $E_{r1} \approx 3.75$ meV and $E_{r2} \approx 6.5$ meV are consistent with the detwinning ratio at elastic position. When the uniaxial pressure is released, we find no difference between $Q_1$ and $Q_2$ at the resonance energy and the
Figure 5.7: Temperature differences of constant energy scans at $Q_1$ and $Q_2$ between 1.5 K and 21 K at (a) $E_{r1} = 3.75$ meV, (b) $E_{r2} = 6.5$ meV in partially detwinned sample, and (c) $E_{r2} = 6.5$ meV in pressure released sample. (d) Comparison of sum of the magnetic scattering at $Q_1$ and $Q_2$ for partially detwinned and twinned sample.
sample goes back to the twinned state [figure 5.7(c)]. Figure 5.7(d) compares the sum of the resonance intensity at $Q_1$ and $Q_2$ for pressured (solid diamonds) and pressure free case (open circles). To within the statistics of our measurements, we find them to be identical.

5.3 Discussion

Several different theories have been proposed to understand the double resonances [132, 133, 134]. In the theory of coexisting static AF order and superconductivity [132, 133], the AF order leads to a reconstruction of the Fermi surface, which gives rise to different resonance energies $E_{r1}$ and $E_{r2}$ at wave vectors $Q_1$ and $Q_2$, respectively. In a twinned sample, double resonances should appear at both $Q_1$ and $Q_2$. Since $E_{r1}$ is expected to be related with the static AF order and its associated spin waves, it should only appear at the AF ordering wave vector $Q_1$ in a detwinned sample, while $E_{r2}$ associated with Fermi surface nesting should appear at both $Q_1$ and $Q_2$ [132, 133]. However, the simultaneously enhancement (suppression) of both resonance peaks at $Q_1$ ($Q_2$) observed in our experiment for a detwinned sample appears to rule out this theory. This is consistent with polarized inelastic neutron scattering experiments, which reveal that low-energy spin waves ($E < 10$ meV) in NaFeAs are dominated by $c$-axis polarized excitations [146], while the neutron spin resonance at $E_{r1}$ has both $a$-axis and $c$-axis polarized spin excitation components [147].

Alternatively, the double resonances may be associated with the gap anisotropy induced by the strong orbital-selective superconducting pairing [134]. In the superconducting phase of the detwinned NaFe$_{0.985}$Co$_{0.015}$As, the splitting between the $d_{xz}$ and $d_{yz}$ orbitals strongly modifies the Fermi surface nesting condition, as shown in figure 5.2(b). As a consequence, the superconducting gaps associated with different
orbitals are also different, i.e., $\Delta_{xz} \neq \Delta_{yz} \neq \Delta_{xy}$. Since the Fermi surfaces have mixed orbital character, such an orbital dependent pairing will give rise to gap anisotropy along the Fermi surfaces. It will also make the resonance energies very different between the intra-orbital ($d_{yz}$-$d_{yz}$) and inter-orbital ($d_{yz}$-$d_{xy/xx}$) scatterings, although both scatterings may take place at the same wave vector. Therefore, it is expected that these intra- and inter-orbital scatterings with different energy scales lead to two spin resonance peaks at $Q_1$, just as observed in our experiment.

In conclusion, our INS experiments on partially detwinned NaFe$_{0.985}$Co$_{0.015}$As shows that neutron spin resonance in this system only appear at the AF wave vector $Q_{AF} = (1,0)$. We connect our observations with the anisotropic band shifting below $T_s$ in NaFe$_{1-x}$Co$_x$As superconductors. The $d_{yz}/d_{xz}$ orbital degeneration breaks at $T_s$ (or higher temperatures under uniaxial pressure), and bands with dominant $d_{yz}$ orbital character shift up in energy and have better nesting conditions [20, 21]. Our analysis agrees with such band structure change and indicates neutron spin resonance in NaFe$_{0.985}$Co$_{0.015}$As reveals a strong orbital dependent superconducting pairing enhanced by the reconstruction of the band structure below $T_s$, in which the scatterings associated with the $d_{yz}$ orbital play a crucial role. These results suggest that intra-orbital quasiparticle scattering of the $d_{yz}$-$d_{yz}$ orbitals are important for superconductivity, similar to magnetic scattering of LiFe$_{1-x}$Co$_x$As family of materials [144].
Appendices
Appendix A

Background signals in neutron scattering experiments

Because the neutron is electrically neutral, it penetrates most substances readily [1]. This penetrability allows samples to be studied under different sample environments (cryostats, furnaces, pressure cells, etc.)[1]. Though all sample environments are carefully designed to minimize the volume exposed to the neutron beam, they may still contribute non-negligible background signals. In this chapter, I will discuss commonly observed background signals in neutron scattering experiments.

A.1 Introduction

Coherent scattering refers to scattering that measured the correlation between different atoms, while incoherent scattering is the scattering due to single atom [2]. As discussed in Chapter 1, we focus on coherent scatterings in most hard condensed experiments, and incoherent scatterings lead to isotropic background. Incoherent scatterings from samples are wave-vector independent and barely change with temperature. In data analysis, they can be handled with (I) including a flat (linear) background term in fitting models, (II) taking subtraction between datasets measured at different temperatures.

Neutron can be scattered several times before hitting the detector, and these events are called multiple-scattering. Since scattered neutrons don’t follow the expected scattering trajectories, the calculated wave-vectors and energies are wrong. As
a result, multiple-scattering backgrounds can appear in both elastic/inelastic channels. In general, multiple scatterings have very small cross-section and can be neglected. In some special geometries/instrument setups, they happen more frequently and form instrument/sample environment signature spurious signals.

Usually, we can use following methods to distinguish background signals from real signals (from samples).

- **Utilize crystal symmetry.** The sample signals exhibit crystal symmetry and periodicity. If we are uncertain whether the measured peak is from the sample, we can measure at equivalent positions. For example, if a “potential” magnetic peak is observed at $Q = (1,0,0.5)$ in iron pnictide with orthorhombic chemical notation (section 2.1.2), we can check at $(-1,0,0.5), (1,0,1.5)$, etc.

- **Measure temperature dependence.** We can measure the temperature dependence of the measured peak, and the measured temperature dependence should agree with underlying physics. For example, if inelastic signal is neutron spin resonance, the signal should behave as superconducting order parameter and disappear at $T_c$. If signal originates from magnetic ordering, the signal should have a clear transition at $T_{mag}$.

- **Utilize magnetic form factor.** As described in section 1.3, magnetic form factor $F(Q)$ ranges from 0 to 1, and it falls off with increasing the magnitude of the scattering vector $Q$. We can use it to distinguish whether newly discovered signals have magnetic origins.

- **Measure background directly.** There are two types of background measurements. First, we can perform “empty can” measurement. By removing the samples and measuring the sample holder alone with exact same setup, we can characterize the background contributed from instrument, sample environment
and sample holders. Second, we can perform the identical measurement in normal state as that in interested state. For a magnetic ordered sample, we can measure at $T > T_{\text{mag}}$, and magnetic signals can be obtained by taking difference between data collected at $T < T_{\text{mag}}$ and $T > T_{\text{mag}}$.

Due to experiment restrictions (insufficient beamtime, limitation of accessible $Q$), we may not be able to perform all required tests. In the following sections, I will introduce several misleading background signals.

### A.2 Helium gas recoil scattering

Helium-4 is widely used as exchange gas in cryogenic devices to reach low temperatures. As a result, helium gas is inevitably exposed to neutron beam. Because helium-4 atom has comparable mass with neutron mass, the energy transfer between neutron and helium atom in scattering process is non-negligible. The recoil scattering can be modeled with

$$I(Q, E) = \left(\frac{\beta}{4\pi E_r}\right)^{1/2} \exp\left(-\frac{\beta}{4E_r} (E - E_r)^2\right)$$

where $E_r = \frac{k^2 Q^2}{2M}$ is the recoil energy and $M$ is the helium atom mass, $\beta = 1/(k_B T)$ with $k_B$ as Boltzmann constant and $T$ as the measured temperature. The scattering intensity is a function of momentum transfer, energy transfer and temperature.

In an triple-axis experiment, we found a peak at $E = 2.5\text{meV}$ in temperature difference constant-$Q$ scan at $Q = 2.2279 \text{ Å}$ between $T = 2.6\text{K}$ and $10\text{K}$. As most background signals are either temperature-independent or stronger at higher temperature, we suspected that this new found peak had magnetic origin. We did a careful inelastic temperature dependence study at $E = 2.5\text{meV}$ and $Q = 2.2279 \text{ Å}$ (figure
Though the measured intensity keeps decreasing with increasing temperature, no clear transition temperature is observed. In figure A.1(b), we show the simulated helium recoil intensities, which achieve a perfect agreement with measured data in figure A.1(a). Figure (c) and (d) exhibit the simulated helium recoil E-Q relation at $T = 2.6K$ and 10K. Figure (e) and (f) show the measurement and the simulation for temperature difference E-Q relation between 2.6K and 10K.

### A.3 Imperfect aluminum powder ring

Aluminum is the mostly widely used material for making sample holder, vacuum chamber in neutron scattering experiment. Aluminum has many advantages for neutron scattering experiment, e.g. not expensive, easy to fabricate, non-magnetic, etc. Moreover, aluminum has very few bragg peaks in low Q region (most measurements for magnetic scatterings take place). Aluminum crystal is face-centered cubic with lattice parameter $a \approx 4.0494 \text{ Å}$. The Bragg peaks in low Q region are summarized in table A.1.

<table>
<thead>
<tr>
<th>(h,k,l)</th>
<th>d (Å)</th>
<th>Q (Å$^{-1}$)</th>
<th>$2\theta$ (degree) $E_i=5\text{ meV}$</th>
<th>$2\theta$ (degree) $E_i=14.7\text{ meV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 1 1)</td>
<td>2.33792</td>
<td>2.6875</td>
<td>119.778</td>
<td>60.598</td>
</tr>
<tr>
<td>(2 0 0)</td>
<td>2.02470</td>
<td>3.1033</td>
<td></td>
<td>71.261</td>
</tr>
<tr>
<td>(2 2 0)</td>
<td>1.43168</td>
<td>4.3887</td>
<td></td>
<td>110.946</td>
</tr>
</tbody>
</table>

Table A.1: **Bragg peak information of aluminum.** In triple-axis experiment, only three aluminum Bragg peaks can be detected at thermal neutron instrument ($E_i = 14.7 \text{ meV}$) and one peak can be measured at cold neutron instrument ($E_i = 5\text{ meV}$).

Ideally, the scattering from aluminum sample holder and vacuum chamber is radial symmetric in reciprocal space (figure A.2(a)), and the rocking scan for such signal
Figure A.1: **Helium gas recoil scattering.** Measurement (a) and simulation (b) for temperature dependence of helium gas scattering at $E = 2.5\text{meV}$ and $Q = 2.2279\,\text{Å}$. (c),(d) are simulated E-Q map for helium recoil at $T = 2.6\text{K}$ and $10\text{K}$ separately. Measurement (e) and simulation (b) for temperature difference E-Q map for helium recoil between 2.6K and 10K. Data in (a) were taken at MACS, NCNR. Data in (e) were taken with $E_i = 15\,\text{meV}$ at HYSPEC, ORNL.
should be flat (figure A.2(b)). In reality, small crystalline domains can form during the manufacturing process, and these small crystals within the aluminum alloy are called "grains". The crystal orientation of grain can be random. As a result, the aluminum powder ring measured by neutron scattering is not perfect (figure A.2(c)). Small peaks appear in rocking scans (figure A.2(d)), and they can be treated as real signals mistakenly in some cases.

Figure A.2 : Schematic for aluminum powder ring. (a) and (c) are schematics for powder ring in reciprocal space for ideal and non-ideal aluminum separately. (b) and (d) show the corresponding rocking scans.

Figure A.3 shows the white beam measurements for aluminum sample can in a time-of-flight experiment at MERLIN, ISIS, UK. We first used a sample can with large amounts of grains (figure A.3(a) and (b)), and we observed huge amount of distinct
peaks in both real space mapping (A.3(a) and (b)) and reciprocal space (not shown). The replaced sample can has much fewer grains A.3(c) and (d).

Figure A.3 : **White beam measurements for aluminum sample can.** (a) and (b) are white beam measurement for a sample can with huge amounts of grains. (c) and (d) show the same mapping for the replace sample can. Data is collected at MERLIN, ISIS, UK.
Bibliography


optimally p-doped bafe 2 (as 0.70 p 0.30) 2 superconductor,” *npj Quantum Materials*, vol. 3, no. 1, p. 47, 2018.


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[57] A. Böhmer, A. Sapkota, A. Kreyssig, S. Budko, G. Drachuck, S. Saunders,


collapse in la 1.2 sr 1.8 mn 2 o 7,” *Physical review letters*, vol. 83, no. 21, p. 4393, 1999.


magnetic order in heavily overdoped $\text{Ba}(\text{Fe}_{1-x}\text{Cu}_x)\text{As}_2$ as 2,” *Physical Review B*, vol. 96, no. 16, p. 161106, 2017.


pnictide high-temperature superconductor \( \text{Ba}(\text{Fe}_{1-x}\text{Co}_x)\text{As}_2 \),” *Physical Review B*, vol. 94, no. 19, p. 195147, 2016.


Carr, O. Sobolev, A. Schneidewind, et al., “Distinguishing s± and s++ electron pairing symmetries by neutron spin resonance in superconducting nafte 0.935 co 0.045 as,” *Physical Review B*, vol. 88, no. 6, p. 064504, 2013.


