RICE UNIVERSITY

Neutron scattering studies of some NaFeAs and BaFe$_2$As$_2$ derivatives and Ce$_{1-x}$Yb$_x$CoIn$_5$

by

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A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE Degree

Doctor of Philosophy

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November, 2016
ABSTRACT

Neutron scattering studies of some NaFeAs and BaFe$_2$As$_2$ derivatives and Ce$_{1-x}$Yb$_x$CoIn$_5$

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Within this thesis I present several neutron scattering works on unconventional superconductors, including derivatives of iron pnictides BaFe$_2$As$_2$, NaFeAs and the heavy fermion compound CeCoIn$_5$. Similar to the cuprates, superconductivity in these systems appear in proximity to magnetically ordered phases and strong magnetic fluctuations persist in paramagnetic superconductors. Neutron scattering is an ideal probe to study spin-spin correlations and hence the interplay between magnetism and superconductivity.

In the iron pnictide parent compounds BaFe$_2$As$_2$ and NaFeAs I demonstrate that while applying uniaxial stress may affect the structural and magnetic transition temperatures, the effect is too small to account for the large temperature range over which resistivity anisotropy has been observed, confirming the resistivity anisotropy is intrinsic rather than being linked to an electronically ordered phase (stripe magnetic order) with broken rotational symmetry. In the underdoped regime of Ni-doped BaFe$_2$As$_2$, I found uniaxial stress can be used to enhance the ordered moment. This is a novel manifestation of the competition between superconductivity and magnetic order since superconductivity is suppressed with uniaxial stress for underdoped samples. Increasing Ni concentration towards optimal doping where long-range magnetic
order is suppressed, I found the anisotropy of spin fluctuations as a function of energy transfer can be described as a power law decay. This result suggests spin fluctuations, rather than orbital ordering drive the Ising-nematic correlations and agrees with proposals of the system being close to magnetic and nematic quantum critical points.

Using polarized neutron scattering I studied the evolution of spin anisotropy in NaFe$_{1-x}$Co$_x$As including the the parent ($x = 0$), underdoped ($x = 0.015$), near-optimal-doped ($x = 0.0215$) and overdoped ($x = 0.05$) compounds. Spin anisotropy in NaFeAs can be described by two spin anisotropy terms similar to BaFe$_2$As$_2$ with $c$-axis being the easy-axis, in addition the likely presence of a longitudinal mode highlight the itinerant aspect of magnetism in iron pnictides. In the underdoped compound polarization analysis reveals the double neutron spin resonance modes seen in this compound has different characteristics, with the first mode being anisotropic and the second mode being isotropic. Near optimal superconductivity the first resonance disappears, but there is still remaining spectral weight that exhibits similar spin anisotropy at the same energy. In the overdoped compound the single resonance is isotropic while excitations at lower energies become fully gapped. In optimal-hole-doped Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$ without static magnetic order, spin anisotropy at $E = 3$ meV persists to $\sim 100$ K, while the resonance has a $c$-axis polarized component as well as an isotropic component. I link the low energy spin anisotropy to deviation from Curie-Weiss behavior seen in elastoresponse measurements and uncover a relationship between the energy scale of spin anisotropy and $T_c$ in BaFe$_2$As$_2$ derived superconductors. While the energy scales of spin anisotropy in these systems are low, they are nevertheless comparable to the superconducting gap and suggests spin-orbit coupling to be an important component of the puzzling superconductivity in iron pnictides.

Iron-based superconductivity develops near an antiferromagnetic order and out of a bad-metal normal state, which has been interpreted as originating from a proximate Mott transition. Whether an actual Mott insulator can be realized in the phase
diagram of the iron pnictides remains an open question. Combining several techniques we demonstrate that NaFe$_{1-x}$Cu$_x$As near $x \approx 0.5$ exhibits real space Fe and Cu ordering, and are antiferromagnetic insulators with the insulating behaviour persisting above the Néel temperature, indicative of a Mott insulator. The discovery of a Mott-insulating state in NaFe$_{1-x}$Cu$_x$As thus makes it the only known Fe-based material, in which superconductivity can be smoothly connected to the Mott-insulating state, highlighting the important role of electron correlations in the high-$T_c$ superconductivity. Magnetic excitations in NaFe$_{1-x}$Cu$_x$As for $x \approx 0.5$ can be interpreted easily in the local moment picture consistent with the system being a Mott insulator, while also exhibiting behavior strikingly similar to superconducting iron pnictides. In addition, I have observed a resonance mode in superconducting NaFe$_{0.98}$Cu$_{0.02}$As, demonstrating its unconventional nature.

CeCoIn$_5$ is believed to be an unconventional superconductor with $d_{x^2-y^2}$-wave pairing symmetry similar to the cuprates. Therefore it is anticipated that the neutron spin resonance in this system should also display a prominent downward dispersion similar to the cuprates. Contrary to such an expectation, I found the resonance mode displays a prominent upward dispersion that is robust against Yb doping, which induces significant changes to the Fermi surface. This result challenges the predominant view that the resonance can be understood as a spin-exciton from an itinerant electron perspective, but instead suggests that a robust nearest-neighbor coupling between Ce$^{3+}$ ions is responsible for the upward dispersion within a magnon-like scenario.

The combination of these works provides a significant advance in the understanding of the interplay between magnetism and unconventional superconductivity, pointing to several directions for future research in these systems.
Acknowledgements

Firstly I would like to thank my advisor Dr. Pengcheng Dai, whose unparalleled passion for science is a lasting motivation for my own scientific endeavors. I am grateful to the former members in the group, with whom I have had many memorable moments and stimulating discussions, Dr. Chenglin Zhang, Dr. Miaoyin Wang, Dr. Meng Wang, Dr. Mengshu Liu, Dr. Xingye Lu, Dr. Jiangang Guo and Dr. Scott Carr. I would also like to acknowledge the current group members, all of whom have taught me important lessons in science as well as life in general, Yu Li, Weiyi Wang, Haoran Man, David Tam, Rui Zhang, Tong Chen and Dr. Ding Hu. I would also like to thank Dr. Guotai Tan, Dr. Chongde Cao and Dr. Li Zhang, who visited our group and with whom I shared many enjoyable collaborations. I appreciate help from undergraduate students who have worked in our lab and contributed significantly to our productivity, Tucker Netherton, Caleb Redding, Zachary Sims, Nickolas F. Luttrell, Chao Zhou and Mengke Liu.

My neutron scattering work would not have been possible without high-quality samples, I would like to thank all of my group members who have helped me synthesize many of the iron pnictide samples that I have worked on. I would like to thank Dr. Xingye Lu and Dr. Huiqian Luo for preparing the Ba-122 samples I worked with. I would like to thank Dr. Brian Maple and his collaborators, I. K. Lum, Dr. B. D. White, Dr. Sooyoung Jang, Dr. Duygu Yazici, Dr. Lei Shu, Dr. Sheng Ran and Naveen Pouse for preparing the Ce-115 samples. I would like to thank my experimental collaborators in studying NaFe$_{1-x}$Cu$_x$As single crystals, Justin Chen, Dr. Jing Tao, Dr. Yimei Zhu, Dr. Yao-Bo Huang, Marcus Dantz, Dr. Thorsten Schmitt and Dr. Emilia Morosan. I would like to thank all the neutron scattering scientists I have worked with for this thesis work, all of whom have taught me the best ways to carry out neutron scattering experiments, Dr. Songxue Chi, Dr. Yang Zhao, Dr. Jeffrey W. Lynn, Dr. D. L. Abernathy, Dr. J. L. Niedziela, Dr. Wei Tian, Dr. Louis-Pierre Regnault, Dr. Frédéric Bourdarot, Dr. Yixi Su, Dr. Haifeng
Li, Dr. M. Enderle, Dr. J. Kulda, Dr. A. D. Christianson, Dr. Zahra Yamani, Dr. Qingzhen Huang, Dr. Hui Wu, Dr. Huibo Cao, Dr. Russell Ewings, Dr. Barry Winn, Dr. Melissa Graves-Brook, Dr. Yiming Qiu, Dr. Astrid Schneidewind and Dr. Petr Čermak. I am grateful to my theory collaborators who helped me to understand my experimental results, Dr. Qimiao Si, Dr. Tao Xiang, Dr. Rong Yu, Dr. Jian Kang, Dr. Rafael Fernandes, Dr. Andriy Nevidomskyy, Dr. Dirk K. Morr and Dr. John Van Dyke.

Finally 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. Kevin Kelly, Dr. Qimiao Si and Dr. Andrea Isella.
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Chapter 1

Basic Neutron Scattering Formalism

In this chapter the formalism of neutron scattering and cross sections are introduced, approximations commonly used experimentally are discussed. Detailed formalism of neutron scattering, corresponding cross sections and relevant experimental techniques can be found in several books [1, 2, 3]. Results deemed most relevant for the present thesis work are presented here.

1.1 Introduction to Neutron Scattering

Neutron is a particle with zero charge and spin $\frac{1}{2}$. Having no charge means neutrons can penetrate well into matter compared to electrons and photons, while the spin can couple to magnetic fields present in matter.

In addition neutrons can interact with atomic nuclei through the strong nuclear force, in contrast to photons that are sensitive to electron density. This means (i) for a specific element the neutron scattering length is isotope-specific, (ii) the scattering length does not vary systematically with atomic number in contrast to photons and (iii) there is no form factor that decreases with increasing $Q$ for neutron scattering from nuclei. Compared to photons, (i) neutrons are much more sensitive to magnetism, (ii) probe the whole bulk of the sample and (iii) allows for simple and reliable measurements in absolute units. Neutron scattering also has several drawbacks compared to photons, (i) neutron scattering is very expensive since the cost for operating
a neutron source is much higher than a photon source, (ii) flux of neutrons is much weaker than photon sources and (iii) while photons can directly probe orders such as charge density wave, neutrons can only indirectly see such an ordering through its coupling with the lattice. Overall neutrons and photons are complementary in many cases but for some measurements one has clear advantage over the other. For measurements of magnetic order and magnetic excitations, especially with $E \lesssim 10$ meV, neutron scattering is undoubtedly the method best suited for the problem.

### 1.2 Nuclear elastic scattering

The double-differential neutron scattering cross section for nuclear scattering is given by

$$
\frac{d^2\sigma}{d\Omega d\omega} = \frac{k'}{k} \frac{1}{2\pi\hbar} \sum_{j,j'} b_j b_{j'} \int_{-\infty}^{\infty} <e^{-iQ \hat{R}_{j'}(0)}e^{iQ \hat{R}_j(t)}> e^{-i\omega t} dt.
$$

$k'$ and $k$ are the outgoing and incident neutron wave vectors ($k'$ and $k$ denote the magnitude of these vectors), $Q = k - k'$ is the measured momentum transfer, $\hbar \omega$ is the measured energy transfer, $b_j$ is the neutron scattering length for the atomic nucleus $j$ and $\hat{R}_j(t)$ is position of the atomic nucleus $j$ at time $t$. For structural determination the time dependence in $\hat{R}_j(t)$ can be ignored and performing the integral over $t$ on the right hand side the cross section becomes

$$
\frac{d^2\sigma}{d\Omega d\omega} = \frac{k'}{k} \sum_{j,j'} b_j b_{j'} <e^{-iQ \hat{R}_{j'}(0)}e^{iQ \hat{R}_j(0)}> \delta(\hbar \omega).
$$

Integrating over $\omega$ on both sides, noting $k = k'$ for elastic scattering and removing the operator notation and time dependence, the single-differential cross section that contains the structural information is obtained
\[ \frac{d\sigma}{d\Omega} = \sum_{j,j'} b_j b_{j'} e^{iQ \cdot (R_j - R_{j'})}. \]  

(1.3)

Neglecting the quantum mechanical operator nature of \( R_j \) results in missing the so-called Debye-Waller factor \( e^{-2W(Q)} \), with \( 2W(Q) = \langle Q \cdot u \rangle^2 \) and \( u(t) \) being the deviation from the average atomic position. While \( \langle u \rangle = 0 \) by definition, \( \langle u^2 \rangle \neq 0 \) and appears in the Debye-Waller factor reflecting the degree of thermal motion. The Debye-Waller factor is therefore temperature-dependent but can be assumed to be close to unity at low temperatures, where measurements of magnetic excitations are typically carried out. The equation above is a general result that can be applied to various systems. In crystalline materials for atom \( \alpha \) in unit cell \( j \), \( R = l_j + d_{\alpha} \), with \( l_j \) being the displacement vector of the unit cell \( j \) and \( d_{\alpha} \) being the displacement vector \textit{inside} the unit cell. The single differential cross section for elastic neutron scatterig becomes

\[ \frac{d\sigma}{d\Omega} = \sum_{j,j'} e^{iQ \cdot (l_j - l_{j'})} \sum_{\alpha,\alpha'} b_\alpha b_{\alpha'} e^{iQ \cdot (d_{\alpha} - d_{\alpha'})}. \]  

(1.4)

It is worth noting \( b_{\alpha} \) here is in fact the average over different unit cells, giving rise to \textit{coherent} scattering. Coherent scattering refers to scattering that measured the correlation between different atoms, and \textit{incoherent} scattering refers to scattering due to single atoms. Different scattering lengths at the same site in a crystalline material can be due to (i) the same isotope and neutrons having different combined spin, (ii) different isotope of the same element having different scattering lengths and (iii) different elements randomly substituted at the same site. It is interesting that the first two cases are categorized as incoherent scattering while the third is called \textit{Laue monotonic} scattering, despite they are all wave-vector-independent. Using \( \sum_j e^{iQ l_j} = \)
\[
\frac{(2\pi)^3}{v_0} \sum_{\tau} \delta(Q - \tau), \sum_{\alpha,\alpha'} b_{\alpha} b_{\alpha'} e^{iQ (d_{\alpha} - d_{\alpha'})} = | \sum_{d} b_d e^{iQ \cdot d} |^2
\]
and restoring the Debye-Waller factor, the single-differential cross section becomes

\[
\frac{d\sigma}{d\Omega} = N_0 \frac{(2\pi)^3}{v_0} \sum_{\tau} \delta(Q - \tau) |F_N(Q)|^2. \tag{1.5}
\]

\[
F_N(Q) = \sum_{d} b_d e^{iQ \cdot d} e^{-W_d(Q)} \text{ is called the nuclear structure factor and reflects intensities of the nuclear Bragg peaks. } N_0 \text{ is the number of unit cells in the sample and } v_0 \text{ is the real space volume of the unit cell. It is also common to exclude the Debye-Waller factor in the definition of the structure factor.}
\]

### 1.3 Magnetic elastic scattering

The spin-only magnetic scattering analogue of Eq. 1.3 with a single species of magnetic atoms for unpolarized neutrons is slightly more complicated,

\[
\frac{d\sigma}{d\Omega} = \frac{(\gamma r_0 g)^2}{2} f(Q)^2 \sum_{\alpha,\beta} (\delta_{\alpha,\beta} - \hat{Q}_\alpha \hat{Q}_\beta) \sum_{j,j'} < S_j^\alpha S_j'^\beta > e^{iQ \cdot (R_j - R_{j'})}. \tag{1.6}
\]

With \( \gamma r_0 = 5.39 \times 10^{-15} \text{m} \), this value is similar to typical scattering lengths for atomic nuclei (also of the order of \( 10^{-15} \text{m} \)) and is the reason why neutron scattering sees similar intensities for nuclear and magnetic scattering (this is certainly true for typical ordered magnets such as MnF\(_2\), but for unconventional superconductors the magnetic signal is usually very weak as a result of small moment and the large energy scales of magnetic excitations). \( f(Q) \) is the magnetic form factor, which is the Fourier transform of the magnetization density of a single atom. It is similar to the atomic form factor seen in X-ray scattering, which is the Fourier transform of the electron density. \( S_j^\alpha \) is the projection of the spin operator along \( \alpha \)-axis (\( \alpha = x,y,z \)). The above expression is quite general and applies to any system with only one type of magnetic
atom. This expression can be easily extended to compounds with multiple types of magnetic atoms, but since such compounds are rarely studied the expressions below are all for systems with a single species of magnetic atoms. $\hat{Q}_\alpha$ is the projection of unit vector $\hat{Q} = \frac{Q}{|Q|}$ on $\alpha$-axis ($\hat{Q} \cdot \hat{\alpha}$). The term $\sum_{\alpha,\beta}(\delta_{\alpha,\beta} - \hat{Q}_\alpha \hat{Q}_\beta)$ reflects that neutrons are only sensitive to spins components perpendicular to $Q$, choosing a Cartesian coordinate system such that $x$ is along $Q$, Eq. 1.6 can be simplified to

$$\frac{d\sigma}{d\Omega} = \left(\frac{\gamma_{0}y}{2}\right)^{2}f(Q)^{2}\sum_{j,j'}\left(<S_{yj}S_{yj'}> + <S_{zj}S_{zj'}>\right)e^{iQ \cdot (R_{j} - R_{j'})}.$$  \hspace{1cm}(1.7)$$

Consider a paramagnet such that $< S_{\alpha j}S_{\alpha j'} > = < S_{\alpha j} > < S_{\alpha j'} > \delta_{j,j'}$, the above expression results in $Q$-independent (aside from the form factor) but nonzero scattering. This is similar to incoherent scattering, with $< S >$ averaging over different sites being zero, but $< S^2 >$ is non-zero. For comparison consider an alloy with completely random site occupation, while there will be incoherent scattering (Laue monotonic) due to site randomness, nuclear Bragg peaks can still be seen. This is different from the analogous paramagnetic phase since $b_j$ averaging over sites is typically non-zero (it is possible to engineer alloys with zero averaged $b_j$, then there would be no Bragg peaks!). The formalism for nuclear and magnetic scattering are very similar, and for collinear ordered magnets or paramagnets there are structural parallels (in both cases the vector nature of the spins can be ignored). 2D spin correlations are rods in $Q$-space since it can be considered to be “paramagnetic” along one direction, and similarly 1D spin correlations are sheets. Since many unconventional superconductors have 2D spin correlations, rods of magnetic excitations are commonly seen.

Starting from Eq. 1.6 the magnetic analog of Eq. 1.5 for a magnet with collinear (therefore commensurate) magnetic order can be found to be
\[
\frac{d\sigma}{d\Omega} = N_m \left(\frac{(2\pi)^3}{v_m}\right) \frac{(\gamma_{0}g)^2}{2} f(Q)^2 (1 - \dot{Q}_z^2) \sum_{\tau_m} \delta(Q - \tau_m)|F_m(Q)|^2.
\]

(1.8)

\[F_m(Q) = \sum_{d} < S_d^z > e^{iQ \cdot d} e^{-W_d(Q)}\] is the magnetic structure factor. Here a Cartesian system with z along the spin directions is chosen and \(< S_d^z >\) can be positive or negative. \(N_m\) is the number of magnetic unit cells in the sample and \(v_m\) is the volume of the magnetic unit cell (may be of the same size or larger than the nuclear unit cell). Comparing Eq. 1.5 and Eq. 1.8 it is clear once both the crystal structure and the magnetic structure are known, by measuring nuclear and magnetic Bragg peak intensities one can extract the ordered moment \(\mu = g\mu_B < S_d^z >\) at each atomic site.

For transition metal systems, the orbital momentum is quenched \((L = 0)\) so the spin-only magnetic scattering cross section is precise. For lanthanides and actinides this is not the case and the cross section becomes rather complicated. An approximation that can be used is to replace the spin operator \(S\) by the total momentum operator \(\frac{g}{2} J\) and apply the spin-only formalism. The magnetic form factor also becomes more complicated and tabulated values (using interpolation in practice) are commonly used for rare earth elements.

### 1.4 Nuclear inelastic scattering

For inelastic neutron scattering, starting from Eq. 1.1 using \(\dot{\mathbf{R}}_j(t) = \mathbf{l}_j + \dot{\mathbf{u}}_j(t)\) where \(\mathbf{l}_j\) is the equilibrium position of atom \(j\) and \(\dot{\mathbf{u}}_j(t)\) is the time-dependent deviation from the equilibrium position which can be decomposed into a sum of phonon modes, the one-phonon neutron energy loss scattering cross section can be obtained as
\[
\frac{d^2 \sigma}{d\Omega d\omega} = \frac{k'}{k} \frac{4\pi^3}{v_0} \sum_{s,q} \frac{1}{\omega_s(q)} \left| \sum_d \frac{b_d}{\sqrt{M_d}} e^{-W_d(q)} e^{iQ \cdot d}(Q \cdot e_{d,s}(q)) \right|^2 \\
\times (n(\omega_s(q)) + 1) \delta(\omega - \omega_s(q)) \sum_\tau \delta(Q - q - \tau).
\] (1.9)

The expression for neutron energy gain is analogous but has \(n(\omega_s(q))\) rather than \(n(\omega_s(q)) + 1\) in the expression with \(n(\omega) = (e^{\frac{\hbar \omega}{kT}} - 1)^{-1}\). Clearly the neutron energy loss side is always larger and experimentally it is usually this side that is measured. With increasing temperature scattering on the neutron energy gain side becomes similar to the neutron energy loss side. On the HB-1A triple axis spectrometer at High-Flux Isotope Reactor, Oak Ridge National Laboratory, the incident energy is fixed, so in order to carry out inelastic neutron scattering one sometimes has to use the neutron energy gain side since otherwise the momentum range would be too small. In such cases phonons can be still measured by raising temperature, while spin excitations that weaken with increasing temperature become very hard to measure.

Summing over \(s\) in the above expression correspond to summing over various phonon branches, for a sample with \(r\) atoms in the unit cell, there are 3 acoustic phonon modes and 3\((r-1)\) optical phonon modes. \(\omega_s(q)\) is the corresponding phonon dispersion with \(Q = \tau + q\). \(\omega_s(q)\) and \(e_{d,s}(q)\) are the eigenvalue and eigenvector for the \(s\) phonon mode at \(q\). \(e_{d,s}(q)\) is in general complex, corresponding to atoms moving out-of-phase with each other. Furthermore \(e_{d,s}(q)\) is orthonormal, with \(\sum_{d,\alpha} (e_{d,s}(q))^* (e_{d,s'}(q)) = \delta_{s,s'}\) (the superscript denote projection along the \(\alpha\)-axis).

Phonon measurements are often carried out for intensity normalization, in such cases one typically chooses acoustic phonons at small \(q\) near a strong nuclear Bragg peak at \(\tau\). This is because for acoustic modes when \(q \to 0\), \(\hat{u}_j(t)\) is the same for all atoms and since \(\hat{u}_d(t) \propto \frac{e_{d,s}(q)}{\sqrt{M_d}}, |e_{d,s}(q)| = \sqrt{\frac{M_d}{M}}\) with \(M = \sum_d M_d\). The neutron
energy loss phonon cross section can be simplified to

\[
\frac{d^2 \sigma}{d\Omega d\omega} = \frac{k'}{k} \frac{4\pi^3}{v_0} \sum_{s,q} \frac{1}{\omega_s(q)} \frac{(Q \cdot \hat{e})^2}{M} |F_N(Q)|^2 \\
\times (n(\omega_s(q)) + 1) \delta(\omega - \omega_s(q)) \sum_{\tau} \delta(Q - q - \tau).
\]

The term \((Q \cdot \hat{e})^2\) can be used to select phonon polarization, for example near \(Q = (200)\) phonons with \(\hat{e}\) along (100) dominates the cross section and experimentally one can ignore the other two phonon polarizations.

### 1.5 Magnetic inelastic scattering

The magnetic analogue of Eq. 1.1 is

\[
\frac{d^2 \sigma}{d\Omega d\omega} = \frac{k'}{k} \frac{1}{2\pi \hbar} (\frac{\gamma r_0 g}{2})^2 f(Q)^2 \sum_{\alpha,\beta} (\delta_{\alpha,\beta} - \hat{Q}_\alpha \hat{Q}_\beta) \\
\times \sum_{j,j'} \int_{-\infty}^{\infty} <e^{-iQ \cdot (R_j - R_{j'}(0))} e^{iQ \cdot R_j(t)}> <S^\alpha_j(0) S^\beta_j(t) > e^{-i\omega t} dt.
\]

It is clear that \((\frac{\gamma r_0 g}{2})^2 f(Q)^2 \sum_{\alpha,\beta} (\delta_{\alpha,\beta} - \hat{Q}_\alpha \hat{Q}_\beta) < S^\alpha_j(0) S^\beta_j(t) >\) replaces the nuclear scattering lengths \(b_j b_{j'}\). Here a single species of magnetic atoms is assumed and a more general result can be easily derived, since the only effect is different \(g\) factors and magnetic form factors (the sum is over magnetic atoms only). It is then customary to neglect the time dependence of \(\hat{R}\) and absorb the quantum mechanical nature of \(\hat{R}\) into the Debye-Waller factor, and the equation becomes

\[
\frac{d^2 \sigma}{d\Omega d\omega} = \frac{k'}{k} \frac{1}{2\pi \hbar} (\frac{\gamma r_0 g}{2})^2 f(Q)^2 e^{-2W(Q)} \sum_{\alpha,\beta} (\delta_{\alpha,\beta} - \hat{Q}_\alpha \hat{Q}_\beta) \\
\times \sum_{j,j'} e^{iQ \cdot (R_j - R_{j'})} \int_{-\infty}^{\infty} <S^\alpha_j(0) S^\beta_j(t) > e^{-i\omega t} dt.
\]
From this equation following what was done for nuclear scattering, Eq. 1.6 can be easily obtained. Introducing the spin-spin correlation or the magnetic scattering function,

\[ S^{\alpha\beta}(Q, \omega) = \frac{1}{2\pi\hbar} \sum_{j,j'} e^{iQ \cdot (R_j - R_{j'})} \int_{-\infty}^{\infty} <S^\alpha_j(0)S^\beta_j(t)> e^{-i\omega t} dt, \quad (1.13) \]

the magnetic scattering cross section then becomes

\[ \frac{d^2\sigma}{d\Omega d\omega} = \frac{k'}{k} (\gamma r g^2 f(Q)^2 e^{-2W(Q)}) \sum_{\alpha,\beta} (\delta_{\alpha,\beta} - \hat{Q}_\alpha \hat{Q}_\beta) S^{\alpha\beta}(Q, \omega). \quad (1.14) \]

From the above equation it is clear that neutron scattering directly measures the spin-spin correlation \( S^{\alpha\beta}(Q, \omega) \), which is proportional to the dynamic spin susceptibility \( \chi''_{\alpha\beta}(Q, \omega) \) through the fluctuation-dissipation theorem.

The spin-spin correlation functions can be derived for various magnetic orders and the corresponding spin waves, for example cross sections of spin waves in La\(_2\)CuO\(_4\) [4] and BaFe\(_2\)As\(_2\) [5] have been discussed in detail. In unconventional superconductors since there are in general no accepted description of the magnetic excitations, it is common to simply report the measured cross sections and model spin-spin correlation functions phenomenologically.

### 1.6 Polarized neutron scattering

The incident neutrons can be polarized along a particular axis, and the scattered neutrons can be analyzed along a particular axis. Typically the choices of polarization axes are the same for incident and scattered neutrons, and this is called *longitudinal neutron polarimetry*. In the derivation of the corresponding scattering cross sections, one then also needs to consider the spin of the neutron. It should be noted that in
the derivation of the neutron scattering cross sections, the neutrons’ final states are
summed over while the initial neutrons’ states are averaged over, therefore the cross
section for unpolarized neutron scattering is

\[ \frac{d^2\sigma}{d\Omega d\omega} = \frac{1}{2}(\frac{d^2\sigma}{d\Omega d\omega_{\uparrow\uparrow}} + \frac{d^2\sigma}{d\Omega d\omega_{\uparrow\downarrow}} + \frac{d^2\sigma}{d\Omega d\omega_{\downarrow\uparrow}} + \frac{d^2\sigma}{d\Omega d\omega_{\downarrow\downarrow}}). \]  
(1.15)

The two up and down arrows in the subscript indicate polarizations of the incident
and scattered neutrons along a particular direction, if the direction of the polariza-
tion changes during the scattering process it is called spin-flip (SF) scattering and
otherwise it is called non-spin-flip (NSF) scattering. In the case of nuclear coherent
scattering, the NSF process have the same cross section as for unpolarized neutron
scattering (say it is 1 for simplicity) while for SF scattering the cross sections are 0,
therefore using the above equation one gets \(\frac{1}{2}(1 + 0 + 0 + 1) = 1\), in agreement with
the expected cross section for unpolarized scattering. From this it appears polarized
neutron scattering is not particular useful for measuring nuclear scattering, indeed
the true power of polarized neutron scattering lies in magnetic neutron scattering.

For magnetic neutron scattering it is convenient to use the coordinate system with
\(x \parallel Q, y \perp Q\) but in the scattering plane, and \(z\) completing the Cartesian coordi-
nate system (perpendicular to the scattering plane). In addition to the fact neutrons
only see magnetic components perpendicular to \(Q\), for NSF scattering only the com-
ponents along the polarization axis is seen while for SF scattering it is components
perpendicular to the polarization axis that are seen. In this coordinate system the
cross sections are then
\[
\begin{pmatrix}
\frac{d^2\sigma}{d\Omega d\omega x, SF} \\
\frac{d^2\sigma}{d\Omega d\omega y, SF} \\
\frac{d^2\sigma}{d\Omega d\omega z, SF} \\
\frac{d^2\sigma}{d\Omega d\omega x, NSF} \\
\frac{d^2\sigma}{d\Omega d\omega y, NSF} \\
\frac{d^2\sigma}{d\Omega d\omega z, NSF}
\end{pmatrix} \propto \begin{pmatrix}
1 & 1 \\
0 & 1 \\
1 & 0 \\
0 & 0 \\
1 & 0 \\
0 & 1
\end{pmatrix} \begin{pmatrix}
S^{yy}(Q, \omega) \\
S^{zz}(Q, \omega)
\end{pmatrix}.
\tag{1.16}
\]

The proportionality factor is the same as in Eq. 1.14. In practice the neutron polarization is not perfect, and the polarization is characterized by the flipping ratio \( R \), with the measured SF cross section consisting of \( \frac{R}{R+1} \) the ideal SF cross section and \( \frac{1}{R+1} \) the ideal NSF cross section. \( R \) can be determined by measuring a strong nuclear Bragg peak through the ratio of intensities seen in experimental NSF and SF channels. In addition, the non-magnetic contribution to SF and NSF channels are different, this is due to nuclear spin incoherent scattering, which has twice the intensity in SF compared to NSF channel.

It can be seen that polarized neutrons can be used to separate magnetic from nuclear scattering and separate different polarizations of magnetic scattering (\( S^{yy} \) and \( S^{zz} \)).

### 1.7 Neutron scattering and complementary experimental techniques

When determining crystal structure and magnetic structure from diffraction measurements, X-ray diffraction, electron diffraction and neutron diffraction are typically used. These techniques are complementary and the best choice is most of the time problem-specific. These three techniques are compared in Table. 1.1. In addition,
Neutron diffraction interacts with nuclei through strong nuclear force. Atomic factor negligible.

Electron diffraction interacts with charged nuclei and electrons through Coulomb interaction. Atomic factor needs to be considered.

X-Ray diffraction interacts with valence electrons. Atomic factor needs to be considered.

Neutrons are expensive to operate. A neutron source is expensive to operate. Sample has to be relatively large. Can measure magnetic moments.

Electrons are relatively cheap to operate. Sample can be nano-sized. Cannot measure magnetic moments.

X-rays are relatively cheap. Synchrotron X-ray is typically cheaper than neutrons. Sample can be relatively small. Can measure magnetic moments.

<table>
<thead>
<tr>
<th>Neutron diffraction</th>
<th>Electron diffraction</th>
<th>X-Ray diffraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>interacts with nuclei through strong nuclear force</td>
<td>interacts with charged nuclei and electrons through Coulomb interaction</td>
<td>interacts with valence electrons</td>
</tr>
<tr>
<td>atomic factor negligible</td>
<td>atomic factor needs to be considered</td>
<td>atomic factor needs to be considered</td>
</tr>
<tr>
<td>expensive to operate a neutron source</td>
<td>relatively cheap to operate</td>
<td>lab X-rays are relatively cheap, synchrotron X-ray is typically cheaper than neutrons</td>
</tr>
<tr>
<td>sample has to be relatively large</td>
<td>sample can be nano-sized</td>
<td>sample can be relatively small</td>
</tr>
<tr>
<td>can measure magnetic moments</td>
<td>cannot measure magnetic moments</td>
<td>can measure magnetic moments</td>
</tr>
</tbody>
</table>

Table 1.1: Comparison of neutron, electron and X-ray diffraction techniques.

Some elements strongly absorb neutrons, so X-ray or electron diffraction should be used. Neutrons also interact strongly with light-elements, compared to X-ray and electrons, therefore neutrons are commonly used to study samples containing hydrogen (samples have to be deuterated) and lithium.

As can be seen in Table 1.1, both neutron and X-ray scattering can be used to study magnetism, therefore it is worthwhile to compare the two techniques. Furthermore, there are differences between resonant and non-resonant X-ray scattering and should be considered separately. The comparison of neutron scattering, non-resonant...
**Table 1.2**: Comparison of neutron, non-resonant and resonant X-ray scattering for studying magnetic order and excitations.

<table>
<thead>
<tr>
<th>Neutron scattering</th>
<th>non-resonant X-ray scattering</th>
<th>resonant X-ray scattering</th>
</tr>
</thead>
<tbody>
<tr>
<td>magnetic form factor needs to be considered</td>
<td>magnetic form factor needs to be considered</td>
<td>magnetic form factor can be ignored</td>
</tr>
<tr>
<td>large sample mass needed</td>
<td>relatively small sample can also be used</td>
<td>can probe small samples with weak magnetic signal</td>
</tr>
<tr>
<td>cross section well-understood and easily interpreted</td>
<td>cross section more complex, but still easily interpreted</td>
<td>cross section not fully understood, harder to interpret results</td>
</tr>
<tr>
<td>can be used to measure spin excitations</td>
<td>too weak to be used for measurement of spin excitations</td>
<td>can be used to measure spin excitations</td>
</tr>
<tr>
<td>not element-specific</td>
<td>not element-specific</td>
<td>element-specific</td>
</tr>
</tbody>
</table>

In recent years resonant inelastic X-ray scattering (RIXS) has emerged as a viable alternative to neutron scattering for studying magnetic excitations [6], especially in cuprates [7, 8, 9] and iron pnictides [10]. However the energy resolution is still much worse than neutron scattering, but the clear advantage of RIXS is that very small samples can be studied much more efficiently than neutron scattering. Even though RIXS with improved energy resolution are scheduled to come online in the near future, it is nearly impossible for it to replace neutron scattering in the study of magnetic
excitations, given the neutron scattering can reach energy order resolution on the order of $\mu$eV. Therefore neutron scattering and RIXS are complementary techniques each with unique applications.
Chapter 2

Introduction

In this chapter an introduction to magnetic order and excitations seen in unconventional superconductors revealed by neutron scattering is given, including cuprates, iron-based superconductors and heavy fermion superconductors. The experimental techniques used in neutron scattering experiments are also discussed to facilitate presentation of the experimental results in later chapters.

2.1 Magnetic Order and Excitations in Unconventional Superconductors

Until the discovery of superconductivity in the heavy fermion compound CeCu$_2$Si$_2$ in 1978, all known superconductors were well described by BCS theory[11] (conventional superconductivity) ans its extensions. Several superconducting heavy fermion compounds were discovered afterwards [12], but the superconducting transition temperatures ($T_c$) is these compounds are typically $\approx 1$ K. These compounds are the first unconventional superconductors, with non-phonon pairing mechanisms. An alternative definition of unconventional superconductivity mandates a superconducting order parameter ($\Delta$) that changes sign on different parts of the Fermi surface.

The discovery of superconductivity in the cuprate La$_{2-x}$Ba$_x$CuO$_4$ in 1986 took the physics community by surprise. It completely goes against the rules set out by Matthias [13] for finding higher $T_c$, the weak electron-phonon coupling in these mate-
rials suggested a non-phonon pairing mechanism. Neutron diffraction soon uncovered
the parent compound La$_2$CuO$_4$ to be a Mott insulator with antiferromagnetic or-
der [14]. This finding highlighted the relevance of magnetism and set the stage for
research in high-temperature superconductivity where neutron scattering played a
key role. With the discovery of superconductivity above 77 K in YBa$_2$Cu$_3$O$_{6+x}$ [15],
both the underlying mechanism and potential application of such high-temperature
superconductors grasped the attention of scientists ever since. In 2008 the physics
community was again pleasantly surprised by the discovery of unconventional su-
perconductivity in iron pnictides [16]. The diversity of compounds and properties
exhibited by iron-based superconductors provide a fertile playground to explore the
nature of superconductivity [17]. Superconductivity in iron-pnictides are also derived
from magnetically ordered parent compounds [18], although whether the magnetism
is due to itinerant or local electrons is still under debate [19].

Heavy fermion superconductors such as CeCu$_2$Si$_2$ [12] and CeCoIn$_5$ [20] are also
in proximity to magnetically ordered phases [21]. CeCu$_2$Si$_2$ is very close to a quan-
tum critical point, and samples obtained via different growth procedures can exhibit
either magnetic order or superconductivity [22]. CeRhIn$_5$ exhibits magnetic order,
and upon gradually replacing Rh by Co magnetic order is suppressed giving way
to superconductivity [23]. In CePd$_2$Si$_2$ superconductivity can be induced by apply-
ing pressure while magnetic order is simultaneously suppressed [24]. Compared to
chemical substitution pressure is a cleaner tuning parameter, and the phase diagram
obtained captures the essence of the intimate relationship between magnetism and
superconductivity in many unconventional superconductors (Fig. 2.1). Very recently
superconductivity with $T_c \sim 2$ mK has also been found in YbRh$_2$Si$_2$, attesting to the
picture of superconductivity emerging near a magnetic quantum critical point [25].
Figure 2.1: **Schematic phase diagram of CePd$_2$Si$_2$.** AFM stands for antiferromagnetic order and SC stands for superconductivity. Whether magnetic order persists into the superconducting state is not known [24].

The typical phase diagram of iron pnictides is very similar to Fig. 2.1 [17], the phase diagram for the prototypical system BaFe$_{2-x}$Ni$_x$As$_2$ is shown in Fig. 2.2 [26]. The transition to stripe antiferromagnetic order at $T_N$ is coincident with or preceded by a tetragonal-to-orthorhombic structural transition at $T_s$. With increasing doping, both transitions are suppressed leading to superconductivity. In the underdoped region superconductivity coexists with antiferromagnetic order while competing with both magnetic order and orthorhombicity [17, 27]. Close to optimal superconductivity there is a region with incommensurate short-range magnetic order [28, 29], in this region $T_N$ becomes ill-defined. It should be noted another structural phase transition well above $T_s$ [30] has been reported, however recent work suggest that internal or inadvertent strain may be causing the apparent symmetry breaking [31].

The phase diagram of cuprates displays a plethora of competing phases and the enigmatic *pseudogap* phase with charge and spin orders. In addition checkerboard
Figure 2.2: \textbf{BaFe}_{2−x}\text{Ni}_x\text{As}_2 \text{ phase diagram.} \ T_S \text{ is the tetragonal-to-orthorhombic transition temperature, } \ T_N \text{ is the magnetic transition temperature and } \ T_c \text{ is the superconducting transition temperature [26]. The region labeled IC correspond to samples with incommensurate short-range glassy magnetic order.}

magnetic order in the parent compound is well suppressed before the appearance of superconductivity [32, 33, 34]. For example in La$_{2−x}$Ba$_x$CuO$_4$ spins order into stripes and strongly suppress superconductivity for doping level $p \sim \frac{1}{8}$ [35]. Recently unidirectional charge ordering has been found to compete with superconductivity in YBa$_2$Cu$_3$O$_{6+y}$ [36, 37, 38].

All the unconventional superconductors mentioned above consist of 2D layers as building blocks (Ce-In plane, Cu-O planes and Fe-As planes). The magnetic structures of La$_2$CuO$_4$, NaFeAs and CeRhIn$_5$ are schematically shown in Fig. 2.3 with the corresponding structural motif. The couplings between neighboring spins are very strong, with spin waves in cuprates and iron pnictides having energies scales well above 200 meV [17, 32, 33]. Such large bandwidths dwarf even the phonon bandwidth in diamond ($\sim 100$ meV). The extraordinary magnetic coupling strengths in cuprates and iron pnictides are likely important for their high $T_c$. The magnetic bandwidth in CeRhIn$_5$ ($\sim 3$ meV) is much smaller in comparison [39, 40], but still large relative to the Fermi energy in a heavy fermion compound. By mapping out the
spectra of spin waves using inelastic neutron scattering, the corresponding exchange coupling constants can be obtained.

Upon doping the magnetic order in the parent compounds are destroyed but magnetic excitations can still persist. In the cuprates while neutron scattering sees magnetic excitations with decreasing intensity as doping level is increased [41, 33], resonant X-ray scattering (RIXS) reports persistent spin excitations that depend weakly on doping [8, 9]. It should be noted RIXS measures near $Q = (0, 0)$ which is inequivalent to $Q_{AF} = (0.5, 0.5)$ in the paramagnetic state of the cuprates. In iron pnictides the doping dependence of magnetic excitations across the superconducting dome has been extensively mapped out by neutron scattering. While low energy excitations are significantly modified by doping, high energy excitations are robust against doping resulting in a total fluctuation moment that only weakly depends on doping [17, 42]. In the case of heavy fermion superconductors, not as much is known but spin waves
in CeRhIn$_5$ [39, 40] are much stronger than normal state spin excitations in CeCoIn$_5$ [43].

In the superconducting state, a strong enhancement of spin fluctuations at the magnetic wave vector with $E(Q) < \min(\Delta_k + \Delta_{k+Q})$ termed the *neutron spin resonance mode* is seen in many unconventional superconductors. The intensity of this mode tracks the superconductivity order parameter and is suggested to be a common thread linking various unconventional superconductors [44, 45]. The energy of the resonance mode is found to scale with the superconducting gap $\Delta$ [46] or the superconducting transition temperature $T_c$ [47]. A common interpretation of the resonance is that it’s a collective bound state within the superconducting gap, termed *spin-exciton*. Within this interpretation the *resonance mode* is a divergence in the dynamic magnetic susceptibility that can only happen when $E(Q) < \min(\Delta_k + \Delta_{k+Q})$.

Within the spin-exciton picture the mode is well captured by the random phase approximation (RPA), including the hour-glass dispersion of the resonance in the cuprates [48] and the upward dispersion of the resonance seen in iron pnictides [49]. In this picture the dynamic susceptibility is obtained by $\chi(Q, \omega) = \frac{\chi_0(Q, \omega)}{1 - \frac{J_Q\chi_0(Q, \omega)}{\epsilon_k\epsilon_{k+Q}}}$, with $\chi_0(Q, \omega)$ being the bare susceptibility and $J_Q$ being the magnetic interaction [50]. For a divergence to occur both the real and imaginary parts of the denominator of the susceptibility have to be zero, $1 - \text{Re}\chi_0(Q, \omega) = 0$ and $\text{Im}\chi_0(Q, \omega) = 0$. For the real part to be zero, the bare susceptibility should be large or divergent, in the superconducting state the BCS coherence factor appears in the expression of $\chi_0(Q, \omega)$ with the form $\sim \frac{1}{2}(1 - \frac{\Delta_k \Delta_{k+Q}}{\epsilon_k \epsilon_{k+Q}})$ which becomes small when there is no a sign change between $\Delta_k$ and $\Delta_{k+Q}$ [45]. For this reason the occurrence of the resonance mode is often used as evidence for sign-changing $\Delta$ [51, 43]. $\text{Im}\chi_0(Q, \omega) = 0$ is the same as $E(Q) < \min(\Delta_k + \Delta_{k+Q})$, namely energy of the resonance mode has to be below the
particle-hole continuum. Take the case of the cuprates with $d_{x^2-y^2}$ superconducting order parameter for example, the resonance is found at $Q_{AF} = (0.5, 0.5)$ and when one moves away from $Q_{AF} = (0.5, 0.5)$ the states connected by $Q$ becomes the nodal points with $\Delta = 0$, which leads to the particle-hole continuum becoming zero at that point. The reason a downward dispersing resonance is seen in the cuprates, is therefore $\min(\Delta_k + \Delta_{k+Q})$ moves towards zero as one moves away from $Q_{AF}$ [50].

While the spin-exciton scenario has been successful in explaining the resonance mode in many cases, it has also been proposed that the mode may be a paramagnon that becomes undamped in the superconducting state [52, 53]. Within this picture the hourglass dispersion of the resonance in the cuprates is explained in terms of magnetic fluctuations associated with spin stripes [35, 54]. So far there is no consensus on the nature of the resonance mode, although the spin-exciton scenario is certainly the most widely accepted interpretation.

Since neutron scattering is the ideal probe to study magnetic ordering and excitations, it has been used extensively to study the interplay between magnetism and superconductivity observed in unconventional superconductors hoping to answer whether spin fluctuations play the role of a pairing glue in unconventional superconductors, similar to phonons in conventional superconductors. Given that unconventional superconductors usually have large magnetic bandwidths and the moment is smaller than rare-earth atoms, successful neutron scattering experiments usually require large sample masses and neutron scattering instruments and facilities with high flux.
Figure 2.4: **Schematic of neutron scattering process.** Incident neutrons with wave number $k_i$ is scattered by the sample to $k_f$, exchanging momentum $Q$ with the sample.

### 2.2 Neutron Scattering Experimental Techniques

The basic idea of neutron scattering is shown schematically in Fig. 2.4. Incident neutrons with wave number $k_i$ strike on the sample, and the scattered neutrons with wave number $k_f$ and a scattering angle of $2\theta$ are counted. The sample exchanges momentum $Q$ and energy $E$ with the neutron, with $Q = k_i - k_f$ and $E = \frac{\hbar^2 k_i^2}{2m_n} - \frac{\hbar^2 k_f^2}{2m_n}$, with $m_n$ being the mass of a neutron. If $E = 0$ the scattering process is called *elastic*, if $E \neq 0$ it is called *inelastic* and measurements that do not select the energy of the scattered neutrons are called *diffraction* measurements.

Neutron scattering measurements are routinely carried out on triple-axis spectrometers and time-of-flight chopper spectrometers. The former is typically installed at reactor neutron sources while the latter at spallation neutron sources, however there are exceptions. A typical triple-axis spectrometer is schematically shown in Fig. 2.5. The neutron beam comes directly from inside a reactor or from a neutron guide. The benefits of neutron guides are to allow instruments to be placed far away
from the reactor, reducing background and allowing for more space to install many instruments. Neutron guides are typically slightly curved to avoid direct high energy neutrons and gamma ray. Furthermore only neutrons below a certain threshold energy will be totally reflected when traveling in the guide. This is because the critical angle for total reflection for neutrons $\gamma_c \propto \lambda$, and for high energy neutrons with small wavelengths, the critical angle becomes too small compared to the curvature of the guide.

Avoiding high energy neutrons is important, since monochromators and analyzers operate based on Bragg’s law $n\lambda = 2d\sin \theta$ and if $\lambda_0 = 2d\sin \theta$ is selected by the monochromator/analyzer then higher order neutrons with $\frac{\lambda_0}{n}$ can also be selected. This is a very serious issue, consider for example diffraction of magnetic Bragg peaks for a simple antiferromagnet. Again based on Bragg’s law $Q = \frac{4\pi \sin \theta}{\lambda}$, if $\lambda_0$ measures a magnetic Bragg peak at $Q$ then $\frac{\lambda_0}{2}$ measuring $2Q$ corresponding to a nuclear Bragg peak will also be seen. One way to reduce such contamination from higher order neutrons is to build an instrument on a neutron guide, but that does not fully solve the problem. A common way to deal with such problems is by using neutron filters. Be and BeO filters are commonly used, these are essentially powders that scattering neutrons according to Bragg’s law $Q = \frac{4\pi \sin \theta}{\lambda}$, where $Q$ is a Bragg reflection. Therefore the maximum wavelength that can be scattered is $\lambda_{max} = \frac{4\pi}{|Q_{min}|}$. Given reasonable thickness, almost all neutrons with wavelength smaller than the critical value will be Bragg scattered and neutrons with wavelengths larger than the critical value are transmitted. Appropriate cooling is often used on these filters to improve transmission of neutrons. Pyrolytic graphite (PG) filters are also commonly used, PG is well-ordered along the $c$-axis, having well-defined $(00l)$ peaks, but orientation of these planes are disordered giving $(hkl)$ peaks that are essentially powder-like.
When used as filters, the incident neutron beam is along the \( c \)-axis of PG filters and Bragg scattering only occurs at particular wavelengths, resulting in a strongly wavelength-dependent transmission function. It happens PG has very high transmission at \( E = 14.7 \) meV and very low transmission at corresponding \( \lambda_0/2 \) and \( \lambda_0/3 \), given that even higher order neutrons will be very few in a thermal neutron white beam, \( \lambda_0/4 \) can be readily ignored. In contrast to Be and BeO powder filters which can work below a certain threshold energy, PG has to operate at fixed energies. An alternative approach in dealing with higher order neutrons is to install a velocity selector before the monochromator. A velocity selector only selects a relatively broad band of neutrons with wavelengths centered at \( \lambda_0 \), with no higher order neutrons to worry about. A monochromator can then select the desired \( \lambda_0 \).

In addition to being used as a filter, PG is regularly used as monochromators/analyzers, especially on thermal triple-axis spectrometers. In this case the (00\( l \)) Bragg peaks are used. The benefit of using PG is that it has a high reflectivity for Bragg scattering on (00\( l \)) peaks, in part because PG can be made to have mosaic spread comparable to the neutron beam spread. Using monochromator/analyzer made of Si \( \lambda_0/2 \) can be avoided, this uses the fact the while (111) Bragg peak is allowed in Si, (222) is forbidden. However \( \lambda_0/3 \) is still present, but since the corresponding energy will be quite high, it presence in a thermal neutron beam should be insignificant. The problem with using Si is that it tend to reduce the neutron flux. Many other crystals can be used as neutron monochromator/analyzer, typically materials with large coherent and small incoherent and absorption cross sections are used.

The monochromator and analyzer are typically curved, focusing the neutrons on the sample. The vertical curvature can be fixed, but the horizontal curvature has to be optimized for the energy to be selected. This is typically motorized and done only
Figure 2.5: **Schematic of a triple-axis spectrometer.** Figure taken from http://nmi3.eu/neutron-research/techniques-for-/dynamics/three-axis-spectroscopy.html. Collimators are made from neutron absorbing materials, monochromator and analyzer are made from crystals prepared with an intentional mosaic. Very often these days, a single detector as depicted here is replaced by multiple detectors or a position-sensitive detector.
for the analyzer. In addition the monochromator and analyzer crystals are designed to have some mosaicity to balance the trade off between neutron flux and resolution.

In addition to collimators, slits are typically used around the sample to cut down unwanted scattering. Experimentally sitting at several Bragg peaks the size of the slits are scanned and the smallest slit in size that does not significantly reduce the intensity of any of the Bragg peaks is chosen. Cadmium sheets, B$_4$C blocks or Gd$_2$O$_3$ powder which absorb neutrons are sometimes used on the sample holder to mask them from the beam to reduce background.

Nowadays newly developed triple-axis spectrometers tend to use multiplexing on the detector side. One way to do this would be to add many detectors situated at different scattering angles ($\theta_S$ in Fig. 2.5), a prime example of this method is the Multi Axis Crystal Spectrometer (MACS) at the NIST center for neutron scattering (NCNR). Such a setup can be realized by using double-bounce analyzers as shown in Fig. 2.6, which allows the scattered beam to go in a straight line after being analyzed. Doing so allows many analyzers to be compactly installed around the sample (Fig. 2.7). It is useful to realize that most neutrons that are not selected by the analyzer goes directly through the analyzer. On MACS a diffraction detector is installed after each analyzer. In principle many analyzers selecting different energies can be built one after another, this is mostly an engineering challenge and with increasing number of analyzers the benefit diminishes. MACS consists of 20 channels each with different $\theta_S$, in each channel there is one analyzer and two detectors (Fig. 2.6), an upgrade to PANDA instrument at FRM-II in Munich will allow for three analyzers selecting three different energies at the same time, but likely the number of channels will be fewer compared to MACS. Alternatively, a position-sensitive detector can be installed to probe a large momentum transfer range when only diffraction is
Figure 2.6: **Schematic of a single channel for a multiplexing triple-axis spectrometer.** On MACS a double crystal analyzer is used which allows many channels to be installed. A detector after the analyzer is used for diffraction. In principle multiple analyzers can be installed in series to measure multiple energy transfers at once.

involved, as realized on the Wide-Angle Neutron Diffractometer (WAND) at Oak Ridge National Laboratory (ORNL).

Time-of-flight neutron spectrometers are designed based on the pulsed structure of the neutron beam, which comes from the pulsed nature of spallation neutron sources or intentionally pulsed beams at reactor sources. Typically the incident neutron energy is selected by Fermi choppers and the scattered neutron energy is calculated based on time of flight (direct geometry). A background chopper is commonly employed to reduce background when the proton pulse initially hits the target. Large
Figure 2.7: Schematic of a multiplexing triple-axis spectrometer with multiple detectors. Using double-bounce analyzers the scattered beam goes in a straight line, allowing the placing of many detectors compactly after the sample.
2D position-sensitive-detector banks are placed after the sample typically inside a evacuated chamber. The distance from the sample to the detectors is a key determining factor of the instrument resolution, the larger distance the better resolution. However this also means larger detectors are needed to cover the same $Q$ range. A time-of-flight chopper spectrometer is conceptually very simple, there are no moving parts other than sample rotation, and for quasi-2D systems the measurement geometry is usually $k_i \parallel c$ so the only parameters that change during an experiment are temperature and incident neutron energy.

With the $k_i \parallel c$ geometry magnetic excitations in the $(H, K)$ plane at various energy transfers (differentiated using time-of-flight) can be probed in a single measurement. However it should be noted that $L$ [this is the reduced lattice units, where $Q = (Q_x, Q_y, Q_z) = (H\frac{2\pi}{a}, K\frac{2\pi}{b}, L\frac{2\pi}{c})$] component of momentum transfer probed cannot be independently varied and is a function of $E_i$, $E$, $H$ and $K$. Using momentum conservation $k_i = k_f + Q$ and energy conservation $(2.072k_i)^2 = (2.072k_f)^2 + E$ ($2.072$ relates neutron energy and momentum in units of meV and Å$^{-1}$), $L$ can be easily obtained from

$$Q_z = L\frac{2\pi}{c} = k_i - \sqrt{k_i^2 - Q_x^2 - Q_y^2} - \frac{E}{2.072}.$$ (2.1)

Even though most unconventional superconductors are quasi-2D, one can check for $L$-dependence by selecting energy transfers that correspond to different $L$, this has been very useful in bi-layer YBa$_2$Cu$_3$O$_{6+y}$ in differentiating acoustic and optical spin wave branches. Moreover by knowing $L$ in addition to $H$ and $K$ one can know the magnetic factor to obtain true strength of the magnetic correlations by correcting for the form factor. It should be noted that for high energy transfers the magnetic form factor involved becomes very small $\sim 0.01$, since experimentally it is very challenging
to determine form factors when it becomes this small, there is some uncertainty when applying the tabulated/calculated magnetic form factor to high-energy time-of-flight data.

Another common way to carry out time-off-flight measurement is to perform a series of measurements, with incident beam $k_i$ at various angles with $c$-axis. By combining all of the measured data it is then possible to obtain four-dimensional $S(Q, \omega)$, compared to $k_i \parallel c$ geometry which only obtains three-dimensional $S(Q, \omega)$ with energy coupled to $L$. The magnetic signal has to be sufficiently strong for such measurements to be feasible.
Chapter 3

Effects of Uniaxial Pressure on Iron Pnictides

In this chapter the effects of uniaxial pressure on iron pnictides is discussed. The background will be briefly introduced, followed by results on NaFeAs, as-grown and annealed BaFe$_2$As$_2$ [55], underdoped BaFe$_{1.925}$Ni$_{0.085}$As$_2$ [56] and optimal-doped BaFe$_{1.9}$Ni$_{0.1}$As$_2$ [57].

3.1 Introduction

The parent compounds of iron pnictide superconductors such as NaFeAs and BaFe$_2$As$_2$ exhibit a tetragonal to-orthorhombic lattice distortion at temperature $T_s$ and a paramagnetic-to-antiferromagnetic phase transition at $T_N$ ($\leq T_s$), forming a low-temperature collinear antiferromagnetic state with ordering wave vectors along the $(\pm 1,0)$ directions of the orthorhombic lattice. Given the similar in-plane lattice parameters, twin domains typically exist in samples large enough for neutron scattering. It is possible to detwin the sample, to favor one of the twin domains by applying uniaxial pressure along one of the orthorhombic axes. Since $b$ axis is shorter than $a$ axis, the domains with $b$ axis along the applied uniaxial pressure direction will be favored. The same applies in doped iron pnictides, up until the orthorhombic phase is fully suppressed.

It is useful to review the notation used in iron pnictides, summarized in Fig. 3.1. The chemical unit cells are most commonly used, although it is useful to note that the magnetic unit cells are different from chemical unit cells because As atoms that
are below and above Fe atoms do not contribute to magnetism. In this thesis only the tetragonal and orthorhombic chemical unit cells will be used, differentiated by subscripts or otherwise specified. In the tetragonal chemical unit cell the in-plane axes are at 45° to the nearest Fe-Fe direction and in the orthorhombic chemical unit cell the axes are along the nearest Fe-Fe directions. The orthorhombic axes are $\sqrt{2}$ times the tetragonal axes. Therefore (200)$_T$ in tetragonal notation correspond to (110)$_O$ in orthorhombic notation. Magnetic peaks are at (0.5, 0.5)$_T$ in tetragonal notation and (1, 0)$_O$ in the orthorhombic notation.

For a twinned crystal in the orthorhombic state magnetic peaks are seen at both (1, 0)$_O$ and (0, 1)$_O$, with (200)$_O$ and (020)$_O$ structural peaks overlapping in reciprocal space. The $d$-spacings of these peaks are slightly different corresponding to the small difference in $a$ and $b$ but typical triple-axis spectrometers cannot resolve them as two peaks, instead a broadening can be seen when the sample enters the orthorhombic state.
Figure 3.2: Schematic of effect of uniaxial pressure on iron pnictides. (a) A twinned crystal and a (b) partially detwinned crystal, the two sets of domains have the same population for the twinned crystal whereas one set of domains dominates in the detwinned crystal. In reciprocal space, the magnetic and structural peaks corresponding to the two sets of domains have equal intensities for a (c) twinned crystal, while for a (d) partially detwinned crystal the dominant set of domains is enhanced while peaks corresponding to the minority set of domains have diminished intensities. Green spheres represent the magnetic $(1, 0, L)O$ peaks, red spheres represent the structural $(2, 0, 0)O/(0, 2, 0)O$ peaks. The blue arrows in (c) and (d) represent applied uniaxial pressure.

phase. In a single-domain sample, magnetic peaks are only seen at $(1, 0)O$, with $(200)O$ and $(020)O$ non-overlapping. In a partially detwinned sample, the magnetic peak at $(1, 0)O$ will be much stronger than the peak at $(0, 1)O$ and longitudinal scans at $(200)O$ and $(020)O$ will reveal an asymmetric lineshape (consisting of a large and a small Gaussian peaks, but a single peak is seen due to limited resolution of neutron spectrometers) as shown in Fig 3.2.

While it is nice to obtain a single-domain sample, it is not necessary for solving magnetic structures or obtaining exchange couplings. The reason that one would want to go through all the effort of applying uniaxial pressure is to study the the intrinsic
response of the system to external stress, in light of the purported electronic nematicity, first observed through transport measurements under uniaxial stress [58]. This electronic anisotropy was later confirmed by many other experimental techniques, including STM [59], resonant ultrasound [60], ARPES [61], Raman scattering [31], optical reflectivity [62], neutron scattering [63] and magnetic torque measurements [30].

Electronic nematicity refers to breaking of rotational symmetry (four-fold to two-fold in this case) due to electronic degrees of freedom, which then couples to the lattice and results in the orthorhombic distortion. In the case of iron pnictides, this refers to the state above the magnetic transition temperature (also below the structural transition temperature for stress-free sample). While the electronic origin of observed anisotropies has been conclusively established [64], it is unclear which electronic degree of freedom is the driver (spin and orbital being the debated candidates) [65]. Currently despite much effort there is no closure on this debate, since spin, orbital and the lattice are always coupled and breaking of symmetry in any one of them would result in anisotropy in the other two [65].

The interest in electronic nematicity first started in the cuprates, when rotational symmetry breaking is found to be associated with the enigmatic pseudogap state [66]. There are proposals of nematic fluctuations in general enhancing superconductivity [67] and for this reason the discovery of electronic nematicity in iron pnictides also generated a great deal of excitement.

The structural and magnetic phase transitions, their response to external stress, as well as the underlying electronic driver are often modeled phenomenologically. For example considering only the lattice and spin, in a Ginzburg-Landau (GL) approach the free energy can be written as [68, 69]
Figure 3.3: **Effect of uniaxial pressure on phase transitions in GL approach.** Using $A = B = C = D = 1$, $T_0 = 1$, $T_{N,0} = 0.8$ and $\lambda = 0.2$ the structural ($\delta$, left) and magnetic ($|M|$, right) order parameters are solved for various applied pressure $\sigma$.

\[ F = F_0 + \frac{A}{2} (T - T_0)\delta^2 + \frac{B}{4} \delta^4 + \frac{C}{2} (T - T_{N,0})M^2 + \frac{D}{4} M^4 - \lambda \delta M^2 - \delta \sigma. \] (3.1)

$\delta$ is the orthorhombic distortion or the shear strain that acts as the order parameter for the structural transition, $M$ is the magnetic order parameter, $\lambda$ is the magnetoelastic coupling, $\sigma$ is applied stress, $T_0$ is the bare structural transition temperature and $T_{N,0}$ is the bare magnetic transition temperature. This model has been successfully applied in parent and electron-doped BaFe$_2$As$_2$ to explain the evolution of the structural and magnetic phase transitions (without considering the effect of stress). Fig. 3.3 shows the behavior of the phase transitions for some arbitrary parameters to qualitatively demonstrate the effect of applied stress. The apparent magnetic transition temperature is different from the bare one, and uniaxial pressure further increases the apparent magnetic transition temperature. The structural order parameter becomes finite at all temperatures under uniaxial stress and can completely lose the kink associated with a phase transition.

Alternatively, it is commonly assumed that the structural transition is secondary to some underlying electronic degree of freedom $\phi$ and the lattice itself does not
soften. In these cases the free energy can be written as (behavior of this model has been discussed in Ref. [70]).

\[ F = F_0 + \frac{A}{2}(T-T_0)\phi^2 + \frac{B}{4}\phi^4 + \frac{C}{2}\delta^2 + \frac{D}{2}(T-T_{N,0})M^2 + \frac{E}{4}M^4 - \lambda \delta \phi - \mu \phi M^2 - \delta \sigma. \] (3.2)

### 3.2 Effect of uniaxial pressure on phase transitions in NaFeAs and BaFe\(_2\)As\(_2\)

A mechanical clamp was used to apply uniaxial pressure on rectangular samples cut along the orthorhombic axes. For NaFeAs, the cutting process is done manually using a scalpel inside an Ar-filled glovebox, doing so means the edges are not perfect and it is hard to apply a uniform uniaxial pressure to the sample, and therefore it is challenging to fully detwin NaFeAs and derived compounds. For BaFe\(_2\)As\(_2\) the cutting is done using a high precision wire saw in air, and the sample edges are flat and highly parallel. Pressure is applied using a spring with known force constants, allowing pressure on the sample to be estimated by measuring the crystal dimensions. A similar device has been employed for resistivity measurements, and resistivity along the two directions are obtained following the Montgomery method [71], using this method the samples should be close to a square to obtain high quality data. The mechanical clamp and measured resistivity anisotropy for NaFeAs is shown in Fig. 3.4. It should be noted that \(T^*\) in the figure is not a phase transition [31, 72], rather resistivity anisotropy has a Curie-Weiss type temperature dependence for constant shear strain, and so it is strictly non-zero at all temperatures under uniaxial pressure [73]. \(T^*\) simply denotes the onset of resistivity anisotropy that can be experimentally resolved.

Neutron scattering experiments were carried out using the BT-7 triple-axis spec-
Figure 3.4: Schematic of a mechanical clamp and resistivity anisotropy in NaFeAs. The mechanical clamp used in neutron scattering experiments is schematically shown on the left. Using a similar device, the resistivity anisotropy has been measured in NaFeAs using the Montgomery method, shown on the right. $T^*$ marks the onset of resistivity anisotropy and the shaded region reflects the change in $T_s$ seen experimentally.

trometer at NIST Center for Neutron Research (NCNR) and HB-1A at High-Flux-Isotope-Reactor (HFIR), Oak Ridge National Laboratory. For HB-1A measurements on BaFe$_2$As$_2$, the collimations are 48'-48'-sample-40'-68'. The measurements for NaFeAs were carried out on BT-7 with open-50'-sample-50'-120' collimation with $E_f = 14.7$ meV. To observe broadening of the (2, 0, 0)$_O$/(0, 2, 0)$_O$ nuclear Bragg peaks in the orthorhombic state of a twinned sample, we used tight collimation of 10'-10'-sample-10'-25' on BT-7 with $E_f = 14.7$ meV.

Measurement of magnetic intensity for NaFeAs is shown in Fig. 3.5, under applied uniaxial pressure the magnetic intensity at $(1032)_O$ is clearly enhanced, this is mostly due to detwinning of the sample, however as the sample is not fully detwinned so the fact the magnetic peak has almost doubled its intensity suggests that the ordered moment may have also increased. Unfortunately, since the sample has to be taken out every time to change the applied pressure, alignment of the sample also changes, so within this experiment it was not possible to conclusively determine whether the ordered moment itself changed. As will be seen in the next section, the ordered mo-
Figure 3.5: Magnetic elastic scattering in NaFeAs under uniaxial stresss. (a) The magnetic order parameter measured at \( Q = (10^3)_O \) for nominally-zero \( (P_0) \), \( \sim 7 \) MPa \( (P_1) \) and \( \sim 15 \) MPa \( (P_2) \). (b) The magnetic order parameters are rescaled to show that there is no discernible shift in \( T_N \). (c) \( H \)-scans at \( Q = (10^3)_O \). (d) \( L \)-scan at \( Q = (10^3)_O \).

The apparent magnetic transition temperature hardly changes as can be seen in the overlay of the magnetic order paramters, this contrasts with BaFe\(_2\)As\(_2\) [74]. The enhanced magnetic intensity at \( (10^3)_O \) is also demonstrated by carrying out scans along \( H \) and \( L \).

Before turning to structural measurements of NaFeAs under uniaxial stress, it is useful to note it is typical to use nuclear extinction to study structural phase transitions in neutron scattering. Due to lowering of symmetry of the crystal and formation of twins, secondary extinction becomes weaker in the orthorhombic state and strong nuclear Bragg peaks gain intensity, this is called nuclear extinction release. For iron pnictides nuclear extinction release very roughly tracks the orthorhombicity of the
system. Especially in the case of doped iron pnictides where the orthorhombicity is very small and it becomes impossible for neutron scattering to resolve, signature of the transition can nonetheless show up in nuclear extinction [75]. For example, measurement of strong nuclear Bragg peaks’ intensities for several doped NaFe$_{1-x}$Co$_x$As obtained on HB-1A are shown in Fig. 3.6. It should be noted that extinction is a general effect, it also occurs in X-ray scattering and magnetic neutron scattering. As can be seen, when the samples enter the orthorhombic phase the intensities of (220)$_T$ clearly increase. There are several details worth noting, as detailed below.

- For some samples the increase of intensity is quite sharp whereas others are rather broad, and there is no clear doping dependence for this behavior. We attribute this to residue strain in the sample or strain that is inadvertently applied during sample mounting. As shear strain will broaden the structural transition, signature of such a broadening can readily be seen in nuclear extinction release. This also explains why it is sample-dependent.

- For samples close to optimal doping, the intensity begins to drop again once the sample enters the superconducting state. This is due to magnetoelastic coupling and the competition between magnetic order and superconductivity resulting in orthorhombicity that also manifestly compete with superconductivity. Similar results has been explicitly demonstrated using high-resolution X-ray scattering in electron-doped BaFe$_2$As$_2$ [27].

- The decrease in the superconducting state appears to saturate below at around 12 K, this could signify an re-entry into the paramagnetic or tetragonal phase but measurement of magnetic peaks indicate otherwise. It is possible that phase separation plays a role since NMR experiments reported phase separation for underdoped NaFe$_{1-x}$Co$_x$As with $x = 0.0175$ [76]. Another possibility is that the orthorhombicity
Figure 3.6: (220)\textsubscript{\textit{T}} **nuclear extinction** in NaFe\textsubscript{1-x}Co\textsubscript{x}As. The intensity of the nuclear Bragg peak (220)\textsubscript{\textit{T}} measured in several dopings of NaFe\textsubscript{1-x}Co\textsubscript{x}As, the green arrows mark the tetragonal-to-orthorhombic structural transition temperature.

 decreases below $T_c$ but saturates at a non-zero value, this is seen by x-ray diffraction in BaFe\textsubscript{2-x}Ni\textsubscript{x}As\textsubscript{2} [26]. The glassy magnetism near optimal superconductivity in iron pnictides [77, 29] complicates the interpretation of these observations.

- While nuclear extinction is very sensitive to structural transition, it can also depend on other factors such as mosaicity of the sample and unintentional strain in the sample, and one can get quite different results depending on the specific sample and thermal cycling. One should therefore be cautious when interpreting such results.

For the measurement on NaFeAs, unfortunately the data at (220)\textsubscript{\textit{T}} was not collected but (110)\textsubscript{\textit{T}} was instead measured. (110)\textsubscript{\textit{T}} is a weak Bragg peak, and we did not see clear extinction release effect. Results on extinction release will be shown later for underdoped BaFe\textsubscript{1.915}Ni\textsubscript{0.085}As\textsubscript{2} under uniaxial pressure.

Using the tighter resolution we were able to resolve the orthorhombic distortion
in NaFeAs as a broadening of (110)\textsubscript{T}. Ideally the ‘intrinsic’ peak width is obtained by fitting a single Gaussian above the structural transition, and two split peaks with the obtained full-width-at-half-maximum (FWHM) and equal heights are used to fit data below the structural transition. When uniaxial pressure is applied, the heights of these two peaks are no longer restrained to be the same. This procedure works well when no uniaxial pressure is applied, but give poor results when the sample is partially detwinned. The reason is when the heights of peaks are no longer required to be the same, splitting of the peaks and their relative intensities are correlated and cannot be reliably and independently obtained, this is largely due to poor resolution of neutron spectrometers. Therefore while the above method is applied for NaFeAs under nominally zero pressure (\(P_0\)), we fit the data with a single Gaussian peak for the cases when pressure is applied (\(P_1\) and \(P_2\)). From the single Gaussian peak fit, \(T_s\) can be extracted as the point then the FWHM of the peak changes and when the center of the peak starts to shift. Results of such an analysis is shown in Fig. 3.7. As can be seen, uniaxial pressure appears to increase the measured structural transition temperature slightly in contrast to the magnetic transition temperature that does not appear to be affected by uniaxial stress. This is in line with the behavior shown in Fig. 3.3 where the magnetic order parameter is affected to a less degree compared to the structural order parameter.

Similar results for BaFe\(_2\)As\(_2\) are shown in Fig. 3.8. Previous neutron scattering experiment found applying uniaxial pressure on BaFe\(_2\)As\(_2\) causes both \(T_N\) and \(T_s\) to increase [74], offering a possible explanation for the observed resistivity anisotropy above \(T_s\) seen in transport measurements [58]. Later transport measurements found that annealing BaFe\(_2\)As\(_2\) causes \(T_N\) to increase and reduces the anisotropy above \(T_s\) [78], suggesting that resistivity anisotropy is related to impurities or defects which in
Figure 3.7: **Structural transition under uniaxial pressure in NaFeAs.** (a) FWHM of the (110)_T peaks when fit with a single peak. (b) Orthorhombicity for NaFeAs with nominally zero stress and center of fits with a single Gaussian peak when stress is applied. The reason for the different analysis is orthorhombicity can only be reliably obtained when equal height can be assumed for the two split peaks.

In summary, uniaxial stress affects \(T_N\) very little in NaFeAs similar to annealed BaFe\(_2\)As\(_2\). On the one hand our results are consistent with previous reports demon-
Figure 3.8: Magnetic and structural transitions under uniaxial pressure in BaFe$_2$As$_2$. (a) The normalized magnetic order parameter for as-grown BaFe$_2$As$_2$. (b) The normalized magnetic order parameter for annealed BaFe$_2$As$_2$. (c) Close-up of the normalized magnetic order parameter for as-grown BaFe$_2$As$_2$. (d) Close-up of the normalized magnetic order parameter for annealed BaFe$_2$As$_2$. (e) FWHM of (200)$_0$ structural peak for as-grown BaFe$_2$As$_2$. (f) FWHM of (200)$_0$ structural peak for annealed BaFe$_2$As$_2$. The arrows mark the transition temperatures with and without applied pressure.
strating $T_N$ and $T_s$ (as seen experimentally) can be affected by applied stress [74]. On the other hand by demonstrating $T_N$ changes little in NaFeAs while resistivity anisotropy is seen up to 70 K, we prove conclusively that the resistivity anisotropy is intrinsic and not related to shift in $T_N$. This work established the intrinsic nature of electronic nematicity in the paramagnetic state (any lattice distortion in these materials are deemed too small to account for the large resistivity anisotropy, so it does not really matter whether the system is actually tetragonal or orthorhombic).

3.3 Enhanced ordered moment in underdoped BaFe$_{1.915}$Ni$_{0.085}$As$_2$ under uniaxial stress

In the previous section effects of uniaxial stress on the structural and magnetic phase transitions in iron pnictides were discussed. While such experiments allowed the influence of stress on the order parameters to be obtained, it is not clear what happens to the ordered moment when $T_N$ is enhanced under uniaxial stress. This is because previous experiments were carried out in the $[H0L]_O$ scattering plane, allowing only $(10L)_O$ to be accessed, so it is not clear what happens to the intensity at $(01L)_O$. Combined with the coarse resolution of neutron triple-axis spectrometers, this means the population of the twin domains cannot be estimated from either nuclear or magnetic Bragg peaks and therefore we were unable to determine whether there is a change to the ordered moment. To overcome this problem, the mechanical clamp used in previous work was modified so that the sample can be aligned in the $[10L]_O \times [01L]_O$ scattering plane [63]. A similar device was used to study the effect of uniaxial pressure on the ordered moment in BaFe$_{1.915}$Ni$_{0.085}$As$_2$ [56]. Experiments were carried out at HB-1A and BT7 instruments. The actual mechanical clamp used is the one on the
Figure 3.9: **Sample holder used for measuring BaFe$_{1.915}$Ni$_{0.085}$As$_2$ under uniaxial stress.** A clamp in the [103]$_O$ × [013]$_O$ scattering plane is shown on the left, allowing (103)$_O$ and (013)$_O$ to be measured in the same experiment. The actual clamp used in the experiment is shown on the right, this clamp uses springs washers rather than springs to apply pressure, making it difficult to estimate the applied pressure.

Right of Fig. 3.9, on the left of Fig. 3.9 another clamp aligned in [10$L$]$_O$ × [01$L$]$_O$ scattering plane is shown.

For the experiment on HB-1A only the results of nuclear extinction release is shown in Fig. 3.10, since this experiment was carried out in the [100]$_O$ × [001]$_O$ scattering plane similar to NaFeAs and BaFe$_2$As$_2$ in the previous section. It is clear that an increase can be clearly seen corresponding to the structural transition when there is nominally no pressure on the sample ($P_0$), similar to the results on NaFe$_{1-x}$Co$_x$As in the previous section. With applied uniaxial pressure ($P_1$) the increase is almost completely gone. This is not due to the sample being detwinned, since in the case of fully detwinned BaFe$_2$As$_2$ nuclear extinction release can still be clearly observed [63]. This result in fact suggest since orthorhombicity is already quite small in BaFe$_{1.915}$Ni$_{0.085}$As$_2$, applying uniaxial pressure can completely smear out the transition similar to the highest stress case shown in Fig. 3.3, whereas in BaFe$_2$As$_2$
Figure 3.10: **Nuclear extinction release in BaFe$_{1.915}$Ni$_{0.085}$As$_2$ under uniaxial pressure.** $P_0$ is nominally zero pressure, $P_1$ is a pressure larger than 40 MPa applied on the sample, but since spring washers were used it is hard to precisely estimate the applied pressure.

a similar stress only slightly smears out the structural transition.

Measurement of magnetic order in BaFe$_{1.915}$Ni$_{0.085}$As$_2$ under uniaxial pressure from BT7 is shown in Fig. 3.11. Under uniaxial stress the sample is completely detwinned, with no intensity at (103)$_O$. Without applied stress equal intensities are seen at (103)$_O$ and (013)$_O$, as expected. Interestingly, comparing the sum of intensities at (103)$_O$ and (013)$_O$ the total intensity with applied stress is double of the total intensity without applied stress. This suggests it is the ordered moment that has increased with applied stress. Since neutron scattering measures the bulk average of the magnetization density, the current results may be interpreted to be due to change in the magnetically ordered volume rather than the moment itself. However, $\mu$SR experiment done under a similar experimental setup has confirmed that the ordered volume does not change with stress (unpublished).

Since for this experiment the sample has to be taken out to change the applied
Figure 3.11: Magnetic order in BaFe$_{1.915}$Ni$_{0.085}$As$_2$ under uniaxial pressure. (a) Rocking scans of (103)$_O$ and (013)$_O$ with pressure ($P_1$), the data is obtained by subtracting 60 K data from 2.5 K data. (b) Similar to (a) but without pressure ($P_0$). (c) Sum of rocking scans at (103)$_O$ and (013)$_O$ with ($P_1$) and without ($P_0$) pressure. (d) Sum of temperature scans at (103)$_O$ and (013)$_O$ with ($P_1$) and without ($P_0$) pressure.
Figure 3.12: **Structural peaks in BaFe$_{1.915}$Ni$_{0.085}$As$_2$ under uniaxial pressure.** Rocking scans at (103)$_O$ and (013)$_O$ with pressure ($P_1$) and without pressure ($P_0$) at 60 K are shown on the left, the measurements were done by removing the filter so that by using $\lambda/2$ the intensity from (206)$_O$ and (026)$_O$ are in fact measured. Similar results of (206)$_O$ and (026)$_O$ are shown on the right by measuring with the filter in.

stress, the alignment will be slightly different every time, care was taken to make sure the enhanced magnetic intensity is not due to changes in alignment. A good way to check the effect of alignment is to remove the filters and use $\lambda/2$ neutrons to repeat the scans at nominally (103)$_O$/(013)$_O$ positions above $T_N$, in this way the signal from (206)$_O$/(026)$_O$ will be measured. The benefit of doing so is that the instrument will be performing identical magnetic and structural scans with all the same instrument angles. The results are shown in Fig. 3.12, with measurement of (206)$_O$/(026)$_O$ also shown. All the structural peaks have similar intensities, with and without applied stress, demonstrating the difference in magnetic intensities can not be due to difference in alignment during sample mounting.

In the case of electron-doped iron pnictides such as BaFe$_{2-x}$(Co,Ni)$_x$As$_2$, long-range commensurate stripe magnetic order in BaFe$_2$As$_2$ evolves into short-range incommensurate magnetic order near optimal superconductivity [79, 80]. While the
incommensurate magnetic order has been suggested to be a signature of SDW arising from itinerant electrons [79], the results are also consistent with a cluster spin glass [77, 29], and therefore complicating the differentiation between local or itinerant origins of the magnetic order near optimal superconductivity. Application of uniaxial pressure provides another route to distinguish between the two cases. In the itinerant scenario, the ordered moment should depend sensitively on distortions of the electronic structure induced by uniaxial pressure and may either increase or decrease whereas in the local moment picture the magnetic order should weaken with applied stress due to enhanced hopping parameters. Our results provide evidence for the magnetic order in iron pnictides being spin-density-waves originating from itinerant electrons that can be tuned by applying uniaxial pressure, similar to the observation of site modulation of Fe moments in holed-doped Sr$_{1-x}$Na$_x$Fe$_2$As$_2$ in the tetragonal magnetically ordered phase [81]. Of course, detailed theoretical analysis is needed to compare the effects of uniaxial pressure within both itinerant and local moment pictures to confirm our conclusion. It should be mentioned that magnetism display dual character in these compounds, and it was suggested while the low energy magnetism has a more itinerant character, the high energy excitations are due to exchange couplings between quasi-localized moments [82].

3.4 Energy dependence of the spin excitation anisotropy in uniaxial-strained BaFe$_{1.9}$Ni$_{0.1}$As$_2$

Following the works of elastic neutron scattering on samples under uniaxial stress, it was shown that magnetic excitations become anisotropic in BaFe$_{2-x}$Ni$_x$As$_2$ well above $T_s$ under uniaxial stress [63]. This observation suggests that anisotropic scattering
due to spin excitations could be responsible for the resistivity anisotropy above $T_s$ \[58\].

It should be noted that it was recently suggested that the change in Drude weight rather than scattering rate is responsible for resistivity anisotropy \[62\]. Previous work studying inelastic magnetic excitations in samples under unaxial stress used a triple-axis neutron spectrometer and was confined to low energies \[63\]. Here our study of the energy dependence of magnetic excitations in BaFe$_{1.9}$Ni$_{0.1}$As$_2$ under uniaxial pressure using a time-of-flight chopper spectrometer is discussed.

Optimal-doped BaFe$_{1.9}$Ni$_{0.1}$As$_2$ single crystals used in previous work \[42\] were cut into rectangular plates with edges along the orthorhombic $a$ and $b$ axes. 9 such single crystals (with a total mass of 6.5 g) were each mounted into a separate aluminum mechanical clamp to apply uniaxial pressure (left of Fig. 3.13). In contrast to earlier experiments, we did not use springs to apply uniaxial pressure but instead compress aluminum pieces to press against the samples and rely on the fact that aluminum contracts more than near-optimal-electron-doped BaFe$_2$As$_2$ \[83\] as temperature is lowered. Based on the change of lattice constants between room temperature and $T < 10$ K and elastic constants for aluminum and Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ \[83, 84\], we estimate the uniaxial pressure experienced by our samples to be larger than 20 MPa, although it is difficult to determine the precise pressure experienced by the samples.

Time-of-flight neutron spectroscopy was carried out on the Wide Angular-Range Chopper Spectrometer (ARCS) at the Spallation Neutron Source, Oak Ridge National Laboratory and elastic neutron scattering was carried out on the Fixed- Incident-Energy Triple-Axis Spectrometer (HB-1A) at the High Flux Isotope Reactor, Oak Ridge National Laboratory. For the experiment on ARCS, incident energies $E_i = 30$, 80, 150 and 250 meV were used. A $T_0$ chopper rotating at 90 Hz was used at all energies to reduce background from prompt neutrons from the source. The samples
are co-aligned with \( k_i \parallel c \) and \( a \)-axis in the horizontal plane, uniaxial pressure is applied along the vertical direction (along \( b \)-axis).

For the elastic neutron scattering experiment on HB-1A the samples are co-aligned in the \([103]_O \times [013]_O\) scattering plane (Right of Fig. 3.13). HB-1A uses two PG monochromators (\( E_i = 14.6 \text{ meV} \)) and two PG filters (before and after the second monochromator) resulting in negligible amount of higher order neutrons. The collimation used was 40'-40'-sample-40'-80'. By removing one of the PG filters, using \( \lambda/2 \) neutrons we measured \((2,0,6)_O\) and \((0,2,6)_O\) (in the identical setup as for measuring \((1,0,3)_O\) and \((0,1,3)_O\) with both filters in) above \( T_N \) and found the intensities for these two nuclear Bragg peaks differ by less than 10%.

Given the debate regarding whether the electronic nematic phase is driven by spin or orbital degrees of freedom [65], we attempt to reveal the energy and temperature dependence of the spin excitation anisotropy to compare the outcome with temperature and electron-doping dependence of the energy splitting of the \( d_{xz} \) and
$d_{yz}$ bands in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [61]. In the tetragonal state without applied stress the Fermi surface is four-fold symmetric [Fig. 3.14(b)]. When the system undergoes a tetragonal-to-orthorhombic structural transition the bands at $X$ and $Y$ with $d_{yz}$ and $d_{xz}$ characters split in energy [Fig. 3.14(c)], a splitting is also seen when uniaxial stress is applied above the stress-free structural transition temperature [Fig. 3.14(d)] [61]. When the system enters the magnetically ordered phase, zone-folding occurs and the Fermi surface becomes more complicated. However given the magnetic order seen in BaFe$_{1.9}$Ni$_{0.1}$As$_2$ is short-ranged, glassy and very weak [26], the Fermi surface reconstruction cannot be experimentally observed and can be ignored in this case. Detwinning ratio as determined from measurement on HB-1A is shown in Fig. 3.14(a).

With the reported band splitting seen in nearly-optimal doped Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$, our goal is to study the splitting of magnetic excitations between (10)$_O$ and (01)$_O$ and compare the energy scales of the two.

Constant-energy maps and cuts along [$H,0$]$_O$ and [0, $K$]$_O$ for several energy transfers at 5 K are shown in Fig. 3.15. Whereas clear anisotropy is seen for $E = 4.5 \pm 0.5$ meV, the anisotropy becomes much smaller for $E = 16 \pm 2$ meV. Further increasing energy to $E = 100 \pm 10$ meV excitations at (1, 0)$_O$ and (01)$_O$ become isotropic. Within a weak-coupling five orbital model the anisotropy of magnetic excitations has been considered in the paramagnetic nematic phase, by assuming a splitting between bands with $d_{yz}$ and $d_{xz}$ characters at $X$ and $Y$ points [85]. The results are qualitatively in agreement with our experiment, the magnetic anisotropy between (10)$_O$ and (01)$_O$ becomes smaller with increasing energy.

In previous work anisotropy of magnetic excitations were studied using a triple-axis spectrometer, the low energy magnetic excitations were found to persist well above $T_N$ [63]. Here we replicate these results using our time-of-flight experiment, the
Figure 3.14: Detwin ratio for BaFe$_{1.9}$Ni$_{0.1}$As$_2$ and schematics for orbital splitting. (a) Detwin ratio of $\delta = (I_{10} - I_{01})/(I_{10} + I_{01}) \approx 0.5$ determined from HB-1A in the [103]$_O \times [013]_O$ scattering plane. (b) Schematic Fermi surface and orbital characters for BaFe$_{1.9}$Ni$_{0.1}$As$_2$ in the paramagnetic state. (c) Schematic of orbital splitting at X and Y points between bands of $d_{yz}$ and $d_{xz}$ orbital characters. (d) Schematic of the orbital splitting as a function of temperature for a sample under uniaxial stress.
Figure 3.15: Constant-energy slices symmetrized along $H$ and $K$ axes at $T = 5$ K for BaFe$_{1.9}$Ni$_{0.1}$As$_2$. (a) $E = 4.5 \pm 0.5$ meV ($E_i = 30$ meV), (c) $E = 16 \pm 2$ meV ($E_i = 80$ meV) and (e) $E = 100 \pm 10$ meV ($E_i = 250$ meV). The black boxes indicate regions that contain non-duplicate data due to symmetrizing. Longitudinal cuts along [$H,0$]$_O$ (red circles) and [0,$K$]$_O$ (blue diamonds) for energy transfers in (a), (c) and (e) are respectively shown in (b), (d) and (f). The solid lines are fits using Gaussian functions and linear backgrounds. [$H,0$]$_O$/$[K,0]_O$ scans are obtained by binning $K/H$ in the range (b) $[-0.15, 0.15]$, (d) $[-0.175, 0.175]$ and (f) $[-0.3, 0.3]$ and folding along [0,$K$]$_O$/$[H,0]_O$. 

E = $4.5 \pm 0.5$ meV, $T = 5$K

E = $16 \pm 2$ meV, $T = 5$K

E = $100 \pm 10$ meV, $T = 5$K
temperature dependence of magnetic anisotropy between $(10)_O$ and $(01)_O$ is shown for $E = 4.5 \pm 0.5$ meV in Fig. 3.16. Similar to earlier report, the magnetic anisotropy persists to well above $T_N$.

The advantage of using of time-of-flight spectroscopy is one can obtain detailed energy dependence from a single measurement. To quantitatively determine the energy and temperature dependence of spin excitation anisotropy, we systematically made constant-energy slices and cuts along $[H, 0]$ and $[0, K]$ at various energies similar to Figs. 3.15 and 3.16. Based on the cuts, we can estimate the energy dependence of the spin excitation anisotropy $\delta = (I_{10} - I_{01})/(I_{10} + I_{01})$. Figure 3.17(a) shows that the spin excitation anisotropy $\delta$ decreases with increasing energy and vanishes for energy transfers above $\sim 60$ meV at $T = 5$ K ($\ll T_c, T_N, T_s$). On warming to 35 K, a temperature above $T_c$, $T_N$, and $T_s$, the energy of the spin excitation anisotropy still persists to about $\sim 60$ meV, similar to 5 K [Fig. 3.17(b)].

We are now in a position to compare and contrast our results with the orbital ordering tendencies indicated by the ARPES measurements [61]. The energy splitting of the $d_{xz}$ and $d_{yz}$ bands in undoped and underdoped Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ is also about $\sim 60$ meV, and is likewise weakly temperature dependent below $T_s$. Upon increasing the doping level to near optimal superconductivity, the ARPES-measured orbital splitting energy in electron-doped iron pnictides decreases to $\sim 20$ meV and vanishes very rapidly above $T_N, T_s$ [61]. Since the ARPES-measured orbital splitting energy [61] and neutron scattering measured spin excitation anisotropy [63] in the paramagnetic state may be uniaxial strain dependent [72], it would be more constructive to compare the doping dependence of the spin excitation anisotropy in the uniaxial strained paramagnetic state with those of APRES measurements. For BaFe$_2$As$_2$, our unpublished results suggest spin excitation anisotropy persists to about 60 meV at
Figure 3.16: Temperature dependence of magnetic anisotropy between (10)₀ and (01)₀ at $E = 4.5 \pm 0.5$ meV for BaFe$_{1.9}$Ni$_{0.1}$As$_2$. Constant-energy slices symmetrized along $H$ and $K$ axes for $E = 4.5 \pm 0.5$ meV ($E_i = 30$ meV) at (a) 20 K, (c) 35 K and (e) 75 K. Corresponding longitudinal cuts along $[H, 0]_O$ (red circles) and $[0, K]_O$ (blue diamonds) are respectively shown in (b), (d) and (f). $[H, 0]_O/[K, 0]_O$ scans are obtained by binning $K/H$ in the range $[-0.15, 0.15]$. (g) Temperature dependence of the anisotropy $\delta = (I_{10} - I_{01})/(I_{10} + I_{01})$ for $E = 4.5 \pm 0.5$ meV. The purple dashed line is a guide to the eye. $T_c$ and stress-free $T_N/T_s$ are marked by vertical dashed lines.
145 K (just above $T_N, T_s$ of 140 K). For BaFe$_{1.9}$Ni$_{0.1}$As$_2$, $\delta$ is also nonzero below $\sim$60 meV both below and above $T_N, T_s$ [Fig. 3.17(a) and 3.17(b)]. This means that spin excitations anisotropy is weakly doping dependent and has a larger anisotropy energy scale than that of the ARPES-measured orbital splitting energy, suggesting that it is likely the spin channel, instead of the orbital sector, that drives electronic nematicity.

To further analyze the energy dependence of the spin correlations, we show in Figures 3.17(c) and 3.17(d) the energy dependence of the sum, $\chi''_{10} + \chi''_{01}$, and difference, $\chi''_{10} - \chi''_{01}$, of the dynamic susceptibilities at the two wave vectors (For the measured energy and temperature range, $\chi''(Q, \omega)$ is directly proportional to the measured neutron scattering intensity assuming the magnetism is essentially two-dimensional and after correcting for the magnetic form factor), respectively. It is seen that both quantities increase as energy is decreased. Within the measured energy range, both the sum and difference can be fit with a power-law dependence on energy, $\sim 1/E^\alpha$, with exponents $\alpha$ being 0.50(5) and 1.0(1) respectively. The ratio, $\delta$, can also be fitted with a power-law divergence, although this divergence must be truncated at frequencies below the measured low-frequency limit, because $\delta$ must be bound by 1. Overall, our data on the sum, $\chi''_{10} + \chi''_{01}$ [Fig. 3.17(c)], are in general agreement with results of the previous studies on twinned samples [86, 87], which fitted the spectra using a model form for the dynamical spin susceptibility $\chi'' \sim E/(E^2 + \Gamma^2) \sim 1/E^\alpha$ with $\alpha = 1$ if $\Gamma \to 0$. In our work, we show that the difference, $\chi''_{10} - \chi''_{01}$ (3.17 (d)), behaves similarly. Within the description of the spin-driven Ising-nematic correlations, the quantum critical behavior in the spin and nematic correlations has been anticipated theoretically [88]. We should caution that the precise values of the exponents are uncertain, because the data below 10 meV is affected by $L$-modulation and, for $T < T_c$, by superconductivity.
It is instructive to contrast the spin nematic scenario with an alternative picture based on orbital ordering. Since the electron-doping evolution of the low-energy spin excitations in BaFe$_{2-x}$Ni$_x$As$_2$ is consistent with quasiparticle excitations between the hole Fermi surfaces near $\Gamma$ and electron Fermi surfaces at $\mathbf{Q}_1 = (1, 0)\,\Omega$ ($\mathbf{Q}_2 = (0, 1)\,\Omega$) [89], an energy splitting of the $d_{xz}$ and $d_{yz}$ bands at these two wave vectors should result in spin excitation anisotropy as seen by INS [85]. However, this picture would require that the tendency towards the orbital ordering is stronger than the spin-excitation anisotropy, which is opposite to our results near optimal electron doping. Nevertheless, since spin and orbital degrees of freedom in iron pnictides are generally coupled, it may not be experimentally possible to conclusively determine if spin or orbital degrees of freedom is the driving force for the enhanced nematic susceptibility.

In summary, we have discovered that the anisotropy of spin excitations at $(1, 0)\,\Omega$ and $(0, 1)\,\Omega$ in BaFe$_{2-x}$Ni$_x$As$_2$ under uniaxial pressure is energy dependent and occurs for energy transfers below about 60 meV in optimal-electron-doped iron pnictides. Since orbital splitting becomes vanishingly small for optimal-electron-doped iron pnictides in the paramagnetic state of uniaxial strained sample, our results would suggest that the spin excitation anisotropy or spin Ising-nematic correlations is the driving force for the electronic nematic correlations in iron pnictides.
Figure 3.17: Summary of energy dependence of anisotropy between $Q_1$ and $Q_2$ in BaFe$_{1.9}$Ni$_{0.1}$As$_2$. Energy dependence of anisotropy between $Q_1$ and $Q_2$ defined as $\delta = (I_{10} - I_{01})/(I_{10} + I_{01})$ for (a) 5 K and (b) 35 K. (c) Energy dependence of $\chi''_{10} + \chi''_{01}$ at 5K, $\chi''_{10}$ and $\chi''_{01}$ are dynamic susceptibilities at $Q_1 = (1,0)_0$ and $Q_2 = (0,1)_0$. (d) $\chi''_{10} - \chi''_{01}$. Data obtained on HB-1A is collected at 6 K, and is plotted together with ARCS data using incident energies $E_i = 30$, 80, 150 and 250meV.
Chapter 4

Polarized Neutron Scattering and Analysis in \( \text{NaFe}_{1-x}\text{Co}_x\text{As} \) and \( \text{Ba}_{0.67}\text{K}_{0.33}\text{Fe}_2\text{As}_2 \)

In this chapter polarized neutron scattering results on \( \text{NaFe}_{1-x}\text{Co}_x\text{As} \) and \( \text{Ba}_{0.67}\text{K}_{0.33}\text{Fe}_2\text{As}_2 \) are presented. The background will be briefly introduced, followed by results on \( \text{NaFeAs} \) [90], underdoped \( \text{NaFe}_{0.985}\text{Co}_{0.015}\text{As} \) [91], near-optimal-doped \( \text{NaFe}_{0.9785}\text{Co}_{0.0215}\text{As} \) (in preparation), overdoped \( \text{NaFe}_{0.95}\text{Co}_{0.05}\text{As} \) [91] and optimal-doped \( \text{Ba}_{0.67}\text{K}_{0.33}\text{Fe}_2\text{As}_2 \) [92].

4.1 Introduction

By polarizing the incident neutron beam and analyzing the scattered neutrons with a particular spin direction, it becomes possible to study the polarization dependence of magnetic excitations as described in Chap. 1.

In optimal-doped \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \), polarized neutron scattering experiments found that the normal state response and the resonance mode are isotropic in spin space (i.e., \( S_{yy} = S_{zz} \)), but low-energy magnetic excitations in the superconducting state are anisotropic with magnetic excitations polarized along \( c \)-axis being suppressed [93]. Another advantage of using polarized neutrons in \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) is that it allows the magnetic signal to be separated from phonons which overlap with the magnetic signal. However, so far there are a limited number of such studies in the cuprates possibly due to the weak magnetic signal of the cuprates and reduced flux for polarized neutron scattering experiments.
In BaFe$_2$As$_2$, significant spin anisotropy was found \cite{94, 95}. The spin waves polarized along $c$-axis have a smaller gap than those polarized in-plane, suggesting that it costs more energy to rotate spins in the $ab$-plane than perpendicular to it \cite{95}. More interestingly, longitudinal magnetic excitations that cannot be explained using spin-wave theory are also observed, highlighting the contribution of itinerant electrons to magnetism in the iron pnictides \cite{94}. Similar anisotropy is also found in NaFeAs, but with smaller spin-anisotropy gaps \cite{90}. Upon electron doping in BaFe$_2$As$_2$ and NaFeAs, a similar anisotropy is found to persist even when antiferromagnetic order is suppressed \cite{91, 96, 97, 98}, and magnetic excitations become isotropic only well into the overdoped side of the phase diagram \cite{91, 99}. For Ba$_{1-x}$K$_x$Fe$_2$As$_2$, significant anisotropy exists in optimal and slightly overdoped samples \cite{100, 101}. Remarkably, using polarized neutron scattering, it was found that the broad resonance mode in near-optimal doped Ba(Fe$_{0.94}$Co$_{0.06}$)$_2$As$_2$ consists of two parts, a low-energy component polarized along $c$-axis and an isotropic component at higher energy \cite{98}.

Similar behavior is also seen in optimal \cite{100} and slightly overdoped Ba$_{1-x}$K$_x$Fe$_x$As$_2$ \cite{101}. In underdoped NaFe$_{0.985}$Co$_{0.015}$As with double resonances coexisting with antiferromagnetic order \cite{102}, the lower-energy resonance is anisotropic, but the resonance at higher energy is isotropic \cite{91}. These findings suggest that the double resonance in NaFe$_{0.985}$Co$_{0.015}$As \cite{102} is actually a common feature of iron pnictides, but in other systems the two modes are too broad and merge into a single mode in unpolarized neutron scattering experiments. The first resonance mode is dispersive along $L$ and anisotropic, while the second resonance is isotropic in spin space and forms a flat band along $L$ \cite{102, 98}.

In-plane spin anisotropy in near-optimal doped BaFe$_{1.904}$Ni$_{0.096}$As$_2$ exists at $E \approx 3$ meV even in the paramagnetic tetragonal state but is enhanced in the superconduct-
Figure 4.1: Schematic for spin anisotropy detected in iron pnictides. Left shows the implications for spin anisotropy detected in the magnetically ordered phase, the corresponding case for the system in the paramagnetic tetragonal state is shown on the right. The red ellipses represent spin anisotropy observed at equivalent wave vectors.

The implications of observed spin anisotropy on electronic nematicity is schematically shown in Fig. 4.1. When the system is in the magnetically ordered phase, the unit cell is the one indicated by green squares shown on the left of Fig. 4.1. In this case $(1, 0)_O$ is equivalent to $(0, 0)_O$ and spin anisotropy observed at $(1, 0)_O$ mandates
spin anisotropy at \((0,0)_{\text{O}}\), which breaks four-fold rotational symmetry. However this is not surprising at all since the system is already in a state that does not have four-fold rotational symmetry. When the system is in the paramagnetic tetragonal state, the magnetic unit cell is the one shown on the right of Fig. 4.1 [104]. In this case \((0.5,0.5)_{\text{T}}\) is at an edge of the Brillouin zone and does not have to obey four-fold rotational symmetry. In this case the spin anisotropy is between longitudinal and transverse directions, rather than the orthorhombic axes \((1,0)_{\text{O}}\) and \((0,1)_{\text{O}}\). This fact is best exemplified by the anisotropic in-plane correlation lengths observed in the paramagnetic state of iron pnictide parent compounds [5, 105].

So far, there are few theoretical studies on the polarization of spin excitations in iron pnictides that considers spin-orbit coupling [106], and no work that explains the experimental observations of spin anisotropy from inelastic neutron scattering. While the energy scale of spin anisotropy is small compared to exchange couplings in the parent compounds, spin anisotropy has an energy scale comparable to the resonance mode. Moreover, ARPES found the largest pairing gaps in iron pnictides reside on Fermi surfaces induced by spin-orbit coupling [103]. These results suggest that spin-orbit coupling and the resulting spin anisotropy may be important ingredients for understanding the origin of high-temperature superconductivity. Further experimental and theoretical efforts are needed to understand the polarization of low-energy magnetic excitations in both the cuprates and iron-based superconductors.
4.2 Extracting $S^{aa}$, $S^{bb}$ and $S^{cc}$ from polarized neutron scattering

In a typical polarized experiment the sample is aligned in the $[H, 0, 0]_O \times [0, 0, L]_O$ scattering plane, with magnetic intensities concentrated at $(1, 0, L)_O$ positions. The geometry of typical setups is shown in Fig. 4.2. Since $S^{yy}$ and $S^{zz}$ are directly measured in neutron scattering experiments, one should consider how to translate them to the more transparent crystallographic axes $S^{aa}$, $S^{bb}$ and $S^{cc}$. Since $[0, 1, 0]_O \parallel z$, the $xyz$ coordinate system can be simply rotated by $\theta$ to go to the $abc$ coordinate system. The conversion can be achieved by considering changing the basis in the term

$$\sum_{\alpha, \beta} (\hat{Q}_\alpha \hat{Q}_\beta) S^{\alpha\beta}$$

(Eq. 1.6). For $xyz$ coordinate system this simply gives $S^{yy} + S^{zz}$ whereas in the $abc$ coordinate system this gives $\sin^2 \theta S^{aa} + \cos^2 \theta S^{cc} - \sin \theta \cos \theta (S^{ac} + S^{ca}) + S^{bb}$. For an ordered magnet with ordered moments along $b$-axis, spin waves correspond to precession of spins in $a-c$ plane so $S^{ac} + S^{ca} = 0$, although off-diagonal components are not zero [1, 3]. It is a reasonable assumption that $S^{ac} + S^{ca} = 0$ holds for iron pnictide at $Q_{AF}$ even in the magnetically disordered phase, because $a$ and $c$ are crystallographic axes with high symmetry. In general $S^{\alpha\beta} + S^{\beta\alpha} = 0$ is not true for arbitrary choice of orthogonal axes. Using $S^{ac} + S^{ca} = 0$ and noting $b$ and $z$ are identical, the following relationships are obtained,

$$S^{yy} = \sin^2 \theta S^{aa} + \cos^2 \theta S^{cc}$$

$$S^{zz} = S^{bb}.$$

It can be seen that while $S^{zz}$ can be uniquely used to determine $S^{bb}$, $S^{yy}$ is a combination of $S^{aa}$ and $S^{cc}$. To obtain $S^{aa}$ and $S^{cc}$ it is therefore necessary to measure at two equivalent wave vectors such as $(1, 0, 0)_O$ and $(1, 0, 2)_O$ to determine the
Figure 4.2: Schematic of geometry used in polarized neutron scattering experiments. The experiment is typically carried out in the $[H, 0, 0]_O \times [0, 0, L]_O$ scattering plane. $x \parallel Q$, $y$ is perpendicular to $Q$ and lies in the scattering plane and $z$ is perpendicular to the scattering plane. The angle between the $[1, 0, 0]_O$ direction and $Q$ is $\theta$. For spin-flip scattering, the $x$ polarization measures $S_{yy} + S_{zz}$, the $y$ polarization measures $S_{zz}$ and the $z$ polarization measures $S_{yy}$.

three diagonal components of $S^{\alpha\beta}$. The detailed relationship between experimentally measured spin-flip cross sections ($\sigma^{SF}_\alpha$) and $S^{\alpha\alpha}$ (denoted as $M_\alpha$ from now on to be consistent with published works [90, 91]) is

\[
\begin{align*}
\sigma^{SF}_x(Q_1) &= F^2(Q_1) \sin^2 \theta Q_1 \frac{R}{R+1} M_a + F^2(Q_1) \frac{R}{R+1} M_b + F^2(Q_1) \cos^2 \theta Q_1 \frac{R}{R+1} M_c + B(Q_1), \\
\sigma^{SF}_y(Q_1) &= F^2(Q_1) \sin^2 \theta Q_1 \frac{1}{R+1} M_a + F^2(Q_1) \frac{R}{R+1} M_b + F^2(Q_1) \cos^2 \theta Q_1 \frac{1}{R+1} M_c + B(Q_1), \\
\sigma^{SF}_z(Q_1) &= F^2(Q_1) \sin^2 \theta Q_1 \frac{R}{R+1} M_a + F^2(Q_1) \frac{1}{R+1} M_b + F^2(Q_1) \cos^2 \theta Q_1 \frac{R}{R+1} M_c + B(Q_1), \\
\sigma^{SF}_x(Q_2) &= r F^2(Q_2) \sin^2 \theta Q_2 \frac{R}{R+1} M_a + r F^2(Q_2) \frac{R}{R+1} M_b + r F^2(Q_2) \cos^2 \theta Q_2 \frac{R}{R+1} M_c + B(Q_2), \\
\sigma^{SF}_y(Q_2) &= r F^2(Q_2) \sin^2 \theta Q_2 \frac{1}{R+1} M_a + r F^2(Q_2) \frac{R}{R+1} M_b + r F^2(Q_2) \cos^2 \theta Q_2 \frac{1}{R+1} M_c + B(Q_2), \\
\sigma^{SF}_z(Q_2) &= r F^2(Q_2) \sin^2 \theta Q_2 \frac{R}{R+1} M_a + r F^2(Q_2) \frac{1}{R+1} M_b + r F^2(Q_2) \cos^2 \theta Q_2 \frac{R}{R+1} M_c + B(Q_2).
\end{align*}
\]
The two equivalent wave vectors are labeled as $Q_1$ and $Q_2$, $F(Q)$ is the magnetic form factor, $R$ is the flipping ratio (typically $R \approx 15$, $R = 1$ for unpolarized neutron beams and $R \rightarrow \infty$ for a perfectly polarized neutron beam) and $\theta_Q$ is the angle between $Q$ and the $[1, 0, 0]_O$ direction. $r$ is a ratio factor that accounts for the different resolution volumes at the two wave vectors, or a scale factor after convolution of the magnetic signal with the instrumental resolution, which should be close to unity if the two wave vectors are reasonably close. $B(Q)$ includes everything else that are not magnetic excitations, including any nuclear scattering, $Q$-independent scattering and instrumental background. This system of equations has 6 measured cross sections and 6 unknowns to be determined, $M_a, M_b, M_c, r, B(Q_1)$ and $B(Q_2)$. Although this system of equations is nonlinear due to $r$, it does have analytical solutions (solution is not unique), specifically

$$r = \frac{F^2(Q_1)[\sigma_{SF}^x(Q_2) - \sigma_{SF}^z(Q_2)]}{F^2(Q_2)[\sigma_{SF}^x(Q_1) - \sigma_{SF}^z(Q_1)]}. \quad (4.1)$$

From this result it is clear that if $M_z = \sigma_{SF}^x - \sigma_{SF}^z = 0$, then $r$ cannot be determined and the analytical solution would fail. Therefore an alternative method is adopted [91] by assuming $r$ has a simple energy-dependence, and the points where $M_z \neq 0$ are used to extrapolate the $r$ values for points that have $M_z = 0$. Having determined $r$, the system of equations is left with 6 equations and only 5 unknowns, an overdetermined system. Casting the system of equations in matrix form $y = Ax$, where $A$ is a $6 \times 5$ matrix, the goal then becomes minimizing $||W^{1/2}(y - Ax)||^2$ with $W = \text{diag}(1/e_1^2, \ldots, 1/e_6^2)$, $e_i^2$ being the experimental error of the $i$th cross section in the above system of equations. The least squares solution is $x = (A^TWA)^{-1}A^TWy$, the error associated with $x$ is similarly propagated from errors in measured $y$ although it should be noted that the error is slightly overestimated since the system is
Figure 4.3 : Determining $r$ for NaFe$_{0.985}$Co$_{0.015}$As. $r$ for NaFe$_{0.985}$Co$_{0.015}$As is determined from $r = \frac{F^2(Q_1)\sigma_{SF}(Q_2) - \sigma_{SF}(Q_2)}{F^2(Q_2)\sigma_{SF}(Q_1) - \sigma_{SF}(Q_1)}$, and since $M_b \approx 0$ for $E \leq 5$ meV, these points are excluded in determining $r$. To obtain reliable results, points with $r > 2$ or $r < 0.5$ are also excluded. The flat line fit gives $r = 0.80 \pm 0.06$ shown as the purple line. This value of $r$ is then used to determine $M_a$, $M_b$ and $M_c$ in the overdetermined system of equations.

overdetermined (assuming $r$ is a known number).

The analysis detailed above was carried out for NaFeAs and underdoped NaFe$_{0.985}$Co$_{0.015}$As [90, 91]. $r$ is fit as an energy-independent constant, and points with $M_z = 0$ or large errors are discarded, an example is shown for NaFe$_{0.985}$Co$_{0.015}$As at $Q_1 = (1, 0, 0.5)_O$ and $Q = (1, 0, 1.5)_O$ as shown in Fig. 4.3. Using obtained $r$ and following the above analysis, $M_a$, $M_b$ and $M_c$ can be obtained (results of $M_a$, $M_b$ and $M_c$ will be shown in the following sections). To check how good the obtained results are, it is useful to plot the components of $W^2(y - Ax)$ as shown in Fig. 4.4. As can be seen, most points are within one standard deviation of the measured intensity and all points are within two standard deviations, attesting to soundness of the analysis detailed above.
Figure 4.4: $W^\frac{1}{2}(y - Ax)$ for NaFe$_{0.985}$Co$_{0.015}$As. Individual components of $W^\frac{1}{2}(y - Ax)$ are shown as a function of energy, since $W^\frac{1}{2} = \text{diag}(1/e_1, ..., 1/e_6)$ the $y$ label of the plots are shown as $(y - Ax)/e$. The results are obtained from energy scans at 2 K at $Q_1 = (1, 0, 0.5)_O$ and $Q_2 = (1, 0, 1.5)_O$.

4.3 Low-energy magnetic excitations in NaFeAs

Following the above analysis, polarized neutron scattering was carried out at $Q = (1, 0, 0)_O$, $(1, 0, 0.5)_O$, $(1, 0, 1)_O$ and $(1, 0, 1.5)_O$ for NaFeAs and $M_a$, $M_b$ and $M_c$ for both the magnetic zone center ($L = 0.5, 1.5$) and zone boundary along $c$-axis ($L = 0, 1$) were determined. The results are summarized together with raw data in Fig. 4.5. The experiment was carried out on IN22 thermal triple-axis spectrometer at the Institut Laue-Langevin, Grenoble, France.

As can be seen the spin waves disperse very little along $c$-axis, dispersing upwards in energy by only about $\sim 3$ meV from $L = 0.5$ to $L = 0$. More importantly, the gaps for the two transverse directions are clearly different, with the mode polarized along $c$-axis exhibiting a much smaller gap compared to the mode polarized along $b$-axis.
This is similar to what was found in BaFe$_2$As$_2$, and contrary to naive expectations this suggests the ordered moment requires a lower energy to rotate out-of-plane than in-plane [95]. An small upturn is observed around 12 meV for $M_a$ at the magnetic zone center, suggesting the presence of longitudinal excitations characteristic of an itinerant magnet. Unfortunately we did not measure to higher energies to fully confirm the longitudinal mode, but later work has confirmed its presence in BaFe$_2$As$_2$ [94].

The result of $c$-axis polarized spin waves having a gap of only $\sim 4$ meV contrasts with earlier measurements that found the gap in Na$_{1-\delta}$FeAs to be $\sim 10$ meV, similar to BaFe$_2$As$_2$ [107]. One possibility is of course that the samples measured are different caused by Na deficiencies, but the similar $T_N$ and $T_s$ of the two measurements suggest this is unlikely to be the reason. Alternatively consider the effect of carrying out unpolarized neutron scattering measurements at different $L$ values, with the measured cross section $\sigma \propto M_y + M_z$. $M_z$ is not affected by changing $L$ and is always $M_b$, but $M_y = \sin^2 \theta M_a + \cos^2 \theta M_c$ ($\theta$ is the angle between $Q$ and the [1,0,0]$_O$ direction) and are $M_y = 0.14M_a + 0.84M_c$ and $M_y = 0.59M_a + 0.41M_c$ for $L = 0.5$ and $L = 1.5$, respectively. Since $M_a = 0$ for $E \leq 10$ meV, only $M_c$ contributes to $M_y$. Clearly then $M_y$ measured for $L = 1.5$ will be only half of $L = 0.5$, combined with a stronger $M_b$ that our data already suggest [Fig. 4.5(e), (f)], the $M_c$ component becomes difficult to resolve near $L = 1.5$ in unpolarized measurements. Given these considerations, it is likely that the larger gap of $\sim 10$ meV was obtained in previous work is because the measurements were done at $L = 1.5$ and the $M_c$ component with a smaller gap was not seen.

We have also carried out unpolarized measurements of NaFeAs near $L = 0.5$ and a mode at $\sim 5$ meV ($L = 0.5$) was clearly seen, as shown in Fig. 4.6. Based on our polarized measurements, this measured mode is mostly $M_c$. Having obtained
Figure 4.5: **Polarization of spin waves in NaFeAs.** (a), (b), (c) and (d) present the spin-flip cross sections $\sigma_{S}^{\alpha}$ ($\alpha = x, y$ and $z$) measured in the magnetically ordered state of NaFeAs at $Q = (1, 0, L)_{0}$ with $L = 0.5, 0, 1.5$, and 1. Following the analysis presented in the previous section, $M_{a}$, $M_{b}$ and $M_{c}$ are shown in (e) and (f) for the magnetic zone center $[Q = (1, 0, 0.5)_{0}]$ and zone boundary along $c$-axis $[Q = (1, 0, 0)_{0}]$, respectively.
the dispersion of the mode from $L = 0$ to $L = 0.5$, it is possible to extract some useful information based on effective Heisenberg models [94] combined with dominant exchange interactions ($J_{1a}$, $J_{1b}$ and $J_2$) from time-of-flight measurements [108].

Spin waves in parent compounds of iron pnictides are typically modeled using a $J_{1a}$-$J_{1b}$-$J_2$-$J_c$ model, plus a single-ion anisotropy term of the form $\sum_i D(S_i^2)$ [109, 110, 5, 108, 111]. Such a model results in degenerate transverse spin wave modes, clearly unable to explain the difference in energy between $M_b$ and $M_c$. To account for the non-degenerate transverse spin waves, a modified anisotropy term of the form $\sum_i D_x(S_i^2) + D_y(S_i^2)$ was introduced [94]. Clearly $D_x < 0$ is necessary for ordered spins to be aligned along $a$-axis and $D_y > 0$ is necessary for $b$-axis polarized spin waves to be at a higher energy than $c$-axis polarized ones. The energy of $c$-axis polarized spin wave modes at the magnetic zone center $Q = (1, 0, 0.5)$ and the zone boundary along $c$-axis $Q = (1, 0, 0)$ are [94]

$$E_{c,L=0.5} = 2S \sqrt{\frac{-D_x(4J_2 + 2J_{1a} + 2J_c + D_y - D_x)}{4J_2 + 2J_{1a}}} \approx 2S \sqrt{-D_x(4J_2 + 2J_{1a})}$$
$$E_{c,L=0} = 2S \sqrt{\frac{(2J_c - D_x)(4J_2 + 2J_{1a} + D_y - D_x)}{(4J_2 + 2J_{1a})}} \approx 2S \sqrt{(2J_c - D_x)(4J_2 + 2J_{1a})}.$$

(4.2)

The approximation made in the above equations is that $D_x$, $D_y$ and $J_c$ are much smaller than $J_{1a}$, $J_{1b}$ and $J_2$, which has been verified experimentally [94]. From the spin wave energy at $L = 0$ ($\approx 7.09$ meV) and $L = 0.5$ ($\approx 4.42$ meV) shown in Fig. 4.6 and in-plane exchange couplings found from time-of-flight measurements [108], it is then possible to obtain $SJ_c \approx 0.025$ meV and $SD_x \approx -0.031$ meV for NaFeAs. Compared with BaFe$_2$As$_2$ with $SJ_c = 0.333$ meV and $SD_x = -0.196$ meV, both the out-of-plane coupling $J_c$ and anistropy $D_x$ are much smaller in NaFeAs compared to BaFe$_2$As$_2$. The smaller $D_x$ might be related to the smaller ordered moment in NaFeAs.
Figure 4.6: Dispersion of c-axis polarized spin waves in NaFeAs. (a) Constant-Q scans at $Q = (1, 0, L)O$ at 4 K for $L = 0, 0.2, 0.3,$ and 0.5 with unpolarized neutrons after background has been subtracted. Solid lines are fits to the response of a damped harmonic oscillator convolved with instrumental resolution with low-energy spin waves modeled as $E(Q) = \sqrt{\Delta(1, 0, L)^2 + v_a^2 h^2 + v_b^2 k^2}$ where $(h, k) = (H, K) - (1, 0)$, $v_a$ and $v_b$ are spin velocities obtained using effective exchange couplings from Ref. [108]. Data points with $E < 11$ meV are used in the fits. (b) Dispersion of the low-energy spin waves along the $(1, 0, L)$ direction, points are fitted gap values $\Delta(1, 0, L)$, the purple solid line is the dispersion from linear spin wave theory using effective exchange couplings from Ref. [108].

[112] compared to BaFe$_2$As$_2$ [113]. Coupling along c-axis is even weaker in LaFeAsO, where no difference was experimentally seen for $L = 0$ and $L = 0.5$, suggesting a vanishing $J_c$ [111]. Therefore NaFeAs is more two-dimensional than BaFe$_2$As$_2$ but less two-dimensional than LaFeAsO, consistent with density functional theory predictions [112]. It should be noted however, for a gap $\sim 10$ meV at $Q = (1, 0, 0.5)O$ as seen in LaFeAsO $SJ_c \approx 0.025$ meV will only give rise to a dispersion along c-axis of $\sim 1$ meV (this is still larger than the reported value for LaFeAsO, after considering the experimental uncertainty). $SJ_c \approx 0.025$ meV obtained in the present work should also be contrasted with $SJ_c = 1.8 \pm 0.1$ meV from time-of-flight measurements of NaFeAs [108], where $SJ_c$ is overestimated by almost two orders of magnitude, this is due to the high energy neutrons used and the coupling between $E$ and $L$ in typical experiments. Clearly, $J_c$ and anisotropy terms should be fixed (obtained from triple-
axis measurements) in the fitting routine rather than allowed to vary when analyzing time-of-flight data. It should be noted that the $c$-axis polarized spin waves correspond to the degenerate spin waves in the model employing the anisotropy term $\sum_i D(S_x)_i^2$, as can be seen in the above equation where $D_y$ plays a very small role (this means $J_c$ obtained would be independent of which type of anisotropy term is used, when analyzing $c$-axis polarized spin waves).

Temperature dependence of anisotropic magnetic excitations was also measured for $L = 0.5$ and $L = 1.5$ (fewer temperatures) at $E = 6$ meV, which allows the temperature dependence of $M_a$, $M_b$ and $M_c$ in NaFeAs to be separated, as shown in Fig. 4.7. In the paramagnetic tetragonal state there is little magnetic anisotropy [Fig. 4.7(a) and (b)], although $M_y > M_z$ is seen at all measured temperatures ($M_y > M_z$ in the paramagnetic tetragonal state is also seen in underdoped BaFe$_{1.904}$Ni$_{0.096}$As$_2$, suggesting a common cause, likely spin-orbit coupling [103] to be responsible for spin anisotropy in the paramagnetic tetragonal state). Examining the temperature dependence of $M_a$, $M_b$ and $M_c$ reveals $M_c$ dominates at low temperature, this is because at $E = 6$ meV there are only $c$-axis polarized spin waves, whereas at $\sim 60$ K the excitations become almost isotropic. Interestingly $M_a$ displays divergent behavior near $T_N$, this can also be readily seen in Fig. 4.7 (d) for $L = 1.5$, where $M_a$ contributes much more to the scattering cross section than $L = 0.5$ [no divergent feature can be seen in Fig. 4.7(c)]. A similar divergence was also seen at $E = 7$ meV and $L = 1.5$ in previous work [107]. In addition, the fact that neither $M_c$ nor $M_b$ shows any divergent behavior reinforces the conclusion that the divergence seen unpolarized neutron scattering [107] must be due to $M_a$. Divergence of $M_a$ at $T_N$ can be interpreted as divergence of longitudinal fluctuations near $T_N$ characteristic of a second-order phase transition [114], or it may be related to the electronic nematic
Figure 4.7: Temperature evolution of polarization of magnetic excitations in NaFeAs. Constant-Q scans at $T = 60$ K for $Q = (1,0,0.5)_O$ and $Q = (1,0,1.5)_O$ are shown in (a) and (b), respectively. Temperature dependence of $\sigma^{SF}_\alpha (\alpha = x,y,z)$ for the magnetic zone centers $Q = (1,0,0.5)_O$ and $Q = (1,0,1.5)_O$ are shown in (c) and (d). (e) The difference of the magnetic components $M_y$ and $M_z$ for $L = 0.5$ determined from $\sigma^{SF}_x$ and $\sigma^{SF}_y$ in (c). The temperature dependence of $M_a$, $M_b$, and $M_c$ at the magnetic zone center are determined and plotted in (f). In cases where only cross sections for $L = 0.5$ are measured, only $M_b$ can be determined, when $\sigma^{SF}_x$ and $\sigma^{SF}_y$ for $L = 1.5$ are in addition measured, all three components along crystal axes can be determined, when all three channels are measured for both $L = 0.5$ and $L = 1.5$, the over-determination is used to improve estimates of $M_a$, $M_b$, and $M_c$. The point at $T \approx 60$ K is obtained by combining raw data from temperatures in the range indicated by horizontal bars and the constant-Q scans in (a) and (b) from $E = 6 \pm 2$ meV, the combined $\sigma^{SF}_x$, $\sigma^{SF}_y$ and $\sigma^{SF}_z$ for $L = 0.5$ and $L = 1.5$ are shown in the inset. The solid vertical gray line through (c), (d), (e), and (f) marks the magnetic transition temperature $T_N$, whereas the dashed gray line marks the structural transition temperature $T_s$. The solid lines in (e) and (f) are guides to the eye.
state found in iron pnictides [65]. From $\sigma^S_z - \sigma^S_y$ one can directly obtain $M_y - M_z$ as shown in Fig. 4.7(e), which becomes $0.14M_a + 0.86M_c - M_b$ for $L = 0.5$. A kink is clearly seen at $T_N$, and another kink possibly exists at $T_s$ although better statistics is needed to prove it beyond doubt. In addition to unpolarized scattering results that showed a line width change at $T_s$ in iron pnictides while the peak intensity evolve continuously through $T_s$ [115], our result adds the possibility that polarization of magnetic excitations also experience a change at $T_s$. Since spin anisotropy is ultimately due to spin-orbit coupling, this suggests spin-orbit coupling is affected by the structural phase transition possibly as a result of the splitting of $d_{xz}$ and $d_{yz}$ orbitals. Our result of $M_a > M_b (\chi''_a > \chi''_b)$ should also be contrasted with the result on static magnetic susceptibility with $\chi_a < \chi_b$ when $T_N < T < T_s$ [116], it should be noted that while static susceptibility is obtained for $Q = (0,0)_O$, our measurements are for $Q = (1,0)_O$.

4.4 Polarization of the double resonance modes in under-doped NaFe$_{0.985}$Co$_{0.015}$As

The double resonance found in NaFe$_{0.985}$Co$_{0.015}$As [102] led to the proposal of different origins for the two modes, with one mode located at $Q = (1,0)_O$ and the other at $Q = (0,1)_O$, however both modes appear at $Q = (1,0)_O$ in neutron scattering measurements due to twinning [117]. The coexistence of superconductivity with antiferromagnetic order results in the excitations at $Q = (1,0)_O$ consisting of a transverse-polarized spin wave mode and a longitudinal-polarized resonance mode, whereas the resonance mode at $Q = (0,1)_O$ is isotropic [117]. Alternatively, the two resonance modes can be due to superconducting gap anisotropy [118, 119]. In this
Figure 4.8: Measured $\sigma^{\text{SF}}_{\alpha}$ ($\alpha = x, y, z$) for electron-underdoped NaFe$_{0.985}$Co$_{0.015}$As. Neutron spin-flip scattering cross sections $\sigma^{\text{SF}}_x$, $\sigma^{\text{SF}}_y$ and $\sigma^{\text{SF}}_z$ at (a) $Q = (1, 0, 0.5)_0$ and (b) $Q = (1, 0, 1.5)_0$ in the superconducting state. Identical scans in the normal state are shown in (c) and (d). (e) and (f) show $\sigma^{\text{SF}}_x$, $\sigma^{\text{SF}}_y$ and $\sigma^{\text{SF}}_z$ at $Q = (1, 0, 0)_0$ and $Q = (1, 0, 1)_0$, respectively.

case the experimental results can be qualitatively reproduced from theory even when $Q = (1, 0)_0$ and $Q = (0, 1)_0$ are equivalent [102], although if orbital splitting between $d_{xz}$ and $d_{yz}$ bands or magnetic ordering are introduced into the model the two wave vectors will become inequivalent.

To better understand the origin of the double resonance in electron-underdoped NaFe$_{0.985}$Co$_{0.015}$As we carried out polarized neutron scattering measurements on IN22 triple-axis spectrometer at the Institut Laue-Langevin, Grenoble, France. The directly measured spin-flip cross sections are shown Fig. 4.8, where it is already clear
that for both $T = 2 \text{ K} \ (T < T_c)$ and $T = 18 \text{ K} \ (T_c < T < T_N)$ the excitations are
anisotropic at low energies ($\approx 4 \text{ meV}$) but become isotropic with increasing energy
($\approx 8 \text{ meV}$). Further it can be seen whereas a clear gap in magnetic excitations is seen
at 2 K, no gap exists at 18 K despite the sample being already in the magnetically
ordered state.

To better understand the polarization of magnetic excitations, using $\sigma_{x}^{\text{SF}}, \sigma_{y}^{\text{SF}}$ and
$\sigma_{z}^{\text{SF}}$ at two equivalent wave vectors $M_a, M_b$ and $M_c$ for the magnetic zone center
$[Q = (1,0,0.5)_O]$ and zone boundary $[Q = (1,0,0)_O]$ along $c$-axis are obtained and
shown in Fig. 4.9. It can be seen whereas the first mode is comprised of excitations
polarized along $c$-axis and $a$-axis, the second mode is isotropic. This can be already
seen by just examining the cross sections $\sigma_{x}^{\text{SF}}, \sigma_{y}^{\text{SF}}$ and $\sigma_{z}^{\text{SF}}$. In the normal state (18
K) at low energies the excitations are mostly polarized along $c$-axis, with $M_b$ and $M_a$
onsetting at higher energies. This is similar to the behavior of spin waves found in
NaFeAs [90] and BaFe$_2$As$_2$ [94]. Given that the $c$-axis polarized mode may be spin
waves linked to magnetic order, it can also display a temperature difference between
2 K and 18 K that is not related to $T_c$ ($T_N \approx 30 \text{ K}$). Indeed, care should be taken
when assigning a mode obtained from subtracting data at different temperatures as a
resonance, especially when there is coexisting magnetic order with superconductivity.

To examine whether the $c$-axis and $a$-axis polarized modes respond to $T_c$, tem-
perature dependence of magnetic excitations at $E = 4 \text{ meV}$ was measured for $Q =
(1,0,0.5)_O$ and $Q = (1,0.1.5)_O$. The measured cross sections and corresponding $M_a,$
$M_b$ and $M_c$ are shown in Fig. 4.10. While magnetic anisotropy is clearly present,
no clear response to $T_c$ can be seen in any of the measured cross sections. This is in
stark contrast to previous results using a lower fixed $E_f$ and therefore better resolu-
tion. Another discrepancy is whereas the first resonance seen previously is very sharp
Figure 4.9: $M_\alpha$ ($\alpha = a, b, c$) for electron-underdoped NaFe$_{0.985}$Co$_{0.015}$As. Energy dependence of the spin-spin correlations (a) $M_a$, (b) $M_b$, and (c) $M_c$ above and below $T_c$ at the magnetic zone center. Energy dependence of $M_a$, $M_b$, and $M_c$ in the superconducting state at (d) AF zone center and (e) zone boundary along $c$-axis. The vertical dashed lines indicate $E_{r1}$ and $E_{r2}$, the energies corresponding to the two resonance modes. The solid lines are guides to the eye.
in energy, the first resonance here is not as sharp and strong. To resolve these differences it should first be noted that while the sharp resonance seen previously is clearly related to superconductivity and well-defined in both energy and momentum, the corresponding spin waves above $T_c$ are broader in both energy and momentum [102]. With this in mind, it is clear the effect of having a worse resolution is to have the broad spin-wave-like excitations dominate the measured cross sections, overwhelming the sharp mode originating from superconductivity. This can then explain why no clear response can be seen at $T_c$ and the mode is no longer sharp and strong in the present experiment. Examining $M_a$, $M_b$ and $M_c$ reveals whereas an anomaly is seen in $M_a$ at $T_c$, $M_c$ evolves smoothly across $T_c$. The clear response to $T_c$ in $M_a$ suggests this corresponds to the sharp resonance seen in previous unpolarized neutron scattering measurements. Whether a resonance also occurs for $M_c$ is unclear even though $M_c$ also increase below $T_c$, since the temperature dependence does not show a clear anomaly at $T_c$. However since the magnetic order parameter decreases below $T_c$, one would expect corresponding spin waves to decrease in intensity as well if $M_c$ is entirely due to magnetic order, contrary to what is experimentally seen.

In conclusion, it is appropriate based on the present results to assign the sharp resonance seen in electron-underdoped NaFe$_{0.985}$Co$_{0.015}$As to be polarized along $a$-axis, with a $c$-axis polarized mode possibly also contributing. While anisotropic resonance modes were seen in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [98] and Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [100], it is not clear if they correspond to $a$-axis or $c$-axis polarized modes seen here. It should be noted both these compounds do not exhibit magnetic order in contrast to NaFe$_{0.985}$Co$_{0.015}$As, therefore resonance modes related to the interplay between superconductivity and magnetic order should not be present.

In summary we observe the first resonance in NaFe$_{0.985}$Co$_{0.015}$As is anisotropic
Figure 4.10: Temperature dependence of $M_\alpha$ ($\alpha = a, b, c$) for electron-underdoped NaFe$_{0.985}$Co$_{0.015}$As. Temperature dependence of measured cross sections $\sigma_{\alpha}^{SF}$ ($\alpha = x, y, z$) at $E = 4$ meV for (a) $Q = (1, 0, 0.5)_O$ and (b) $Q = (1, 0, 1.5)_O$. The black solid line is a guide-to-the-eye. (c) $M_\alpha$ ($\alpha = a, b, c$) obtained from results in (a) and (b). The star symbols are obtained from binning data points with energy close to 4 meV (from constant-$Q$ scans). The solid lines are guides-to-the-eye. The vertical gray dashed lines represent $T_c$ and $T_N$. 
(with a contribution polarized along $a$-axis and possibly a contribution polarized along $c$-axis), highlighting the role of itinerant electrons in iron pnictides. While an isotropic mode and a longitudinal mode is expected from the model where the two resonance modes occur at different $Q$, the longitudinal mode is seen at higher energies in the model, reversed from the experimental result. Further measurements on detwinned NaFe$_{0.985}$Co$_{0.015}$As are needed to confirm which wave vectors the two modes come from.

4.5 Spin anisotropy of magnetic excitations in near-optimal-doped NaFe$_{0.9785}$Co$_{0.0215}$As

With increasing Co-doping, the resonance at lower energy in underdoped NaFe$_{0.985}$Co$_{0.015}$As loses spectral weight and disappears near optimal doping and only the resonance mode at higher energy remains in NaFe$_{0.975}$Co$_{0.025}$As [120]. Combining polarized and unpolarized neutron scattering we show that the first resonance already disappears in NaFe$_{0.9785}$Co$_{0.0215}$As which exhibits magnetic order [121], and the remaining resonance at higher energy is mostly isotropic in spin space. By measuring detailed temperature dependence of the resonance in NaFe$_{0.9785}$Co$_{0.0215}$As we found that while the integrated intensity of the mode closely tracks the superconducting order parameter, energy of the resonance mode depends only weakly on temperature. Polarized neutron scattering further reveals while the resonance is mostly isotropic, spin anisotropy is present below the resonance and persists above $T_c$, disappearing at or slightly above the magnetic ordering temperature $T_N$.

Unpolarized neutron scattering experiment was carried out on the HB-3 triple-axis spectrometer at the High-Flux Isotope reactor, Oak Ridge National Laboratory. Po-
Figure 4.11: **Unpolarized neutron scattering study of NaFe_{0.9785}Co_{0.0215}As.**

(a) Constant-Q scans at $Q = (1, 0, 1)\Omega$ for $T = 4$ K ($T < T_c$), $T = 22$ K ($T_c < T < T_N$) and $T = 35$ K ($T > T_N$). The solid line is a fit to 35 K data using a Gaussian peak centered at $E = 0$ meV and a polynomial function of energy transfer. (b) Constant-Q scans at $Q = (1, 0, 1)\Omega$ for several temperatures, after subtracting the fit to 35 K data shown in (a). The solid lines are fits to Gaussian peaks for data with $5 \leq E \leq 10$ meV. (c) Temperature dependence for $E = 4$, 8 and 12 meV at $Q = (1, 0, 1)\Omega$. The solids lines are guides-to-the-eye, and the dashed vertical line marks $T_c$. (d) Constant-Q scans at $Q = (1, 0, 1)\Omega$ and $Q = (1, 0, 1.5)\Omega$ at $T = 4$ K after subtracting data at $T = 35$ K. The solids lines are guides-to-the-eye.

Polarized neutron scattering was carried out on IN22 triple-axis spectrometer at Institut Laue-Langevin. Time-of-flight neutron spectroscopy studies of the same sample has been reported [122].

Results from unpolarized neutron scattering are summarized in Fig. 4.11 and Fig. 4.12, mostly carried out $Q = (1, 0, 1)\Omega$, corresponding to the magnetic zone boundary along $c$-axis in antiferromagnetically ordered NaFeAs. Comparing constant-Q scans at $T = 4$ K ($T < T_c$), $T = 22$ K ($T_c < T < T_N$) and $T = 35$ K ($T > T_N$) in
Fig. 4.11(a) reveals a clear resonance mode and opening of a spin gap below the resonance in the superconducting state, while little difference is seen between 22 K and 35 K, suggesting the magnetic excitations are hardly affected by the magnetic transition with an ordered moment of $\sim 0.02 \mu_B$/Fe. These results are corroborated by temperatures scans at $Q = (1, 0, 1)_O$ and $E = 4, 8$ and 12 meV in Fig. 4.11(c), with the resonance mode and the spin gap displaying a clear response to $T_c$ but weak/no response to $T_N$ in all cases. Given that data at 22 K and 35 K are similar, we fit the data at 35 K using a phenomenological expression and plot constant-$Q$ scans at several temperatures with the fit at 35 K subtracted in Fig. 4.11(b). To parametrize temperature dependence of the resonance mode, we fit the data shown in Fig. 4.11 with Gaussian peaks to capture temperature dependence of both the center and integrated intensity. The fit results are shown in Fig. 4.12(a), whereas the integrated intensity of the resonance closely tracks the superconducting order parameter [123], the peak center of the resonance mode only decreases slightly upon approaching $T_c \approx 19$ K. A color-coded temperature-energy map of the magnetic excitations at $Q = (1, 0, 1)_O$ is shown in Fig. 4.12(b), further demonstrating that excitations become weakly temperature-dependent above $T_c$.

To compare the difference between integer and half-integer $L$, corresponding to the magnetic zone boundary and zone center along $c$-axis in NaFeAs, we plot the resonance modes at $Q = (1, 0, 1)_O$ and $Q = (1, 0, 1.5)_O$ in Fig. 4.11(d). As can be clearly seen, the resonance mode displays little/no $L$-dependence, although the spin gap appears to be larger for $L = 1$. The fact the resonance mode displays little $L$-dependence is consistent with previous studies on NaFe$_{1-x}$Co$_x$As [102, 120]. $L$-dependence of the gap is also observed in Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$ [124], in both cases it is likely due to $L$-dependence of $a/c$ polarized excitations that are not fully suppressed.
Figure 4.12: Temperature dependence of the resonance mode in NaFe$_{0.9785}$Co$_{0.0215}$As. (a) Temperature dependence of the peak center and integrated area of the resonance mode, obtained from fits in Fig. 4.11(b). The solid line is a fit to BCS superconducting order parameter, and the vertical dashed line marks $T_c$. (b) Color-coded temperature-energy map of the resonance mode at $Q = (1, 0, 1)_0$, the fit to 35 K data has been subtracted. The circles represent data points from which the interpolated map is constructed, and the dashed vertical line marks $T_c$. 
inside the superconducting state.

Polarized neutron scattering results on NaFe$_{0.9785}$Co$_{0.0215}$As are summarized in Fig. 4.13 and Fig. 4.14. We have carried out constant-$Q$ scans of $\sigma^\text{SF}_x$, $\sigma^\text{SF}_y$ and $\sigma^\text{SF}_z$ at $Q = (1, 0, 0.5)_O$ and $Q = (1, 0, 1.5)_O$ at $T = 2$ K and $T = 21$ K. In the superconducting state at 2 K, we observed a clear resonance mode and opening of a partial spin gap, in agreement with unpolarized neutron scattering results. Polarized neutron scattering further reveals both below and above $T_c$, spin anisotropy with $\sigma^\text{SF}_z > \sigma^\text{SF}_y$ is present for $E \lesssim 6$ meV as can be seen in Fig. 4.13(a)-(d). Using data at $Q = (1, 0, 0.5)_O$ [Fig. 4.13(a)-(b)] and $Q = (1, 0, 1.5)_O$ [Fig. 4.13(c)-(d)] we obtained $M_a$, $M_b$ and $M_c$ at $T = 2$ K [Fig. 4.13(e)] and $T = 21$ K [Fig. 4.13(f)]. $r = 0.82$ is used to account for differences in effective illuminated volume between the two wave vectors, this value is similar to $r = 0.8$ used for underdoped NaFe$_{0.985}$Co$_{0.015}$As [91].

While a clear gap develops in the superconducting state below $E \approx 6$ meV in $M_b$, significant spectral weight remains in $M_c$ down to 2 meV [Fig. 4.13(e)]. At 21 K $M_c$ is also stronger than $M_b$ below $E \approx 6$ meV, while both channels display significant spectral weight, indicating the absence of a spin gap due to magnetic ordering.

To gain further insight into the spin anisotropy of NaFe$_{0.9785}$Co$_{0.0215}$As, we carried out temperature scans at $Q_{\text{AF}} = (1, 0, 0.5)_O$ for $E = 3$ meV and $E = 5$ meV, as shown in Figs. 4.14(a) and 4.14(b). At both energies, the spin anisotropy with $\sigma^\text{SF}_z > \sigma^\text{SF}_y$ persists up to $\sim 30$ K. At $E = 3$ meV the magnetic signal is suppressed in all three SF cross sections below $T_c$ [Fig. 4.14(a)], at $E = 5$ meV only $\sigma^\text{SF}_y$ is slightly suppressed. In Figs. 4.14(c) and 4.14(d), $\sigma^\text{SF}_x - \sigma^\text{SF}_y \propto M_y$ and $\sigma^\text{SF}_x - \sigma^\text{SF}_z \propto M_z$ are shown. At $E = 3$ meV, $M_y > M_z$ for $T \lesssim 30$ K and both are suppressed below $T_c$. At $E = 5$ meV, $M_y > M_z$ for $T \lesssim 30$ K is also observed but only $M_z$ displays clear response to $T_c$. The temperature onset of spin anisotropy is more clearly seen in Fig. 4.14(e) and
Figure 4.13: Polarized neutron scattering constant-Q scans on NaFe$_{0.9785}$Co$_{0.0215}$As. Constant-Q scans of $\sigma^x_{SF}$, $\sigma^y_{SF}$ and $\sigma^z_{SF}$ at $Q = (1,0,0.5)$ for (a) $T = 2$ K and (b) $T = 21$ K. Similar results at $Q = (1,0,1.5)$ are also shown for (c) $T = 2$ K and (d) $T = 21$ K. Based on results in (a) and (c), $M_a$, $M_b$ and $M_c$ are obtained for half-integer $L$ for $T = 2$ K, shown in (e). Similarly, $M_a$, $M_b$ and $M_c$ are shown for $T = 21$ K in (f). The inset in (b) shows constant-Q scan at $Q = (1,0,0.5)$ at $T = 35$ K. The solid lines are guides-to-the-eye.
(f), which plots $\sigma_z^{SF} - \sigma_y^{SF} \propto M_y - M_z$ for $E = 3$ meV and $E = 5$ meV, respectively.

In summary, by measuring detailed temperature dependence of the resonance mode in NaFe$_{0.9785}$Co$_{0.0215}$As using unpolarized neutron scattering, we found the peak center of the resonance only weakly decreases upon approaching $T_c$ whereas the integrated intensity tracks the superconducting order parameter. This is in agreement with findings in Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$ [82], FeTe$_{0.6}$Se$_{0.6}$ [125] and NaFe$_{0.95}$Co$_{0.05}$As [126], but different from BaFe$_{1.85}$Co$_{0.15}$As$_2$ [86]. One possible reason that energy of the resonance does not track the superconducting order parameter is that it remains well below $2\Delta$ at low temperatures, upon approaching $T_c$ calculations based on the resonance being a spin-exciton shows that its energy only decreases when $2\Delta$ becomes similar to the resonance energy [126], therefore clear decrease in energy of the resonance may happen only extremely close to $T_c$, by which time the mode may have become too weak to observe experimentally. Using polarized neutron scattering, we find moving from NaFe$_{0.985}$Co$_{0.015}$As to NaFe$_{0.9785}$Co$_{0.0215}$As, the first anisotropic resonance is suppressed but spin anisotropy remains at similar energies. However in contrast to BaFe$_{1.904}$Ni$_{0.096}$As$_2$ [96] such anisotropy disappears right above $T_N$, suggesting NaFe$_{0.9785}$Co$_{0.0215}$As to be an ideal system to compare with BaFe$_{1.904}$Ni$_{0.096}$As$_2$ to elucidate the origin of in-plane spin anisotropy in the paramagnetic iron pnictides and its possible link with transport measurements [73]. Elastoresistance measurements on NaFe$_{1-x}$Co$_x$As, as done for doped BaFe$_2$As$_2$ [73], would be highly beneficial for such an understanding.

4.6 Isotropic resonance mode in overdoped NaFe$_{0.95}$Co$_{0.05}$As

Compared to underdoped NaFe$_{0.985}$Co$_{0.015}$As that exhibits double resonance modes, overdoped NaFe$_{0.95}$Co$_{0.05}$As has a single resonance mode with at an energy corre-
Figure 4.14: Polarized neutron scattering temperature scans on NaFe$_{0.9785}$Co$_{0.0215}$As. Temperature scans of $\sigma_x^{SF}$, $\sigma_y^{SF}$ and $\sigma_z^{SF}$ at $Q = (1,0,0.5)_0$ with (a) $E = 3$ meV and (b) $E = 5$ meV. The differences $\sigma_x^{SF} - \sigma_y^{SF}$ and $\sigma_x^{SF} - \sigma_z^{SF}$ which are respectively proportional to $M_y$ and $M_z$ are shown for (c) $E = 3$ meV and (d) $E = 5$ meV. The differences $\sigma_y^{SF} - \sigma_z^{SF}$ which is proportional to $M_y - M_z$ are shown for (e) $E = 3$ meV and (f) $E = 5$ meV. The solid lines are guides-to-the-eye. The dashed vertical lines mark $T_c$. 
sponding to the second resonance mode in NaFe$_{0.985}$Co$_{0.015}$As [126]. Therefore we expect this single resonance mode to be isotropic in terms of polarizations, similar to the second resonance in NaFe$_{0.985}$Co$_{0.015}$As. To confirm if this is indeed the case, we carried out a polarized neutron scattering experiment on IN20 triple-axis spectrometer at the Institut Laue-Langevin, Grenoble, France. The results are shown in Fig. 4.15, as can be seen in the measured spin-flip cross sections the excitations are isotropic both at 1.5 K and 25 K [Fig. 4.15(a) and (b)]. The same results are also verified by measuring non-spin-flip cross sections. Whereas $M_y \approx \sigma_y^\text{SF} - \sigma_y^\text{SF}$ and $M_z \approx \sigma_z^\text{SF} - \sigma_z^\text{SF}$ for spin-flip cross sections, $M_y \approx \sigma_y^\text{NSF} - \sigma_y^\text{NSF}$ and $M_z \approx \sigma_z^\text{NSF} - \sigma_z^\text{NSF}$ for non-spin-flip cross sections. $M_y$ and $M_z$ obtained from spin-flip and non-spin-flip cross sections are consistent and are shown in Fig. 4.15(e) and (f) for 1.5 K and 25 K. In agreement with the observation from the cross sections, $M_y$ and $M_z$ are isotropic, with $M_z$ possibly being slightly stronger than $M_y$. The same conclusion is obtained by looking at constant-$E$ scans shown in Fig. 4.15(g) and (h).

This work shows that the resonance in overdoped NaFe$_{0.95}$Co$_{0.05}$As corresponds to the second resonance in underdoped NaFe$_{0.985}$Co$_{0.015}$As and is expected to be present across the superconducting phase diagram. The fact the resonance is isotropic is consistent with the spin-exciton picture, where a magnetic field is expected to split the resonance into triplets [127]. Furthermore, the spin gap below the resonance becomes complete and no spin anisotropy is observed compared to near-optimal-doped NaFe$_{0.9785}$Co$_{0.0215}$As, similar to the evolution of spin anisotropy from near-optimal-doped BaFe$_{1.904}$Ni$_{0.096}$As$_2$ [96] to overdoped BaFe$_{1.85}$Ni$_{0.15}$As$_2$ [99].
Figure 4.15: Polarized neutron scattering on electron-overdoped NaFe$_{0.95}$Co$_{0.05}$As. Energy dependence of the measured cross sections $\sigma_{x}^{\text{SF}}$, $\sigma_{y}^{\text{SF}}$ and $\sigma_{z}^{\text{SF}}$ at $Q = (1, 0, 0.5)_{0}$ (a) below ($T = 1.5$ K) and (b) above ($T = 25$ K) $T_{c} = 18$ K for NaFe$_{0.95}$Co$_{0.05}$As. Identical scans as in (a) and (b) are shown in (c) and (d) for $\sigma_{x}^{\text{NSF}}$, $\sigma_{y}^{\text{NSF}}$ and $\sigma_{z}^{\text{NSF}}$. Energy dependence of (e) $M_{y}$ and (f) $M_{z}$ above and below $T_{c}$. The solid lines are the same guide to the eye for 1.5 K, whereas the dashed lines are the same fit of the form $A \frac{1}{E^2 + E_{0}^2}$. Constant-energy scans of $\sigma_{x}^{\text{SF}}$, $\sigma_{y}^{\text{SF}}$ and $\sigma_{z}^{\text{SF}}$ along the $[H, 0, 0.5]_{0}$ direction at (g) $E = 7.5$ meV and 1.5 K and (h) $E = 4$ meV and 25 K. The data are fit globally using Gaussian peaks, with the constraint the peak in $\sigma_{x}^{\text{SF}}$ being twice as strong as the peaks in $\sigma_{y}^{\text{SF}}$ and $\sigma_{z}^{\text{SF}}$. 
4.7 Spin anisotropy due to spin-orbit coupling in optimally hole-doped \( \text{Ba}_{0.67}\text{K}_{0.33}\text{Fe}_2\text{As}_2 \)

The parent compounds of iron pnictide superconductors, such as \( \text{LaFeAsO} \) and \( \text{BaFe}_2\text{As}_2 \), form stripe antiferromagnetic (AF) order at \( T_N \) below a tetragonal-to-orthorhombic structural transition temperature \( T_s \) [inset in Fig. 4.16(b)] [16, 18, 128, 17]. Superconductivity can be induced by partially replacing Ba by K in \( \text{BaFe}_2\text{As}_2 \) to form hole-doped \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) [129, 130, 131, 81, 132] or by partially replacing Fe by \( \text{TM} \) (\( \text{TM} = \text{Co, Ni} \)) to form electron-doped \( \text{BaFe}_{2-x}\text{TM}_x\text{As}_2 \) [133, 134, 79, 26]. Importantly, the resulting phase diagrams exhibit significant asymmetry between electron- and hole-doping [Figs. 4.16(a) and 4.16(b)] [128, 17]. For instance, while near optimal doping the stripe AF order becomes incommensurate for electron-doped \( \text{BaFe}_{2-x}\text{TM}_x\text{As}_2 \) [79, 26][see arrow in Fig. 4.16(b)], a double-\( Q \) tetragonal magnetic structure with ordered moments along the \( c \)-axis is observed in hole-doped \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) [inset in Fig. 4.16(a)] [130, 131, 81, 132].

Nevertheless, upon entering the superconducting state, a magnetic resonance mode appears in the magnetic spectrum in both cases at the AF wave vector (\( Q_{AF} \)) [51, 124, 136, 137]. Furthermore, by measuring the splitting of the electronic states at high-symmetry points in reciprocal space [138], angle-resolved photoemission spectroscopy (ARPES) measurements find that spin-orbit coupling (SOC) is present in both electron- and hole-doped iron pnictides with a similar energy scale \( \sim 10 \text{ meV} \) [103]. Also common to both optimally electron-doped \( \text{BaFe}_{2-x}\text{TM}_x\text{As}_2 \) [58, 139] and hole-doped \( \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 \) [140, 141] is the presence of electronic nematic fluctuations, as revealed by the elastoresistance – i.e. the rate of change of the resistivity anisotropy with respect to applied in-plane uniaxial strain [Fig. 4.16(c)] [65]. The
Figure 4.16: Relevant previous results on optimal-doped \( \text{Ba}_{0.67}\text{K}_{0.33}\text{Fe}_2\text{As}_2 \). The electronic phase diagrams of (a) hole- and (b) electron-doped \( \text{BaFe}_2\text{As}_2 \). While parent compounds of iron pnictides have stripe AF order [inset in (b)] [18], the tetragonal double-Q \( C_4 \) AF order is found in hole-doped \( \text{BaFe}_2\text{As}_2 \) near optimal superconductivity [inset in (a)] [130, 131, 81, 132]. \( T_s \), \( T_N \), \( T_c \) and \( T_r \) mark the tetragonal-to-orthorhombic structural transition, the paramagnetic-to-AF transition, the superconducting transition and the transition into the \( C_4 \) magnetic phase. The phase diagrams in (a) and (b) are adapted from Refs. [135] and [17]. (c) Resistivity anisotropy \( (\rho_a - \rho_b)/(\rho_a + \rho_b) \) of \( \text{BaFe}_{1.904}\text{Ni}_{0.096}\text{As}_2 \) and \( \text{Ba}_{0.67}\text{K}_{0.33}\text{Fe}_2\text{As}_2 \) under uniaxial pressure of \( P = 15 \text{ MPa} \) measured using a mechanical clamp that can vary applied pressure \textit{in-situ} [72]. (d) Elastoresistance \( |2m_{66}| \) for optimally-doped \( \text{BaFe}_{1.91}\text{Ni}_{0.09}\text{As}_2 \), \( \text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2 \), and \( \text{BaFe}_2\text{As}_1\text{P}_{0.6} \), adapted from Ref. [73]. The solid lines are Curie-Weiss fits to the data and dashed lines represent deviations from the Curie-Weiss form. Vertical arrows mark the temperature at which such deviations begin.
elastoresistance diverges with a Curie-Weiss form for both classes of materials as well as for isovalent-doped BaFe$_2$As$_{1.4}$P$_{0.6}$ [73]. Deviation from the Curie-Weiss behavior is seen in both optimally electron- and hole-doped BaFe$_2$As$_2$ at low temperatures, while no deviation is seen in BaFe$_2$As$_{1.4}$P$_{0.6}$ down to $T_c$ [Fig. 4.16(d)] [73].

In addition to its impact on the electronic spectrum [103, 142], SOC also converts crystalline anisotropies into anisotropies in spin space, as seen from nuclear magnetic resonance studies [143]. The spin anisotropy resulting from SOC plays an essential role for the double-$Q$ magnetic phase [130, 131, 81, 132], in which the ordered moments align along the $c$-axis [106]. If SOC was absent, the spin excitations in the paramagnetic tetragonal state of the iron pnictides would be isotropic in spin space [Fig. 4.16(e)]. However, due to the presence of a sizable SOC, an anisotropy is developed in the spin excitations, which can be quantitatively determined by neutron polarization analysis [144]. In the antiferromagnetically ordered phases of the parent compounds BaFe$_2$As$_2$ and NaFeAs [113, 112], where the ordered moments point parallel to the orthorhombic $a$-axis [inset in Fig. 4.16(b)], spin waves exhibit significant anisotropy, with $c$-axis polarized spin waves occurring at lower energy compared to $b$-axis polarized spin waves [95, 94, 90]. To elucidate the relevance of SOC to superconductivity, it is instructive to compare the behavior of the spin anisotropy in hole-doped and electron-doped BaFe$_2$As$_2$, since the maximum values of $T_c$ are quite different in these two cases – $T_c \approx 38$ K for optimally hole-doped Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$ and $T_c \approx 25$ K for optimally electron-doped BaFe$_{1.86}$Co$_{0.14}$As$_2$. Previous analysis of the electron-doped case revealed that the spin anisotropy persists in the paramagnetic tetragonal phase for doping levels up to or slightly beyond optimal doping [97, 96, 98, 100, 101, 91], but vanishes in the well-overdoped regime [99, 91].

Here we present polarized neutron scattering studies of spin excitations in opti-
mally hole-doped Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$ [100, 124]. In the normal state, we find that the spin anisotropy of Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$ persists to $\sim 100$ K for $E = 3$ meV, similarly to the case of near-optimally electron-doped BaFe$_{2-x}$TM$_x$As$_2$, where spin anisotropy at $Q_{AF} = (1, 0, 1)_0$ was found below $E \approx 7$ meV and up to $\sim 70$ K [96, 98]. We associate the onset of normal state spin anisotropy with the nematic susceptibility deviating from Curie-Weiss behavior measured via elastoresistance [see vertical arrows in Fig. 4.16(d)] [73], indicating an important role of spin excitations in transport properties of iron pnictides.

Upon entering the superconducting state, we find that while at high energies ($E \geq 14$ meV) the spectrum is nearly isotropic as found in previous work [100], at low energies the resonance mode is strongly anisotropic, being dominated by a $c$-axis polarized component. We attribute this behavior to the fact that the superconducting state is close to the double-$Q$ magnetic phase, in which the magnetic moments point out-of-plane [131, 81]. Indeed, by adding a spin-anisotropic term that favors $c$-axis spin orientation in a simple two-band theoretical model, we find that the resonance mode in the $c$-axis polarized channel has in general a lower energy than in other channels, and that this energy difference increases as the magnetically ordered state is approached. Our analysis also reveals an interesting correlation between the energy scale of the spin anisotropy in the superconducting state and $T_c$ [97, 96, 98, 100, 101, 91], suggesting that SOC is an integral part of the superconductivity of iron pnictides.

Previous measurements of resistivity anisotropy in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ demonstrated that compared to their electron-doped counterparts, the hole-doped compounds have much smaller and reversed resistivity anisotropy [140, 141]. Near optimal doping resistivity anisotropy was found to disappear in Ba$_{0.66}$K$_{0.34}$Fe$_2$As$_2$ [141], however recent measurements revealed significant elastoresistance in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ [73]. To
resolve this puzzling difference, we measured resistivity anisotropy on single crystals of Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$ and BaFe$_{1.904}$Ni$_{0.096}$As$_2$ using the Montgomery method with a mechanical clamp that can vary the applied pressure *in-situ* as described in Ref. [72]. Prefactors due to samples not being perfect squares were corrected for at 200 K [72], where no/negligible resistivity anisotropy is present. Several nominal pressures were applied and the actual zero pressure is determined by performing a linear fit of the change in resistivity anisotropy as a function of nominal pressure. Measured resistivity anisotropy is then scaled to $P = 15$ MPa for both samples to allow for direct comparison under the same applied pressure. Resistivity anisotropy is linearly proportional to the applied pressure in the pressure range we studied, as shown in Fig. 4.17 for Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$, similar to BaFe$_2$As$_2$ in which linear response persists up to 90 MPa in the paramagnetic state [72]. Our results are presented in Fig. 4.16(c) and resolves a discrepancy in the literature.

Polarized inelastic neutron scattering measurements were carried out using the IN22 triple-axis spectrometer at Institut Laue-Langevin, Grenoble, France. We studied Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$ single crystals ($a = b \approx 5.56$ Å, $c = 13.29$ Å) co-aligned in the $[H, 0, L]_O$ scattering plane used in previous works [100, 82]. We use the orthorhombic notation suitable for AF ordered iron pnictides even though Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$ has a tetragonal structure and is paramagnetic at all temperatures [124, 100]. Thus, the momentum transfer is $Q = Ha^* + Kb^* + Lc^*$, with $a^* = \frac{2\pi}{a}\hat{a}$, $b^* = \frac{2\pi}{b}\hat{b}$ and $c^* = \frac{2\pi}{c}\hat{c}$, where $H$, $K$ and $L$ are Miller indices. In this notation, magnetic order in BaFe$_2$As$_2$ occurs at $Q_{AF} = (1, 0, L)_O$ with $L = 1, 3, 5, \ldots$. Three neutron spin-flip (SF) cross sections $\sigma^S_F$, $\sigma^S_y$ and $\sigma^S_z$ were measured, with the usual convention $x \parallel Q$, $y \perp Q$ and in the scattering plane, and $z$ perpendicular to the scattering plane. Magnetic neutron scattering directly measures the magnetic scattering function $S^{\alpha\beta}(Q, E)$, which
Figure 4.17: Determining resistivity anisotropy in optimal-doped Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$ under 15 MPa uniaxial pressure. Resistivity anisotropy as a function of applied pressure. Data is obtained by combining measured points with 50 $\leq$ T $\leq$ 60 K, a scaling factor used to normalize resistivity anisotropy to $P = 15$ MPa is obtained by a linear fit as shown.

is proportional to the imaginary part of the dynamic susceptibility through the Bose factor, $S^{\alpha\beta}(Q, E) \propto [1 - \exp(-E/k_BT)]^{-1}\text{Im}\chi^{\alpha\beta}(Q, E)$ [3]. We denote the diagonal components of the magnetic scattering function $S^{\alpha\alpha}$ as $M_\alpha$.

Figure 4.18 summarizes constant-$Q$ scans at 2 K and $Q = (1, 0, L)_O$ with $L = 0, 1, 2$ and 3. From Fig. 4.18(a)-(d), it is clear that $\sigma_x^{SF} > \sigma_z^{SF} \geq \sigma_y^{SF}$ below $E \approx 14$ meV, meaning that spin anisotropy exists below this energy while excitations above this energy are isotropic as shown in previous work [100]. Although magnetic order is fully suppressed in Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$, the spin gap $E_g$ in the superconducting state displays strong $L$ dependence, with $E_g \approx 0.75$ meV for odd $L$ and $E_g \approx 5$ meV for even $L$ [124, 100]. From Figs. 4.18 (b) and 4.18(d), we observe that the small gap for odd $L$ is due to $M_y$, with $\sigma_x^{SF} \approx \sigma_z^{SF} > \sigma_y^{SF}$ for $E \lesssim 5$ meV. Magnetic excitations are gapped in the same energy range for even $L$ as can be seen in Figs. 4.18(a) and 4.18(c), with
Figure 4.18: Constant-Q scans on optimal-doped Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$. Constant-Q scans of $\sigma_{x}^{SF}$, $\sigma_{y}^{SF}$ and $\sigma_{z}^{SF}$ at $Q = (1, 0, L)$ for (a) $L = 0$, (b) $L = 1$, (c) $L = 2$ and (d) $L = 3$ measured at 2 K. Using the measured cross sections in (a) - (d), $M_a$, $M_b$ and $M_c$ are obtained for (e) even and (f) odd $L$. The solid lines are guides to the eye.
\( \sigma_x^{SF} \approx \sigma_y^{SF} \approx \sigma_z^{SF} \). \( M_a, M_b \) and \( M_c \) for even and odd \( L \) are shown in Figs. 4.18(e) and 4.18(f), respectively. While \( M_b \) is weakly \( L \)-dependent, \( M_c \) clearly displays different behaviors for even and odd \( L \). Because in the energy range \( 5 \lesssim E \lesssim 10 \) meV \( M_c \) dominates and is dispersive along \( L \), we uniquely identify it with the the anisotropic resonance that disperses along \( L \) which was previously observed in the same sample [100].

To gain further insight into the spin anisotropy of \( \text{Ba}_{0.67}\text{K}_{0.33}\text{Fe}_2\text{As}_2 \), we carried out temperature scans at \( Q_{AF} = (1, 0, 1)_0 \) for \( E = 3 \) meV and \( E = 9 \) meV, as shown in Figs. 4.19(a) and 4.19(b). At \( E = 3 \) meV, the spin anisotropy with \( \sigma_z^{SF} > \sigma_y^{SF} \) persists up to \( \sim 100 \) K. Although below \( T_c \) the magnetic signal is suppressed in all three SF cross sections, the normal-state anisotropy persists [Fig. 4.19(a)]. At \( E = 9 \) meV, the spin anisotropy disappears above \( T_c \), suggesting that the main contribution to the spin anisotropy in the superconducting state arises from the anisotropic resonance mode [100]. In Figs. 4.19(c) and 4.19(d), \( \sigma_x^{SF} - \sigma_y^{SF} \propto M_y \) and \( \sigma_x^{SF} - \sigma_z^{SF} \propto M_z \) are shown. At \( E = 3 \) meV, \( M_y > M_z \) for \( T \lesssim 100 \) K and both are suppressed below \( T_c \). At \( E = 9 \) meV, while a clear resonance mode with an order-parameter-like temperature dependence is seen in \( M_y, M_z \) remains constant across \( T_c \). The temperature onset of spin anisotropy is more clearly seen in Fig. 4.19(e) and (f), which plots \( \sigma_z^{SF} - \sigma_y^{SF} \propto M_y - M_z \) for \( E = 3 \) meV and \( E = 9 \) meV, respectively.

To obtain the temperature dependence of \( M_a, M_b \) and \( M_c \), we measured \( \sigma_x^{SF}, \sigma_y^{SF} \) and \( \sigma_z^{SF} \) at \( Q_{AF} = (1, 0, 3)_0 \) for \( E = 3 \) meV and \( E = 9 \) meV [Fig. 4.20]. Using the method described in 4.2 and data for \( Q = (1, 0, L)_0 \) with \( L = 1 \) and 3 (\( L = 0 \) and 2), we extracted \( M_a, M_b \) and \( M_c \) for the magnetic zone center (zone boundary along \( L \)) with odd (even) \( L \) [results in Figs. 4.18(e)-(f) above are obtained similarly]. The data with \( L = 3 \) used in combination with the \( L = 1 \) data [Fig.
Figure 4.19: Temperature scans on optimal-doped Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$ at Q = (1, 0, 1)°. Temperature scans of $\sigma_{x}^{\text{SF}}$, $\sigma_{y}^{\text{SF}}$ and $\sigma_{z}^{\text{SF}}$ at Q = (1, 0, 1)° with (a) $E = 3$ meV and (b) $E = 9$ meV. The differences $\sigma_{y}^{\text{SF}} - \sigma_{y}^{\text{SF}}$ and $\sigma_{x}^{\text{SF}} - \sigma_{z}^{\text{SF}}$ which are respectively proportional to $M_y$ and $M_z$ are shown for (c) $E = 3$ meV and (d) $E = 9$ meV. The differences $\sigma_{z}^{\text{SF}} - \sigma_{y}^{\text{SF}}$ which is proportional to $M_y - M_z$ are shown for (e) $E = 3$ meV and (f) $E = 9$ meV. The solid lines are guides to the eye. The dashed vertical lines mark $T_c$. 
4.19(a)-(b)] to obtain $M_a$, $M_b$ and $M_c$ in Fig. 4.21(a)-(b) are shown here 4.20. In the analysis we ignored the differences of sample illumination volume and convolution with instrumental resolution between $L = 1$ and 3, and set the scale factor that accounts for these differences to be $r = 1$ [100]. In previous works [100, 96, 94, 90] $r$ is found to be close to unity in all cases and our results are qualitatively robust when $r$ deviates slightly from 1.

Combining the temperature dependence for $L = 1$ and $L = 3$, $M_a$, $M_b$ and $M_c$ are obtained for odd $L$ as shown in Fig. 4.21(a) and 4.21(b). At $E = 3$ meV, $M_a \approx M_c > M_b$ within the probed temperature range, and all three channels decrease in intensity below $T_c$. At $E = 9$ meV, $M_a$ and $M_b$ display a weak temperature dependence while $M_c$ is sharply affected by $T_c$. To corroborate our conclusion, we binned data points in Fig. 4.21(a) and 4.21(b) that are well below $T_c (T \leq 25 \text{ K})$ and above $T_c (T \geq 40 \text{ K})$, as shown in the insets of Figs. 4.21(a) and 4.21(b). While magnetic excitations at $E = 3$ meV are suppressed upon entering the superconducting state,
Figure 4.21: Summary of polarized neutron scattering results on \( \text{Ba}_{0.67}\text{K}_{0.33}\text{Fe}_2\text{As}_2 \). Temperature dependence of \( M_a \), \( M_b \) and \( M_c \) for (a) \( E = 3 \) meV and (b) \( E = 9 \) meV. The solid lines are guides to the eye and dashed vertical lines mark \( T_c \). The insets in (a) and (b) show binned \( M_a \), \( M_b \) and \( M_c \) from (a) and (b) for \( T \leq 25 \) K and \( T \geq 38 \) K. The insets share the same \( y \)-axis label as (a) and (b). (c) Difference between the energies of the \( ab \)-polarized and the \( c \)-polarized resonance modes obtained in our theoretical model. \( U \) is the electronic interaction that triggers long-range magnetic order with the moments pointing along the \( c \)-axis when \( U = U_c^* \). (d) Maximum energy at which spin anisotropy is observed in the superconducting state of several doped \( \text{BaFe}_2\text{As}_2 \) compounds. Results are obtained from Refs. [98, 100, 101, 96, 99]. For overdoped \( \text{BaFe}_{1.85}\text{Ni}_{0.15}\text{As}_2 \) the excitations are isotropic but low energy excitations are gapped below \( E \approx 4 \) meV [99], therefore for this compound we assign the maximum spin anisotropy energy to be 0, but with an error bar of 4 meV. The results on \( \text{BaFe}_2\text{As}_{1.4}\text{P}_{0.6} \) are from unpublished data.
the polarization of these magnetic excitations seems to remain the same, persisting up to \( T \approx 100 \text{ K} \). On the other hand, at \( E = 9 \text{ meV} \), magnetic excitations are nearly isotropic above \( T_c \), while \( M_c > M_a \approx M_b \) well below \( T_c \). Therefore, the \( c \)-axis polarized anisotropic resonance is directly coupled to superconductivity with an order-parameter-like temperature dependence.

To understand the origin of this \( c \)-axis polarized spin resonance, we consider a simple two band model in which the resonance mode arises due to the sign change of the gap function between a hole pocket and an electron pocket displaced from each other by the AF ordering vector \( Q_{\text{AF}} \) [145, 146, 147]. Without SOC, the energy of the resonance mode is the same for all polarizations, being close to \( 2\Delta \) far from the putative magnetic quantum phase transition inside the superconducting dome \([U \ll U'_c \text{ in Fig. 4.21(c)}]\), but vanishing as the transition is approached \([U \rightarrow U'_c \text{ in Fig. 4.21(c)}]\). SOC, however, promotes a spin anisotropy term that makes the magnetic moments point along the \( c \)-axis for hole-doped compounds [106]. As a result, the energy of the resonance mode polarized along the \( c \)-axis is suppressed much faster as the magnetic transition is approached, yielding \( \omega_c < \omega_{ab} \) [Fig. 4.21(c)]. This behavior is in qualitative agreement with our experimental results, with the resonance seen in \( M_c \) indeed at lower energies. It should also be noted that our model does not capture the broadening of the resonance, which is rather pronounced in the experimental data. Our simple model has two additional consequences: first, as the system is overdoped and moves farther from the magnetically ordered state, the resonance mode should become more isotropic. While spin anisotropy persists in slightly overdoped \( \text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2 \) \((T_c = 36 \text{ K})\) [101], how it evolves in K-well-overdoped samples remains to be seen.

Furthermore, because in electron-doped compounds the moments point along the \( a \) direction, the resonance is expected to be polarized along the \( a \)-axis. Although this is
the case in electron-doped NaFe$_{0.985}$Co$_{0.015}$As [91], the sample studied had long-range AF order. For electron-doped Ba(Fe$_{0.94}$Co$_{0.06}$)$_2$As$_2$ [98], the anisotropic resonance was argued to be also polarized along c-axis, based on the assumption $M_a=M_b$ and the observation $M_y > M_z = 0$ for the anisotropic resonance. As we have shown here and in previous work [96], even in the tetragonal state $M_a$ and $M_b$ are not necessarily the same and it is unclear whether there is also significant resonance spectral weight polarized along the a-axis in previous work [98]. Spin anisotropy of spin excitations has also been detected in the superconducting states of LiFeAs [148] and FeSe$_{0.5}$Te$_{0.5}$ [149], consistent with significant spin-orbit coupling detected by ARPES [103, 142] in these systems.

The normal state spin anisotropy at low energies persists to a temperature significantly higher than $T_c$ [$\sim 70$ K in BaFe$_{1.094}$Ni$_{0.096}$As$_2$ [96] and $\sim 100$ K in Ba$_{0.67}$K$_{0.33}$Fe$_2$As$_2$, Fig. 4.19(e)] for both electron- and hole-doped BaFe$_2$As$_2$ near optimal doping. The temperature at which spin anisotropy onsets is similar to the temperature at which the nematic susceptibility deviates from Curie-Weiss behavior [73], suggesting a common origin for both phenomena [Fig. 4.16(d)]. For optimally-doped BaFe$_2$As$_{1.4}$P$_{0.6}$ [from unpublished results], whose nematic susceptibility shows no deviation from the Curie-Weiss form [Fig. 4.16(d)] [73], no spin anisotropy is observed right above $T_c$.

While disorder is likely to play an important role in explaining this deviation from Curie-Weiss behavior in the elastoresistance [73], our results suggest that the spin anisotropy may also be important. Indeed, previous INS experiments revealed the intimate relationship between nematicity and magnetic fluctuations [63, 115, 150]. Theoretically, the nematic susceptibility increases with increasing magnetic fluctuations in all polarization channels [65]. However, once a spin anisotropy sets in, fluctuations related to the spin components perpendicular to the easy axis increase more
slowly with decreasing temperature. As a result, the nematic susceptibility should also increase more slowly, which may contribute to the deviation from Curie-Weiss behavior observed experimentally.

Finally, the maximum energies at which spin anisotropy is observed in the superconducting states of several doped BaFe$_2$As$_2$ compounds are plotted as function of $T_c$ in Fig. 4.21(d). Note that the spin anisotropy of the resonance in the superconducting state is also present in BaFe$_2$As$_{1.4}$P$_{0.6}$, despite the absence of spin anisotropy in the normal state [from unpublished results]. We note a clear positive correlation between the energy scale of the spin anisotropy and $T_c$, suggesting SOC to be an important ingredient for understanding superconductivity in iron pnictides.
Chapter 5

Antiferromagnetically Ordered Insulating Phase in \( \text{NaFe}_{1-x}\text{Cu}_x\text{As} \) with \( x \approx 50\% \)

In this chapter the phase diagram of \( \text{NaFe}_{1-x}\text{Cu}_x\text{As} \) will be discussed. A neutron spin resonance mode is observed in superconducting \( \text{NaFe}_{0.98}\text{Cu}_{0.02}\text{As} \) [151]. Upon further increasing \( x \) beyond \( \sim 10\% \), the ground state becomes insulating with short-range Fe-Cu cation order and magnetic order of Fe, both of which approach long-range for \( x \approx 50\% \) [152]. Time-of-flight neutron spectroscopy on \( \text{NaFe}_{0.53}\text{Cu}_{0.47}\text{As} \) reveals highly one-dimensional magnetic excitations that provide clues for understanding spin waves in \( \text{NaFeAs} \) (unpublished).

5.1 Introduction

At the heart of understanding the physics of the iron-based superconductors is the interplay of superconductivity, magnetism and bad-metal behavior [16, 153, 45, 17, 19, 154], a key question is whether superconductivity emerges due to strong electronic correlations [154, 155, 156, 157, 158, 159] or nested Fermi surfaces [13, 160, 161]. Superconductivity occurs in the vicinity of antiferromagnetic (AF) order, both in the iron pnictides and iron chalcogenides [153, 45, 17, 19]. In addition, the normal state has a very large room-temperature resistivity, which reaches the Ioffe-Mott-Regel limit [153, 17, 19]. This bad-metal behavior has been attributed to the proximity to a Mott transition [155, 156, 157, 158, 159], with the Coulomb repulsion of the multi-orbital 3\( d \) electrons of the Fe ions being close to the threshold for electronic localization.
In the iron chalcogenide family, several compounds have been found to be AF and insulating with characteristic features of a Mott insulator [162, 163, 164, 165]. There is also evidence for an orbital-selective Mott phase in $A_xFe_{2-y}Se_2$ ($A = K, Rb$) [166]. However, in these iron chalcogenide materials, one cannot continuously tune the AF Mott insulating state into a superconductor.

On the other hand, the iron pnictide NaFe$_{1-x}$Cu$_x$As is a plausible candidate for a Mott insulator based on transport and scanning tunneling microscopy (STM) measurements near $x = 0.3$ [167, 168], however the insulating behavior may also be induced by Anderson localization via Cu-disorder. Here we demonstrate that heavily Cu-doped NaFe$_{1-x}$Cu$_x$As becomes an AF insulator when $x$ approaches 0.5 and the insulating behavior persists into the paramagnetic state, providing strong evidence for a Mott insulating state. This conclusion is corroborated by theoretical calculations based on a slave-spin approach, which show that a Cu-site blockage of the kinetic motion of the Fe 3$d$ electrons reduces the electron bandwidth and thus enhances the effect of electron correlations. We also demonstrate that Cu is in 3$d^{10}$ state resulting in hole-doping which also enhances electronic correlations [157, 158, 159], both effects are responsible for pushing the system towards Mott localization.

The parent compounds of iron pnictide superconductors such as AFe$_2$As$_2$ ($A = $Ba, Sr, Ca) and NaFeAs have crystal structures shown in Fig. 5.1(a) and 5.1(b), respectively [153]. They exhibit a tetragonal-to-orthorhombic structural phase transition at temperature $T_s$, followed by a paramagnetic to AF phase transition at $T_N$ ($T_s \geq T_N$) with a collinear magnetic structure where the spins are aligned antiferromagnetically along the $a$-axis of the orthorhombic lattice [Fig. 5.1(c)] [112]. When Fe in AFe$_2$As$_2$ is replaced by Cu to form ACu$_2$As$_2$, the Cu atoms have a nonmagnetic 3$d^{10}$ electronic configuration with Cu$^{1+}$ and a filled $d$ shell due to the presence of a co-
Figure 5.1: Structure and resistivity of NaFe$_{1-x}$Cu$_x$As. (a) The crystal structure of ACu$_2$As$_2$ in the tetragonal state, where $a_T$ is the in-plane lattice parameter. The As-As covalent bonding distance is $\sim 2.5$ Å. (b) The crystal structure of NaFe$_{1-x}$Cu$_x$As, where similar As-As covalent bonding is not possible. (c) The collinear magnetic structure of NaFeAs, where the AF order and moment direction are along the orthorhombic $a$ axis [112, 121]. Only Fe atoms are plotted in the figure for clarity. (d) Real space structure and spin arrangements of NaFe$_{0.5}$Cu$_{0.5}$As in the AF orthorhombic unit cell similar to NaFeAs. In NaFe$_{0.5}$Cu$_{0.5}$As, since Fe and Cu form stripes, Na and As also shift slightly from their high symmetry positions. (e) In-plane resistivity for $x = 0.016$ sample where bulk superconductivity occurs below $T_c = 11$ K [167]. (f) Temperature dependence of the in-plane resistivity for $x = 0.18, 0.39, 0.44$ and 0.48 samples. The vertical arrow marks the position of $T_N$ for the $x = 0.44$ sample determined from neutron scattering. (g) Evolution of ordered moment with doping in NaFe$_{1-x}$Cu$_x$As. The two ordered phases are separated by the superconducting dome marked as SC, with no magnetic order for $x = 0.016$ near optimal superconductivity. The right and left insets show the in-plane magnetic structures of NaFeAs and the new AF insulating phase, respectively. For $x \leq 0.05$, the phase diagram from Ref. [167] is plotted. Vertical error bars are from least-square fits (1 s. d.).
valent bond between the As atoms within the same unit cell $[\text{As}]^{-3} \equiv [\text{As-As}]^{-4}/2$ [169, 170, 171, 172], as predicted by band structure calculations [173]. Since the crystal structure of NaFe$_{1-x}$Cu$_x$As does not allow a similar covalent bond [167], it would be interesting to explore the magnetic state of NaFe$_{1-x}$Cu$_x$As in the heavily Cu-doped regime. From transport measurements on single crystals of NaFe$_{1-x}$Cu$_x$As with $x \leq 0.3$, it was found that the in-plane resistivity of the system becomes insulating-like for $x \geq 0.11$ [167]. STM showed that local density-of-states for NaFe$_{1-x}$Cu$_x$As with $x = 0.3$ resembles electron-doped Mott insulators [168], although it is unclear what the undoped Mott insulating state is or whether it exhibits AF order.

Using transport, neutron scattering, transmission electron microscopy (TEM), X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) we demonstrate that NaFe$_{1-x}$Cu$_x$As with $x \approx 0.5$ exhibits Fe and Cu ordering and is a Mott insulator with AF order. Upon decreasing $x$ from $x \approx 0.5$, the correlation lengths of Fe and Cu ordering and magnetic ordering, as well as the ordered magnetic moment continuously decrease, connecting smoothly with the superconducting phase in NaFe$_{1-x}$Cu$_x$As appearing near $x = 0.05$, highlighting the role of electronic correlations in iron pnictides.

Using inelastic neutron scattering we studied magnetic excitations in the antiferromagnetically ordered NaFe$_{1-x}$Cu$_x$As ($x = 0.47$) with Fe and Cu forming stripes, a structural analog of magnetic order in NaFeAs [112]. Consistent with the stripe structure of Fe, the magnetic excitations are highly one-dimensional dominated by the nearest neighbor exchange coupling along the chain direction. Surprisingly, magnetic excitations in NaFe$_{1-x}$Cu$_x$As ($x = 0.47$) reveal clues for understanding spin waves in NaFeAs.

In NaFe$_{1-x}$Cu$_x$As with $x \approx 50\%$ magnetic order is long-range, however for lower
Cu concentration magnetic order is short-range and has clear quasi-elastic contribution. Therefore in the phase diagram of NaFe$_{1-x}$Cu$_x$As, with increasing Cu concentration the spin-density-wave order in NaFeAs is suppressed giving way to superconductivity near $x \approx 2\%$, above $x \approx 5\%$ superconductivity disappears and above $x \approx 10\%$ the system becomes insulating-like and at the same time short-range magnetic order and presumably also cation order appears, finally when $x \approx 50\%$ magnetic and cation orders become long-range, culminating in an antiferromagnetically ordered insulating phase. Therefore, the superconducting phase in NaFe$_{1-x}$Cu$_x$As is continuously connected to an antiferromagnetically ordered insulating phase through a region of short-range quasi-static magnetic correlations. The ordered moment estimated evolves continuously as shown in Fig. 5.1(g).

Moreover we observed a neutron spin resonance mode in the superconducting state of NaFe$_{0.98}$Cu$_{0.02}$As, similar to other iron pnictides [17, 51, 45, 174], suggesting electronic correlations to be an important part of iron pnictides in general. The superconducting dome in NaFe$_{1-x}$Cu$_x$As [167] is also unique in the sense that such a dome is absent in Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ and SrFe$_{2-x}$Cu$_x$As$_2$ [175, 170], allowing us to compare energy of the resonance $E_r$ with NaFe$_{1-x}$Co$_x$As [126, 120], leading to the observation that in doped NaFeAs there is no apparent scaling of $E_r$ with $T_c$ [120], rather both the concentration of dopants and the impurity potential seem to increase the ratio $E_r/k_B T_c$.

Our systematic studies demonstrate the superconducting phase in NaFe$_{0.98}$Cu$_{0.02}$As is similar to other iron pnictides, while being continuously connected to an antiferromagnetically ordered insulating phase, highlighting the role of electronic correlations in the generic phase diagram of iron pnictides.
5.2 Crystal Structure of NaFe$_{1-x}$Cu$_x$As with $x \approx 0.5$

NaFe$_{1-x}$Cu$_x$As single crystals were grown by the self-flux method using the same growth procedure as for NaFe$_{1-x}$Co$_x$As described in earlier work [176]. The Cu doping levels used in this paper were determined by inductively coupled plasma (ICP) atomic-emission spectroscopy. Samples with nominal Cu concentrations of $x = 2\%$, 20\%, 50\%, 75\% and 90\% were prepared, resulting in actual Cu concentrations of $x = 1.6\%$, 18.4(0.4)\%, 38.9(2.8)\%, 44.2(1.7)\% and 48.4(3.4)\%. For each nominal doping except $x = 2\%$, 5-6 samples were measured and the standard deviation in these measurements are taken as the uncertainty of the actual concentrations. For simplicity, the actual concentrations are noted as $x = 1.6\%$, 18\%, 39\%, 44\% and 48\% in this chapter, unless otherwise specified. This suggests that the solubility limit of Cu in NaFe$_{1-x}$Cu$_x$As single crystals by our growth method is $\approx 50\%$.

For single crystal elastic neutron scattering measurements, samples were covered with a hydrogen-free glue and then stored in a vacuum bottle at all times except during sample loading before the neutron scattering experiment. While our largest crystals grown are up to 2 grams, we typically used thin plate-like samples around $5 \times 5$ mm$^2$ in size with mass $\approx 0.2$ grams for elastic neutron scattering measurements. Measurement of the sample with $x = 0.18$ was carried out on the N5 triple-axis spectrometer at the Canadian Neutron Beam Center (CNBC), Chalk River Laboratories. Pyrolitic graphite (PG) monochromator and analyzer ($E_i = 14.56$ meV) were used with none-36'-sample-33'-144' collimation setup. A PG filter was placed after the sample to eliminate contamination from higher order neutron wavelengths. The experiment on $x = 0.39$ and 0.44 samples were done on the HB-3 triple-axis spectrometer and the HB-1A fixed-incident-energy triple axis spectrometer, respectively, at the High Flux Isotope Reactor, Oak Ridge National Laboratory. On HB-3, a PG
monochromator \((E_i = 14.7 \text{ meV})\), analyzer and two PG filters (one before and the other after the sample) were used with collimation setup 48'-60'-sample-80'-120'. HB-1A uses 2 PG monochromators \((E_i = 14.6 \text{ meV})\) and 2 PG filters (mounted before and after second monochromator) resulting in negligible higher order wavelengths. Neutrons in the incident beam. A PG analyzer is placed after the sample. The collimation used was 48'-48'-sample-40'-68'. In all cases above, the samples were aligned in the \([H, 0, L]_\text{O}\) scattering plane.

The polarized single crystal neutron scattering measurements were carried out on the C5 polarized-beam triple-axis spectrometer at CNBC, Chalk River Laboratories. The neutron beams were polarized with Heusler \((1, 1, 1)\) crystals with a vertically focusing monochromator and a flat analyzer \((E_f = 13.70 \text{ meV})\). A PG filter was placed after the sample and none-48'-51'-144' collimation was used. Neutron polarization was maintained by using permanent magnet guide fields. Mezei flippers were placed before the sample to allow the measurement of neutron SF and NSF scattering cross-sections. A 5-coil Helmholtz assembly was used to control the neutron spin-orientation at the sample position by producing a magnetic field of the order of 10 G. The orientation of the magnetic field at the sample position was automatically adjusted to allow the measurements to be performed for the neutron spin to be parallel or perpendicular to the momentum transfer. The flipping ratio, defined as the ratio of nuclear Bragg peak intensities in NSF and SF channels, was measured to be about 10:1 for various field configurations. The sample was studied in both \([H, 0, L]\) and \([H, H, L]\) scattering planes.

The XAS and RIXS measurements on the \(x = 0.44\) samples were carried out at the Advanced Resonant Spectroscopy (ADRESS) beam-line of the Swiss Light Source, Paul Scherrer Institut, Switzerland [177]. Samples were cleaved \textit{in-situ} and
measured in a vacuum better than $1 \times 10^{-10}$ mbar. X-ray absorption was measured in total electron yield mode by recording the drain current from the samples and in total fluorescence yield with a photodiode. Linearly polarized X-rays with $E = 931.8$ eV resonant at the Cu $L_3$ edge were used for the RIXS measurements. The total momentum transfer was kept constant, but the component of momentum transfer in the $ab$ plane has been varied.

For neutron powder diffraction (NPD) measurements, the samples were ground from $\sim 2$ grams ($x = 0.016, 0.18, 0.39, 0.44$) of single crystals and sealed in vanadium sample cans inside a He filled glove box. NPD measurements were carried out at room temperature (300 K) on the BT1 high resolution powder diffractometer at NIST Center for Neutron Research. The Ge$(3,1,1)$ monochromator was used to yield the highest neutron intensity and best resolution at low scattering angles. For the $x = 0.44$ sample, measurement at 4 K using a Cu$(3,1,1)$ monochromator was also carried out.

For the single crystal neutron diffraction measurement, a sample with $x = 0.44$ (25 mg) was used. The experiment was carried out at the four-circle diffractometer HB-3A at the High Flux Isotope Reactor, Oak Ridge National Laboratory. The data was measured at 250 K with neutron wavelength of 1.003 Å from a bent Si$(3,3,1)$ monochromator using an Anger camera detector. Bragg peaks associated with the NaFeAs structure were measured with 1 second per point by carrying out rocking scans. Super-lattice peaks were measured with 10 minutes per point at each position.

Figure 5.1(e) shows temperature dependence of the in-plane resistivity for the $x = 0.016$ sample. In addition to superconductivity at $T_c = 11$ K, the normal state resistivity $\rho$ is $\sim 0.4$ m$\Omega \cdot$ cm at room temperature, consistent with previous work [167]. Figure 5.1(f) plots the temperature dependence of the resistivity on a log
scale for samples with \( x = 0.18, 0.38, 0.44 \) and 0.48. Resistivity in the \( x = 0.18 \) sample exhibits insulating-like behavior consistent with earlier work [167]. For the \( x \geq 0.39 \) samples, resistivity further increases by more than an order of magnitude compared to the \( x = 0.18 \) sample, signifying that electrons become much more localized in NaFe\(_{1-x}\)Cu\(_x\)As when \( x \) approaches 0.5. It is worth noting that resistivity in SrFe\(_{2-x}\)Cu\(_x\)As\(_2\) does not go above 1 mΩ · cm for similar doping levels [170], and as discussed below there is in fact less disorder in NaFe\(_{1-x}\)Cu\(_x\)As compared to SrFe\(_{2-x}\)Cu\(_x\)As\(_2\), therefore the enhanced resistivity in NaFe\(_{1-x}\)Cu\(_x\)As cannot be due to any disorder effects.

For triple-axis instruments measurements, we use the orthorhombic unit cell notation suitable for the AF ordered state of NaFeAs [112, 121], and define momentum transfer \( \mathbf{Q} \) in three-dimensional reciprocal space in Å\(^{-1}\) as \( \mathbf{Q} = H \mathbf{a}^* + K \mathbf{b}^* + L \mathbf{c}^* \), where \( H, K, \) and \( L \) are Miller indices and \( \mathbf{a}^* = \hat{a} 2\pi / a, \mathbf{b}^* = \hat{b} 2\pi / b, \mathbf{c}^* = \hat{c} 2\pi / c \) [Fig. 5.1(c)]. Single crystals are aligned in the \((H,0,L)\) and \((H,H,L)\) scattering planes in these measurements. In the \((H,0,L)\) scattering geometry, the collinear magnetic structure in NaFeAs [Fig. 5.1(c)] gives magnetic Bragg peaks below \( T_N \) at \( \mathbf{Q}_{AF} = (H,0,L) \), where \( H = 1, 3, \cdots \) and \( L = 0.5, 1.5, \cdots \), positions [112, 121].

Figure 5.2(c) shows typical elastic scans for NaFe\(_{0.56}\)Cu\(_{0.44}\)As along the \([H,0,0.5]\) direction at \( T = 3.6 \) K and 300 K. Because of twinning in the orthorhombic state, this is equivalent to elastic scans along the \([0,K,0.5]\) direction. While the scattering has a clear peak centered around \( \mathbf{Q} = (1,0,0.5)/(0,1,0.5) \) at room temperature, the scattering is enhanced dramatically on cooling to 3.6 K, suggesting the presence of static AF order. The temperature difference plot between 3.6 K and 300 K in Fig. 5.2(d) indicates that the low-temperature intensity gain is essentially instrumental resolution limited (horizontal bar). Figure 5.2(e) shows the temperature difference
Figure 5.2: TEM and elastic neutron scattering on NaFe$_{0.56}$Cu$_{0.44}$As. (a) Using 200 keV incident electrons, an electron diffraction pattern in the $[H, K]$ plane was obtained from a NaFe$_{0.56}$Cu$_{0.44}$As particle with its TEM real-space image shown in the inset. The scale bar is 1 µm. (b) Cuts of (a) along the $[H, 0]$ and $[0, K]$ directions. (c) Unpolarized neutron diffraction scans along the $[H, 0, 0.5]/[0, K, 0.5]$ direction for the $x = 0.44$ sample at 300 K and 3.6 K. The peak at 300 K is a super-lattice peak arising from Fe-Cu ordering. Temperature difference plots between 3.6 K and 300 K along the (d) $[H, 0, 0.5]/[0, K, 0.5]$ and (e) $[1, 0, L]/[0, 1, L]$ directions. Solid lines are Gaussian fits and the horizontal bars indicate instrumental resolution. (f) Temperature dependence of the scattering at $Q = (1, 0, 0.5)/(0, 1, 0.5)$ shows $T_N \approx 200$ K. (g) Neutron polarization analysis of the magnetic Bragg peak at $(1, 0, 0.5)/(0, 1, 0.5)$. Neutron SF and NSF cross sections are measured at 2 K and 240 K. The peak at 240 K is nonmagnetic nuclear scattering giving rise to NSF scattering. (h) Similar scans for the $(1, 1, 0)$ peak. The inset shows positions of these two peaks in reciprocal space. All vertical error bars represent statistical error (1 s. d.).
along the \([1, 0, L]/[0, 1, L]\) direction which apparently is not resolution limited. The temperature dependence of the scattering at \((1, 0, 0.5)/(0, 1, 0.5)\) plotted in Fig. 5.2(f) reveals clear evidence of magnetic ordering below \(T_N \approx 200\) K, suggesting that the small peak observed at room temperature in Fig. 5.2(c) occurs in the paramagnetic phase and is thus of structural (super-lattice) origin induced by Cu substitution, since such a peak is forbidden for NaFeAs.

While the above results indicate ordering of Fe and Cu, it is unclear if the superstructure has four-fold or two-fold rotation symmetry in the \(ab\)-plane. To answer this question we have carried out high-resolution TEM measurements. The inset in Fig. 5.2(a) shows an image of the sample, and the electron diffraction patterns were collected from areas about 100 nm in diameter within a single domain of the sample [see the arrow in the inset of Fig. 5.2(a)]. A typical diffraction pattern along the \([001]\) zone axis at room temperature is shown in Fig. 5.2(a). While we see clear super-lattice reflections at \(H = 1, 3, \cdots\) positions along the \([H, 0, 0]\) direction, they are absent at the \(K = 1, 3, \cdots\) positions along the \([0, K, 0]\) direction [Fig. 5.2(b)]. This means that the crystal structure of \(\text{NaFe}_{0.56}\text{Cu}_{0.44}\text{As}\) is orthorhombic and obeys two-fold rotational symmetry.

To fully determine the structure of \(\text{NaFe}_{0.56}\text{Cu}_{0.44}\text{As}\), we carried out single crystal neutron diffraction refinement on HB-3A. The crystal structure of \(\text{NaFe}_{0.56}\text{Cu}_{0.44}\text{As}\) obtained from single crystal neutron diffraction refinement is shown in Table 5.1. We collected 120 reflections at Bragg peaks associated with the NaFeAs structure and measured 95 super-lattice peak positions. 22 super-lattice peaks with measurable intensities are identified [Table 5.2], these peaks are refined together with Bragg peaks associated with the NaFeAs structure (not shown). Due to twinning the measured intensity at \((H, K, L)\) have contributions from \((H, K, L)\) from twin 1 and \((H, L, K)\)
Table 5.1: Structure of NaFe$_{0.56}$Cu$_{0.44}$As with Fe-Cu stripe order with the space group $Ibam$ from single crystal neutron diffraction refinement at 250K. The notation used is different from Fig. 5.1(d). The fit lattice parameters are $a = 13.85(2)$ Å, $b = c = 5.723(9)$ Å. Twin 1 scale factor = 1.821(78), twin 2 scale factor = 0.960(59). $R_f = 3.13\%$, $R_{f2} = 4.46\%$, $\chi^2 = 0.794$.

from twin 2. Population of the twins is roughly 2:1 for this particular sample. Due to formation of Fe-Cu stripes, $y$ positions of Na and As also shift from their high symmetry position 0.25 by $\delta_{\text{Na}}$ and $\delta_{\text{As}}$, respectively.

The crystal structure for NaFe$_{0.56}$Cu$_{0.44}$As in Table 1 5.1 approximates the ideal structure of NaFe$_{0.5}$Cu$_{0.5}$As as shown in Figure 5.1(d), where Fe and Cu order into stripes forming a structural analog of the stripe magnetic order in NaFeAs. This reduces the symmetry of the system to $Ibam$ space group. We adopt a unit cell similar to the orthorhombic structural unit cell of NaFeAs throughout the rest of the chapter as shown in Figure 5.1(d) unless otherwise stated. Compared to the $Ibam$ notation used in Table 5.1, $a$, $b$ and $c$ in this notation correspond to $b$, $c$, and half of $a$ in the $Ibam$ notation. In the notation used in Figure 5.1(d), super-lattice peaks due to Fe-Cu ordering occur at $(H,K,L)$ with $H = 1,3,5\ldots$, $K = 0,2,4\ldots$ and $L = 0.5,1.5,2.5\ldots$. Magnetic peaks in this notation occur at $(H,K,L)$ with $H =
From these information and from intensities of the super-lattice peaks in \((H, 0, L)\) scattering plane, we conclude that Fe and Cu atoms in NaFe\(_{0.5}\)Cu\(_{0.5}\)As (which is approximated by NaFe\(_{0.56}\)Cu\(_{0.44}\)As) form a real space stripe-like ordered structure in Fig. 5.1(d) in the space group \(Ibam\). The Fe-Cu ordering is a structural analogue of the magnetic order in NaFeAs and structural super-lattice peaks occur at the same positions as magnetic peaks in NaFeAs.

Fe and Cu ordering in NaFe\(_{1-x}\)Cu\(_x\)As affects the intensities of Bragg peaks already present in NaFeAs very little, and the induced super-lattice are relatively weak. To illustrate the effect of Fe-Cu ordering seen in neutron diffraction experiments, calculated neutron powder diffraction profiles for NaFe\(_{0.5}\)Cu\(_{0.5}\)As with (i) disordered Fe and Cu and \(\delta_{As} = \delta_{Na} = 0\), (ii) ordered Fe and Cu and \(\delta_{As} = \delta_{Na} = 0\) and (iii) ordered Fe and Cu with \(\delta_{As} = \delta_{Na} = -0.01\) are compared in Figure 5.3 assuming \(b = c\) (\(Ibam\) notation). With this assumption, case (i) becomes tetragonal with \(P4/nmm\) symmetry. In case (ii) where Fe-Cu order into stripes, the only effect is to induce super-lattice peaks without affecting the intensity of nuclear Bragg peaks already present in case (i). For case (iii), introducing non-zero \(\delta_{As}\) and \(\delta_{Na}\), nuclear Bragg peaks already present in case (i) change only slightly.

Given these considerations and for NaFe\(_{1-x}\)Cu\(_x\)As with \(x < 0.5\) the already weak super-lattice peaks become weaker and broader with decreasing doping [Figure 5.7(f)], we use \(P4/nmm\) space group appropriate for NaFeAs in the tetragonal state [112] to fit the our room temperature neutron powder diffraction (NPD) data for NaFe\(_{1-x}\)Cu\(_x\)As. Doing so the information related to Fe-Cu ordering is neglected but other aspects of the structure can still be reliably obtained. Since the Fe-Cu ordering exists already
Table 5.2: Measured and calculated super-lattice peak intensities for NaFe$_{0.56}$Cu$_{0.44}$As with the space group Ibam from single crystal neutron diffraction. Due to twinning measured intensity at $(H,K,L)$ has contributions from $(H,K,L)$ from twin 1 and $(H,L,K)$ from twin 2. Peaks with no measurable intensities are not listed.

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Figure 5.3: Calculated neutron powder diffraction profiles for NaFe$_{0.5}$Cu$_{0.5}$As. (a) Case (i) where Fe and Cu are completely disordered and $\delta_{\text{As}} = \delta_{\text{Na}} = 0$, corresponding to the $P4/nmm$ space group when $a = c$ (Ibam notation). Case (ii) has Fe-Cu stripe order and $\delta_{\text{As}} = \delta_{\text{Na}} = 0$, case (iii) further has non-zero $\delta_{\text{As}}$ and $\delta_{\text{Na}}$. The black arrows mark some super-lattice peak positions. (b) Difference between case (ii) and case (i), when Fe and Cu order into stripes, only super-lattice peaks are formed without affecting nuclear Bragg peaks already present in case (i). (c) Difference between case (iii) and case (i), having non-zero $\delta_{\text{As}}$ and $\delta_{\text{Na}}$ only slightly affects the intensities of nuclear peaks already present in case (i). Note the intensity range is much smaller in (b) and (c) compared to (a).
at room temperature (Figure 5.2(c)), it will be interesting in future work to see if an order-disorder transition occurs at elevated temperatures where $P4/nmm$ symmetry can be recovered with Fe and Cu becoming disordered and $\delta_{\text{As}} = \delta_{\text{Na}} = 0$ corresponding to case (i).

The NPD refinement results for NaFe$_{1-x}$Cu$_x$As with $x = 0.016, 0.18, 0.39$ and $0.44$ at room temperature are shown in Fig. 5.4(a)-(d) and the refined structural parameters are shown in Table 5.3. Na and As occupancies are assumed to be 1, refinements of their occupancies also yield values close to 1. Given the similar scattering lengths of Fe and Cu, the occupancies of these two elements are set to values determined from ICP. The NPD data at 4K for NaFe$_{1-x}$Cu$_x$As with $x = 0.44$ is shown in Figure 5.4(e). Only one super-lattice/magnetic peak is clearly seen as shown in the inset, so it is not possible to reliably refine $\delta_{\text{As}}$ and $\delta_{\text{Na}}$ from NPD data. Instead this data is used to estimate size of the ordered moment, refining the ordered moment for the magnetic structure in Figure 5.1(d) [discussed below] assuming Fe-Cu ordering we find $1.12(9) \mu_B$ [Fig. 5.4(e)], whereas assuming disordered Fe and Cu we obtain $1.4(1) \mu_B$. (0,0,1), (1,0,1) and (1,1,0) shown in the inset of Figure 5.4(e) are in Ibam notation [Table 5.1], corresponding to (0,1,0), (0,1,0.5) and (1,0,0.5) respectively in the notation of Figure 5.1(d). Therefore aside from ordering of Fe and Cu, other aspects of the structure of NaFe$_{1-x}$Cu$_x$As remain identical to that of NaFeAs and that the samples are of single phases with little/no impurity phases, corroborated by the similar neutron powder diffraction patterns.

### 5.3 Magnetic Structure of NaFe$_{1-x}$Cu$_x$As with $x \approx 0.5$

Having solved the structure of NaFe$_{1-x}$Cu$_x$As with $x \approx 0.5$, it becomes possible to solve its magnetic structure. The first step in doing so is to find out between Fe and
Figure 5.4: Neutron powder diffraction data for NaFe$_{1-x}$Cu$_x$As measured at 300K and 4K. (a) Observed (black crosses) and calculated (red lines) neutron powder diffraction intensities for NaFe$_{0.984}$Cu$_{0.016}$As at 300 K using space group $P4/nmm$. Short magenta vertical lines represent nuclear Bragg peak positions, the blue trace is the difference between measured and calculated intensities. (b), (c) and (d) show similar results for NaFe$_{1-x}$Cu$_x$As with $x =$ 0.18, 0.39 and 0.44 respectively. Despite the observation of super-lattice peaks in samples with $x =$ 0.39 and 0.44 at 300K, such peaks are not visible in neutron powder diffraction data and all data sets at 300K are fit with the same tetragonal structure as undoped NaFeAs in the paramagnetic state with space group $P4/nmm$. (e) NaFe$_{0.56}$Cu$_{0.44}$As at 4K fit with $Ibam$ structure described in Table 5.1 and the magnetic structure in Fig. 5.1(d), magenta vertical lines correspond to nuclear Bragg peak positions and orange vertical lines are magnetic Bragg peak positions. The inset zooms in on a super-lattice/magnetic peak.
Table 5.3: Refinement results from neutron powder diffraction data on NaFe$_{1-x}$Cu$_x$As. All measurements are taken at 300 K and are fit using P4/nmm space group as super-lattice peaks are too weak to be seen in powder diffraction data. For NaFe$_{0.984}$Cu$_{0.016}$As, $R_p = 5.08\%$, $wR_p = 6.38\%$ and $\chi^2 = 1.130$. For NaFe$_{0.82}$Cu$_{0.18}$As, $R_p = 4.20\%$, $wR_p = 5.14\%$ and $\chi^2 = 1.270$. For NaFe$_{0.61}$Cu$_{0.39}$As, $R_p = 4.11\%$, $wR_p = 5.02\%$ and $\chi^2 = 1.123$. For NaFe$_{0.56}$Cu$_{0.44}$As, $R_p = 4.79\%$, $wR_p = 5.97\%$, $\chi^2 = 1.098$. 

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<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
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Figure 5.5: **XAS and RIXS measurements on NaFe_{0.56}Cu_{0.44}As.** (a) X-ray absorption spectroscopy (XAS) measurements on NaFe_{0.56}Cu_{0.44}As (solid lines) and SrCuO_2 (dashed line) obtained at 10 K. (b) Typical resonant inelastic X-ray scattering (RIXS) measurement on the same compound with incident energy E_i = 931.8 eV and in-plane momentum transfer q_∥ = 0.498 Å^{-1} obtained at 10 K. Light green lines are measurements with π polarization and red lines are measurements with σ polarization.

Cu, which is or if both are magnetic. We carried out XAS and RIXS measurements using ADRESS beamline as shown in Fig. 5.5. XAS for NaFe_{1-x}Cu_xAs (x = 0.44) is shown in Figure 5.5(a) for both π and σ polarizations [10], compared with XAS of SrCuO_2 (dashed line) measured with identical experimental configuration. The absorption peak at 930.7 eV in SrCuO_2 due to Cu^{2+} is absent in NaFe_{1-x}Cu_xAs (x = 0.44), demonstrating Cu^{1+} valence in heavily Cu-doped NaFe_{1-x}Cu_xAs samples. Previous results on Cu in different valence states [178] show a chemical shift of ∼2 eV between the absorption peaks for Cu^{1+} and Cu^{2+}. This agrees with our observation that the sharp absorption peak (931.8 eV) in NaFe_{1-x}Cu_xAs (x = 0.44) is higher than the Cu^{2+} absorption peak in SrCuO_2, suggesting that Cu in NaFe_{1-x}Cu_xAs assumes the Cu^{1+} oxidation state. The two overlapping peaks at ∼935.5 eV and 936.5 eV are likely due to traces of unreacted elemental Cu. We have further searched for magnetic excitations with resonant inelastic X-ray scattering (RIXS) Cu L_3 edge, but did not observe indication for magnetic modes for any of the sampled momentum transfers,
Figure 5.6: Scans at several wave-vectors equivalent to \((1, 0, 0.5)/(0, 1, 0.5)\) for NaFe\(_{0.56}\)Cu\(_{0.44}\)As at 3.6 K and 300 K. These scans were measured with unpolarized neutrons. Scans at 3.6 K are shown as blue squares and scans measured at 300 K are shown as red circles. Scans centered at \(Q = (1, 0, L)/(0, 1, L)\) with \(L = 1.5, 2.5, 3.5\) and 4.5 are respectively plotted in (a), (b), (c) and (d). Similarly scans centered at \(Q = (3, 0, L)/(0, 3, L)\) with \(L = 0.5, 1.5, 2.5\) and 3.5 are shown in (e), (f), (g) and (h), respectively. Scan along \([H, 0, 0.5]/[0, K, 0.5]\) at 3.6 K centered at \(Q = (3, 0, 3.5)/(0, 3, 3.5)\) was not measured, instead a rocking scan is plotted to show that there is no observable intensity at this wave-vector and temperature. Scan along \([H, 0, 3.5]/[0, K, 3.5]\) at 3.6 K centered at \(Q = (3, 0, 3.5)/(0, 3, 3.5)\) was not measured.

All vertical error bars represent statistical error (1 s. d.).

typical scans at \(Q = (0.23, 0.23)\) are shown in Figure 5.5(b). The absence of magnetic excitations is expected for Cu\(^{1+}\) with a Cu 3d\(^{10}\) electronic configuration. Thus, both XAS and RIXS results confirm that Cu is in the nonmagnetic Cu\(^{1+}\) state and the elastic magnetic order observed by neutron scattering is entirely due to Fe.

To determine the magnetic structure we carried out scans along the \([H, 0, L]/[0, K, L]\) directions at 3.6 K and 300 K for the \(x = 0.44\) sample at several different \(L\)-values as shown in Fig. 5.6. Assuming that the magnetic structure is collinear and based on the presence of magnetic peaks at these wave vectors and the position of Fe atoms,
Figure 5.7: Wave vector dependence of super-lattice peaks and magnetic peaks of NaFe$_{0.56}$Cu$_{0.44}$As

(a) The magnetic intensities for equivalent wave-vectors $(0, 1, L)$ (solid blue circles) and $(0, 3, L)$ (solid red squares) are summarized for NaFe$_{0.56}$Cu$_{0.44}$As. The intensities were obtained from rocking scans at 3.6 K, correcting for contributions from super-lattice peaks estimated from $[H, 0, L]/[0, K, L]$ scans presented in Figure 5.6. (b) Assuming Fe$^{2+}$ magnetic form factor, the expected intensities for $(0, 1, L)$ wave-vectors are shown depending on the orientation of the magnetic moment. The magnetic moment along $a$ axis (orange diamonds), $b$ axis (cyan circles) and $c$ axis (magenta squares) are compared. (c) Expected magnetic intensities are similarly shown for $(0, 3, L)$. (d) Super-lattice peak intensities for equivalent wave-vectors $(1, 0, L)$ (empty red squares) and $(3, 0, L)$ (empty blue circles) obtained from scans at 300 K in Figure 5.6, (e) shows the corresponding calculated intensity for NaFe$_{0.56}$Cu$_{0.44}$As using the structure in Table 5.1. (f) Scan along the $[1, 0, L]$ direction for NaFe$_{0.61}$Cu$_{0.39}$As at 240 K (magenta diamonds), the instrument resolution (black line) is obtained by performing the same scan after removing the filters. Vertical error bars in (a), (d) and (e) are from least-square fits (1 s. d.). Vertical error bars in (f) represent statistical error (1 s. d.).
we conclude that only the magnetic structure shown in Figure 5.1(d) is consistent with our experimental observations. This magnetic structure also has Bragg peaks at $Q = (1, 1, 0)$, and this is corroborated by our polarized neutron scattering measurements. Figure 5.2(g) shows SF and NSF scans along the $[H, 0, 0.5]/[0, K, 0.5]$ direction at $T = 2$ K and 240 K. Inspection of the data reveals clear magnetic scattering at 2 K that disappears at 240 K, in addition to the temperature independent NSF nuclear super-lattice reflection. Figure 5.2(h) shows the SF and NSF scans along the $[H, H, 0]$ direction at 2 K and 240 K. While the SF scattering shows a clear peak at 2 K that disappears on warming to 240 K, the NSF scattering shows no evidence of the super-lattice peaks.

Another part of the magnetic structure is the orientation of the moments, to obtain this information we show in Figure 5.7(a) the $Q$-dependence of magnetic peak intensities. The magnetic intensities are obtained from rocking scans at 3.6 K after correcting for the super-lattice contributions using the ratio of peak intensities at 3.6 K and 300 K shown in Figure 5.6 and the Lorentz factor. In Figure 5.7(b)-(c), the calculated $Q$-dependence of magnetic peak intensities are plotted for spins oriented along $a$, $b$ and $c$ assuming Fe$^{2+}$ magnetic form factor. Comparing the measured $Q$-dependence in Figure 5.7(a) and the calculated $Q$-dependence in Figure 5.7(b)-(c), we conclude that the ordered magnetic moments are oriented predominantly along the $a$ axis.

To conclusively determine the orientation of the ordered magnetic moment, we carried out detailed polarized neutron scattering experiments. Since in our notation magnetic peaks occur at $(0, K, L)$ with $K = 1, 3, 5\ldots$ and $L = 0.5, 1.5, 2.5\ldots$ but not $(H, 0, L)$ positions, we only see magnetic signal from $[0, K, L]$ scattering plane. We define neutron polarization directions along momentum transfer $Q$ as $x$, perpendicular
Figure 5.8: Determining the spin direction in NaFe$_{0.56}$Cu$_{0.44}$As using polarized neutron scattering. (a) Definition of $x$, $y$ and $z$ directions with respect to the crystallographic axes. (b) Wave vectors probed in $[0, K, L]$ scattering plane and the corresponding $\theta$. $M_y$ (open red circles) and $M_z$ (open cyan diamonds) for $Q_1 = (0, 1, 3.5)$, $Q_2 = (0, 1, 2.5)$, $Q_3 = (0, 1, 0.5)$ and $Q_4 = (0, 3, 0.5)$ are shown in (c), (d), (e) and (f), respectively. All vertical error bars represent statistical error (1 s. d.).
to $Q$ but in the $[0, K, L]$ scattering plane as $y$ and perpendicular to the scattering plane as $z$, as shown in Figure 5.8(a). As our neutron scattering samples have twin domains, we cannot distinguish the $(H, 0, L)$ from the $(0, K, L)$ positions in these measurements.

Since SF neutron diffraction is only sensitive to spin components perpendicular to both momentum transfer $Q$ and neutron polarization direction, one can conclusively determine the spin components along all crystallographic axes $M_a$, $M_b$ and $M_c$ from the observed magnetic peaks. $M_a$, $M_b$ and $M_c$ can be obtained via $\sigma_x^{SF} - \sigma_y^{SF} \propto M_y = \sin \theta^2 M_b + \cos \theta^2 M_c$ and $\sigma_x^{SF} - \sigma_z^{SF} \propto M_z = M_a$ where $\sigma_x^{SF}$, $\sigma_y^{SF}$ and $\sigma_z^{SF}$ are neutron SF scattering cross sections with polarization directions along $x$, $y$ and $z$, respectively, and $\theta$ is the angle between momentum transfer $Q$ and $(0, 1, 0)$. Figure 5.8(b) shows the wave vectors probed in $[0, K, L]$ scattering plane and the corresponding $\theta$. In all cases $M_z = M_a$ while for momentum transfer with small $\theta$, $M_y$ is most sensitive to $M_c$ and for momentum with larger $\theta$, $M_y$ is most sensitive to $M_b$. Measuring at the momentum transfers shown in Figure 5.8(b), it can be seen in Figure 5.8(c)-(f) that a clear peak can be seen for $M_z$ but no peak is seen for $M_y$ in all cases. These results conclusively show that spins are along the $a$ axis, with negligible spin components along the other two directions, in agreement with our conclusion from unpolarized neutron diffraction results in Figure 5.7(a)-(c).

In Figure 5.9(a)-(b), the temperature dependence of magnetic and super-lattice peaks of NaFe$_{0.56}$Cu$_{0.44}$As are shown for $Q = (1, 0, 0.5)/(0, 1, 0.5)$ and $Q = (1, 1, 0)$ respectively. At both wave-vectors, the SF channel shows magnetic signal with $T_N \sim 200$ K. At $Q = (1, 0, 0.5)$, the super-lattice peak appears in the NSF channel and is weakly temperature dependent. At $Q = (1, 1, 0)$, there is no signal in the NSF channel below 200K, consistent with this wave-vector being forbidden in the structures
Figure 5.9: Temperature dependence of magnetic and super-lattice peaks in NaFe$_{0.56}$Cu$_{0.44}$As using polarized neutron scattering. (a) Temperature dependence of SF (blue squares) and NSF (orange circles) channels for NaFe$_{0.56}$Cu$_{0.44}$As at $Q = (1,0,0.5)/(0,1,0.5)$. Magnetic signal coming from $Q = (0,1,0.5)$ is seen in the SF channel whereas super-lattice signal coming from $Q = (1,0,0.5)$ is seen in the NSF signal. (b) Similar temperature dependence of SF and NSF channels at $Q = (1,1,0)$. All vertical error bars represent statistical error (1 s. d.).
of NaFeAs and NaFe_{0.5}Cu_{0.5}As in Figure 5.1(c) and (d). From these results and from systematic determination of magnetic and super-lattice scattering intensity at different wave vectors, we conclude that NaFe_{0.56}Cu_{0.44}As forms a collinear magnetic structure with moments aligned along the $a$ axis as shown in the right inset in Fig. 5.1(g). The ordered magnetic moment is $1.12 \pm 0.09 \mu_B/Fe$ at 4 K determined from neutron powder diffraction [Fig. 5.4(e)]. For this magnetic structure, magnetic peaks are expected and observed at $(0,1,0.5)$ and $(1,1,0)$ as shown in Fig. 5.2(g)-(h) and Figure 5.9. The magnetic peaks at $(0,1,0.5)$ overlap with super-lattice peaks at $(1,0,0.5)$ due to twinning.

### 5.4 Doping dependence of magnetic order and Mott insulating phase in NaFe$_{1-x}$Cu$_x$As

To determine the Cu-doping dependence of the NaFe$_{1-x}$Cu$_x$As phase diagram, we carried out additional measurements on single crystals of NaFe$_{1-x}$Cu$_x$As with $x = 0.18$ and 0.39. Figures 5.10(a) and 5.10(b) compare the wave vector scans along the $[H,0,0.5]/[0,K,0.5]$ and $[1,0,L]/[0,1,L]$ directions for $x = 0.18, 0.39,$ and 0.44. In each case, the scattering intensity is normalized to the $(2,0,0)$ nuclear Bragg peak. With increasing Cu-doping, the scattering profile becomes narrower and stronger, changing from a broad peak indicative of the short-range magnetic order in $x = 0.18, 0.39$ to an essentially instrument resolution limited peak with long-range magnetic order at $x = 0.44$. Figure 5.10(c) shows the doping evolution of the spin-spin correlation length $\xi$ in NaFe$_{1-x}$Cu$_x$As, suggesting that the increasing spin-spin correlation lengths in NaFe$_{1-x}$Cu$_x$As is related to the increasing Cu-doping and the concomitant increase in correlation length of Fe and Cu ordering [Figure 5.7(f)]. The
Figure 5.10: **Cu-doping evolution of the magnetic order in NaFe$_{1-x}$Cu$_x$As.**

(a) Comparison of wave vector scans along the $[H,0,0.5]/[0,K,0.5]$ direction for NaFe$_{1-x}$Cu$_x$As single crystals with $x = 0.18, 0.39,$ and $0.44$. The data are normalized to the $(2,0,0)$ nuclear Bragg peak. Note that intensity in the $x = 0.18$ and $0.39$ samples are multiplied by 200 and 5 times, respectively. (b) Similar scans along the $[1,0,L]/[0,1,L]$ direction. (c) Cu-doping evolution of the spin-spin correlation length. The correlation length along $(1,0,0)$ for the $x = 0.44$ sample is resolution limited. (d) Cu-doping evolution of the magnetic order parameter for NaFe$_{1-x}$Cu$_x$As. All error bars represent statistical error (1 s. d.).
evolution of the temperature dependent magnetic order parameter with Cu doping is shown in Fig. 5.10(d). For \( x \) well below 0.5, the magnetic transition is gradual and spin-glass-like. However with \( x \) approaching 0.5, the transition at \( T_N \) becomes more well-defined. In the undoped state, NaFeAs has a small ordered moment of \( 0.17 \pm 0.03 \, \mu_B/\text{Fe} \) [121]. Upon small Cu-doping, superconductivity is induced at \( x = 0.02 \) and the static AF order is suppressed [167]. With further Cu doping, the system becomes an AF insulator, where the ordered moment reaches \( \sim 1.1 \, \mu_B/\text{Fe} \) at \( x = 0.44 \) (the ordered moment per Fe site was determined in the structure for NaFe\(_{0.5}\)Cu\(_{0.5}\)As [Fig. 5.1(d)]). Since the iron moment in NaFe\(_{1-x}\)Cu\(_x\)As increases with increasing Cu-doping, our determined moment is therefore a lower bound for the ordered moment for Fe in the ideal NaFe\(_{0.5}\)Cu\(_{0.5}\)As, which for Fe 3\(d^5\) can be in either \( S = 3/2 \) or \( S = 5/2 \) spin state.

The behavior in NaFe\(_{1-x}\)Cu\(_x\)As is entirely different from the bipartite magnetic parent phases seen in the iron oxypnictide superconductor LaFeAsO\(_{1-x}\)H\(_x\), where magnetic parent phases on both sides of the superconducting dome are metallic anti-ferromagnets [179]. In Cu-doped Fe\(_{1-x}\)Cu\(_x\)Se, a metal-insulator transition has been observed around 4\% Cu-doping, and a localized moment with spin glass behavior is found near \( x \approx 0.12 \) [180, 181]. Although the density functional theory (DFT) calculations suggest that Cu occurs in the 3\(d^{10}\) configuration and the metal-insulator transition is by a disorder induced Anderson localization in Fe\(_{1-x}\)Cu\(_x\)Se [182], the 20-30\% solubility limit of the system [180] means it is unclear whether Fe\(_{1-x}\)Cu\(_x\)Se is also an AF insulator at \( x \approx 0.5 \).

It is useful to compare our experimental findings with the results of the band structure calculations based on DFT [152]. Both the DFT and DFT+\(U\) calculations clearly predict the paramagnetic phase of NaFe\(_{0.5}\)Cu\(_{0.5}\)As to be a metal [152]. By
Figure 5.11: Summary of the schematic Cu and Fe electronic states and parameter regimes of a Mott insulator in the phase diagram of NaFe$_{1-x}$Cu$_x$As. Schematic of the electronic states of a Cu ion alongside those of an Fe ion, shown in terms of the atomic levels (a) and the electronic density of states (b). The relative potential difference associated with the two ions is specified in terms of an energy shift, $\Delta$, as illustrated in (b). (c) The ground-state phase diagram of a multiorbital Hubbard model for NaFe$_{0.5}$Cu$_{0.5}$As. $U_{\text{OSM}}$ and $U_{\text{MT}}$ refer to the critical $U$ values for an orbital-selective Mott (OSM) transition and a Mott transition (MT), respectively into an orbital-selective Mott phase (OSMP) and a Mott insulator. The shaded region shows the physical parameter regime as determined by comparing the theoretically calculated bandwidth renormalization factors of the three $t_{2g}$ orbitals with those determined by the ARPES results [183].
contrast, our measurements have shown that the insulating behavior of the resistivity persists above the Néel temperature [Fig. 5.1(f)], implying that NaFe$_{0.5}$Cu$_{0.5}$As is a Mott insulator. This is also consistent with STM measurements on lower Cu-doping NaFe$_{1-x}$Cu$_x$As where the overall line shape of the electronic spectrum at $x = 0.3$ is similar to those of lightly electron-doped copper oxides close to the parent Mott insulator [168].

To understand the origin of the Mott insulating behavior, we address how Cu-doping affects the strength of electron correlations [152]. Our starting point is that the local (ionization) potential difference between the Fe and Cu ions, as illustrated in Fig. 5.11(a) and described by the energy shift $\Delta$ in Fig. 5.11(b), will suppress the hopping integral between Fe and Cu sites. This causes a reduction in the kinetic energy or, equivalently, the electron bandwidth. The ratio of the on-site Coulomb repulsion $U$ (including the Hund’s coupling $J_H$) relative to the bandwidth will effectively increase, even if the raw values of $U$ and $J_H$ remain the same as in pure NaFeAs. This would enhance the tendency of electron localization even without considering the disorder effects with increasing $x$ [184, 185].

The case of $x = 0.5$ allows a detailed theoretical analysis. Here, the Cu and Fe ions in NaFe$_{1-x}$Cu$_x$As have real space ordering, as discussed above. We study the metal-insulator transition in multi-orbital Hubbard models for NaFe$_{0.5}$Cu$_{0.5}$As via the $U(1)$ slave-spin mean-field theory [186]. We use the tight-binding parameters for NaFeAs, and consider the limit of a large local potential difference between Cu and Fe, which transfers charge from Fe to Cu to Cu$^{1+}$ ($n = 10$). The fully occupied Cu 3$d$ shell makes the Cu ions essentially as vacancies. Reduction of the Fe 3$d$ electron bandwidth is caused by this kinetic blocking effect [152]. The resulting ground state phase diagram is shown in Fig. 5.11(c). For realistic parameters, illustrated by the
shaded region, a Mott localization takes place. Our understanding is in line with
the general theoretical identification of a Mott insulating phase in an overall phase
diagram [186], which takes into account a kinetic-energy-reduction induced increase
of the effective interactions and a decrease of the 3d-electron filling from 6 per Fe\(^{2+}\)
to 5 per Fe\(^{3+}\) [186, 19, 157, 158, 159].

Our work uncovers a Mott insulator, NaFe\(_{0.5}\)Cu\(_{0.5}\)As, and provides its under-
standing in an overall phase diagram of both bandwidth and electron-filling controls
[186]. Our results suggest that the electron correlations of the iron pnictides, while
weaker than those of the iron chalcogenides, are sufficiently strong to place these
materials in proximity to the Mott localization. This finding makes it natural that
the electron correlations and the associated bad-metal behavior and magnetism in-
duce a similarly high superconducting transition temperature in the iron pnictides as
in the iron chalcogenide family. Such a commonality, in spite of the very different
chemical composition and electronic structure of these two broad classes of mate-
rials, introduces considerable simplicity in the quest for a unified framework of the
iron-based superconductivity. More generally, the proximity to the Mott transition
links the superconductivity of the iron pnictides to that arising in the copper ox-
ides, organic charge-transfer salts [187] and alkali-doped fullerides [188], and suggests
that the same framework may apply to all these strongly correlated electronic sys-
tems. Very recently, angle-resolved photoemission spectroscopy measurements on our
NaFe\(_{0.56}\)Cu\(_{0.44}\)As samples also confirmed its Mott insulating nature [189].

5.5 Magnetic excitations in NaFe\(_{0.53}\)Cu\(_{0.47}\)As single crystals

Having established the nature of magnetic order in NaFe\(_{1-x}\)Cu\(_x\)As with \(x \approx 50\%\),
it would be interesting to study the magnetic excitations in such a compound and
Figure 5.12: Comparing in-plane magnetic structures of NaFeAs and NaFe_{0.5}Cu_{0.5}As. Relative spin orientations are represented using + and − symbols, the ordered moment directions are different for the two compounds. Antiferromagnetic (AF) and ferromagnetic (FM) coupling are labeled.

compare the results with NaFeAs. To this end we synthesized and co-aligned 4.3g of NaFe_{1-x}Cu_{x}As single crystals with nominal Cu concentration of 85%. Since ICP measurements reveal that nominal Cu concentrations of 75% and 90% correspond to actual concentrations of 44% and 48%, we designate the actual concentration of the present samples to be 47%. The neutron scattering measurements were carried out on the MAPS chopper spectrometer at Rutherford-Appleton Laboratory, UK. Incident energies $E_i = 50, 80$ and $250$ meV were used with $k_i \parallel c$ and orthorhombic $a/b$ in the horizontal plane. For $E_i = 50$ meV, data was also collected by rotating the sample at successive angles to construct a 4-dimensional map of scattering in energy-momentum space as discussed in Chap. 2.

Before examining the experimental results, it is useful to consider what the excitations will look like based on the magnetic structure derived in the previous sections. The in-plane magnetic structures of NaFeAs and NaFe_{0.5}Cu_{0.5}As are compared in Fig.
Figure 5.13: Comparing magnetic Brillouin zones of magnetically ordered NaFeAs and NaFe$_{0.5}$Cu$_{0.5}$As. Boxes represent magnetic Brillouin zones, whereas red circles represent where magnetic Bragg peaks are expected. This schematic is shown for a single domain sample, whereas typical real samples are twinned.

5.12, as can be seen both structures can be viewed as consisting of ferromagnetically aligned antiferromagnetic stripes, the difference is that the distance between these stripes is doubled in the case of NaFe$_{0.5}$Cu$_{0.5}$As compared to NaFeAs. In fact the magnetic structure of NaFe$_{0.5}$Cu$_{0.5}$As can be obtained from the magnetic structure of NaFeAs by replacing Fe with Cu, as can be seen by examining the full magnetic structures shown in Fig. 5.19(c) and (d), although the direction of ordered spins differ by 90°. Since the distance between stripes is doubled in NaFe$_{0.5}$Cu$_{0.5}$As compared to NaFeAs, the Brillouin zone would be halved along that direction, which is why in addition to observing magnetic peaks at $Q = (1, 0)/(0, 1)$ positions, peaks are also seen at $Q = (1, 1)$ positions.

It should be noted in previous sections, to highlight the structural order of NaFe$_{0.5}$Cu$_{0.5}$As being similar to the magnetic order in NaFeAs, $a$ and $b$ axes are chosen as shown in
Fig. 5.19(d). In this notation magnetic peaks in NaFe$_{0.5}$Cu$_{0.5}$As occur at $Q = (0,1)$ rather than $Q = (1,0)$. Following this notation the magnetic Brillouin of magnetically ordered NaFeAs and NaFe$_{0.5}$Cu$_{0.5}$As are compared in Fig. 5.13, as can be seen the Brillouin zone of NaFe$_{0.5}$Cu$_{0.5}$As can be seen as the NaFeAs Brillouin zone compressed along the ferromagnetic direction.

From the in-plane magnetic structure of NaFe$_{0.5}$Cu$_{0.5}$As [Fig. 5.12] it is clear that the antiferromagnetic exchange coupling along the Fe stripe should be quite strong whereas the coupling between stripes should be quite weak. Given that the coupling along $c$ axis is weak for iron pnictides in general as discussed in Chap. 4 for NaFeAs, magnetic excitations in NaFe$_{0.5}$Cu$_{0.5}$As should exhibit one-dimensional characteristics forming sheets perpendicular to the antiferromagnetic direction in reciprocal space.

Experimentally measured low energy magnetic excitations are summarized in Fig. 5.14. At very low energies magnetic excitations stem from magnetic Bragg peaks, for $L = 0.5$ the excitations are at $Q = (1,0)/ (0,1)$ [Fig. 5.14(a)] whereas for $L = 1$ the excitations are at $Q = (1,1)$ [Fig. 5.14(b)]. For a single domain sample, excitations should only be seen at $Q = (0,1)$ as shown in Fig. 5.13, the signal at $Q = (1,0)$ is due to the other twin 90° away. As can already be seen at $E = 5$ meV, the dispersion of magnetic excitations is highly anisotropic in the $[H,K]$ plane, with a much higher velocity along the longitudinal direction [Fig. 5.14(a), for $Q = (0,1)$, the longitudinal direction is along $K$]. This is readily understood as the longitudinal direction corresponds to along the antiferromagnetic Fe chains with a strong coupling [$J$ in Fig. 5.12] whereas the transverse direction [for $Q = (0,1)$ this is along $H$] corresponds to the ferromagnetic coupling between chains. With increasing energy, the broadening along the transverse direction becomes more evident as can be seen in Fig. 5.14(c) and (d). Furthermore, the excitations becomes less $L$-dependent,
Figure 5.14: Low energy magnetic excitations in NaFe$_{0.53}$Cu$_{0.47}$As at $T = 4$ K. By rotating the sample, data in 4-dimensional energy-momentum space was measured, and 2-dimensional slices in $[H,K]$-plane are obtained are binning $L$ and $E$. $[H,K]$ Slice for (a) $E = 5 \pm 1$ meV and $L = 0.5 \pm 0.1$, (b) $E = 5 \pm 1$ meV and $L = 1 \pm 0.1$, (c) $E = 14 \pm 2$ meV and $L = 0.5 \pm 0.1$ and (d) $E = 18 \pm 2$ meV and $L = 1 \pm 0.1$. Color bars are shown for each slice, normalized to absolute units of mbarn $\cdot$ steradian$^{-1} \cdot$ meV$^{-1} \cdot$ f.u.$^{-1}$, where f.u. stands for formula unit.
Figure 5.15: **Sheet-like magnetic excitations in NaFe$_{0.53}$Cu$_{0.47}$As.** Data is obtained by measuring with $k_i \parallel c$, and data within the energy range $E = 60 \pm 10$ meV are binned. Energy is coupled to $L$ in this setup, but the excitations are $L$-independent aside from the magnetic form factor. The intensities are normalized to absolute units of mbarn $\cdot$ steradian$^{-1} \cdot$ meV$^{-1} \cdot$ f.u.$^{-1}$, where f.u. stands for formula unit.

Excitations at both $Q = (1, 0)/(0, 1)$ and $Q = (1, 1)$ are seen for $E = 18$ meV and $L = 1$ [Fig. 5.14(d)]. Therefore measurement of low energy excitations in NaFe$_{0.53}$Cu$_{0.47}$As confirms the expectation from the magnetic structure shown in Fig. 5.1(d), that $J$ [Fig. 5.12] corresponding to dispersion along the in-plane longitudinal direction is dominant.

With increasing energy, the magnetic excitations become sheets in reciprocal space as shown in Fig. 5.15 for $E = 60 \pm 10$ meV. Excitations centered at $Q = (0, 1)$ at low energies [Fig. 5.14(a)] become independent of $H$, moreover since the excitations also do not depend on $L$, they indeed are sheets in momentum space. The two
Figure 5.16: Constant-energy slices of magnetic excitations in NaFe$_{0.53}$Cu$_{0.47}$As. Data is obtained by measuring with $k_i \parallel c$, and data within the energy ranges $E = 40 \pm 10$, $60 \pm 10$, $80 \pm 10$, $100 \pm 10, 120 \pm 10$ and $140 \pm 10$ meV are binned shown in (a) through (f). The data have been folded into a quadrant to improve statistics. The dashed box represent the width in $K$ that $H$-scans shown below are binned. The intensities are normalized to absolute units of mbarn \cdot steradian$^{-1}$ \cdot meV$^{-1}$ \cdot f.u.$^{-1}$, where f.u. stands for formula unit.

sets of perpendicular sheets are due to twinning. This is again consistent with the expectation that the antiferromagnetic coupling $J$ along Fe chains is dominant.

With increasing energy the excitations begin to disperse also along the longitudinal direction [along the Fe chains], as summarized in Fig. 5.16 and Fig. 5.17. As can be seen the excitations evolve from a single peak for $E = 40$ meV and $E = 60$ meV [Fig. 5.17(a) and (b)] to two peaks along the in-plane longitudinal direction for $E = 80, 100, 120$ and $140$ meV [Fig. 5.17(c)-(f)]. At $E = 40$ meV and $E = 60$ meV [Fig. 5.16(a) and (b)] there are still some modulation along the transverse direction
Figure 5.17: **Longitudinal cuts of magnetic excitations in NaFe$_{0.53}$Cu$_{0.47}$As.** Data in the dashed boxed in Fig. 5.16 are cut along $H$, binned along $K$ and shown here. The background has been subtracted and the form factor has been corrected for. The solids lines are either fits to a single Gaussian peak or two symmetric Gaussian peaks. Cuts for the energy ranges $E = 40 \pm 10$, $60 \pm 10$, $80 \pm 10$, $100 \pm 10, 120 \pm 10$ and $140 \pm 10$ meV are shown in (a) through (f).

[in-plane ferromagnetic coupling between Fe chains], which completely disappears for $E = 80$ meV [Fig. 5.16(c)] and above, becoming sheets of excitations typical for a one-dimensional magnet.

From these results it becomes possible to obtain the nearest-neighbor exchange coupling $J$ along the antiferromagnetic Fe chains. The fit Gaussian peak positions from Fig. 5.17 are summarized in Fig. 5.18 and fit to the expression $E(H) = 2J|\sin \pi H|$. This is applicable because $J$ is dominant compared to couplings along other directions, and the energy range shown in Fig. 5.18 exceeds the energy range of these couplings. The obtained exchange coupling is $SJ \approx 100$ meV, suggesting the band top of magnetic excitations going up to 200 meV. It should be noted that Figs. 5.16, 5.17 and 5.18 are shown for the domain with magnetic Bragg peaks occurring
Figure 5.18: Dispersion of magnetic excitations in NaFe$_{0.53}$Cu$_{0.47}$As along the antiferromagnetic chain direction. The points are obtained from fits shown in Fig. 5.17, with vertical error bars present the range of energy binned in Fig. 5.17 and horizontal error bars representing the widths of fit peaks. The solid line is a fit to the expression $E(H) = 2J|\sin \pi H|$. The obtained $SJ$ is $98(3)$ meV.
at $\mathbf{Q} = (1, 0)$ and in spin wave theory $SJ$ is obtained from fitting inelastic neutron scattering data rather than $J$.

Our inelastic neutron scattering results on NaFe$_{0.53}$Cu$_{0.47}$As are easily interpreted in the local moment exchange coupling picture, consistent with NaFe$_{0.5}$Cu$_{0.5}$As being a Mott insulator with localized moments, but in contrast to prototypical iron pnictide compounds in which the excitations can be modeled using either local or itinerant models (neither fully satisfactorily) [17]. It has been proposed that low energy excitations in iron pnictides are due to itinerant electrons whereas high energy excitations are due to localized moments [82], in light of this it is interesting to note that a recurring pattern in the spin excitation spectrum of iron pnictides is transversely elongated ellipses, which can be interpreted as the result of a stronger antiferromagnetic coupling $J_{1a}$ in compounds such as BaFe$_2$As$_2$ [5]. This has in fact been revealed to be the case for most iron pnictides such as NaFeAs, BaFe$_2$As$_2$, CaFe$_2$As$_2$ and SrFe$_2$As$_2$, with $J_{1a}$ being the largest exchange coupling, although $J_{1b}$ and $J_2$ are also comparable in magnitude [17]. Furthermore, in electron-doped iron pnictides such elongation along the transverse direction becomes more pronounced [82] whereas in hole-doped iron pnictides the excitations are longitudinally elongated at low energies [82]. However detailed studied of overdoped Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ and KFe$_2$As$_2$ reveal that with increasing energy the excitation again become transversely elongated [190]. Assuming that high energy excitations are indeed due to localized moments as proposed in earlier work [82], this means transversely elongated excitations are common to all iron pnictides. Therefore the case of NaFe$_{0.5}$Cu$_{0.5}$As is an extreme of spin excitations being elongated along the transverse direction [being independent of the transverse direction, Fig. 5.15] and suggests an approach to tackle the magnetism of iron pnictides, is to approach the magnetic order of the parent compounds such as NaFeAs
as consisting of ferromagnetically aligned antiferromagnetic spins chains (the actual case will be quite complicated because $J_{1b}$ and $J_2$ are of similar magnitude) and consider short antiferromagnetic stripes as the structural motif that high-temperature superconductivity is derived from.

5.6 Neutron resonance mode in slightly overdoped NaFe$_{0.98}$Cu$_{0.02}$As

One hallmark of unconventional superconductivity in iron pnictides is the appearance of a neutron spin resonance mode in the superconducting state at the antiferromagnetic (AF) ordering wave vector of their parent compounds [51, 17, 45, 174]. The energy of the resonance is approximately related to the superconducting transition temperature $T_c$ or the superconducting gap $\Delta$ [174, 46]. The resonance in BaFe$_2$As$_2$-derived superconductors display significant dispersion along $c$-axis in the underdoped regime [136], and becomes $L$-independent in the well-overdoped region [191]. In electron-doped NaFe$_{1-x}$Co$_x$As, two resonance modes are seen in underdoped compositions [102], with the lower-energy-mode gradually losing spectral weight upon further doping before disappearing near optimal doping [120, 126]. The energy of the single resonance mode in well-overdoped NaFe$_{1-x}$Co$_x$As does not scale with $T_c$, likely due to multi-orbital physics and impurity effects [120]. Since superconducting domes are absent in Cu-doped AFe$_2$As$_2$ [175, 170], it is unclear if superconductivity induced by Cu-doping is similar to their electron/hole-doped counterparts. As NaFe$_{1-x}$Cu$_x$As exhibits bulk superconductivity similar to NaFe$_{1-x}$Co$_x$As [167], superconducting NaFe$_{1-x}$Cu$_x$As offers a unique case to study effect of the stronger impurity potential of Cu [167, 192] on the resonance mode.

Single crystals of NaFe$_{1-x}$Cu$_x$As were prepared using the self-flux method as described in previous work [176]. We quote nominal concentrations throughout this
section, which is consistent with previous report on NaFe\textsubscript{1-\textit{x}}Cu\textsubscript{\textit{x}}As in the superconducting region [167]. Inelastic neutron scattering experiments were carried out using the HB-3 triple-axis spectrometer at the High Flux Isotope Reactor (HFIR) and the Hybrid Spectrometer (HYSPEC) at the Spallation Neutron Source, both at Oak Ridge National Laboratory. The experiment at HB-3 used a pyrolitic graphite monochromator, analyzer and filter after the sample, the collimation used is 48'-40'-sample-40'-120' and the final neutron energy is fixed to $E_f = 14.7$ meV. HYSPEC is a time-of-flight chopper spectrometer with a movable strip-shaped detector bank that has much fewer pixels along the vertical direction compared to the horizontal direction. Detected neutron counts from the middle third of the pixels along the vertical direction are binned making it function like a triple-axis spectrometer with a position-sensitive-detector, and by rotating the sample and the detector bank, maps of the scattering plane can be obtained. Fixed incident energy $E_i = 15$ meV is used for the experiment on HYSPEC. Momentum transfer $\mathbf{Q} = (Q_x, Q_y, Q_z)$ is presented in reciprocal lattice units (r.l.u.) as $(H, K, L)$, with $H = Q_x a / 2\pi$, $K = Q_y b / 2\pi$ and $L = Q_z c / 2\pi$. We adopt the chemical unit cell for the orthorhombic phase of NaFe\textsubscript{1-\textit{x}}Cu\textsubscript{\textit{x}}As, in this notation $a \approx b \approx 5.56$ and $c \approx 7.05$ for NaFeAs [112]. The orthorhombic unit cell is twice the volume of the tetragonal unit cell, and magnetic Bragg peaks are seen at $\mathbf{Q} = (1, 0, L)$ with $L = 0.5, 1.5, 2.5 \ldots$ 8 high-quality single crystals with a total mass of 6.04 grams were co-aligned in the $[H, 0, L]$ scattering plane.

Constant-\textit{Q} scans at $\mathbf{Q} = (1, 0, L)$ for slightly overdoped NaFe\textsubscript{0.98}Cu\textsubscript{0.02}As ($T_c = 11.8$ K) measured using HB-3 are summarized in Figure 5.19. Scans above ($T = 14$ K) and below ($T = 2$ K) $T_c$ for $L = 0, 0.5$ and 1 are shown in Fig. 5.19(a), (c) and (e), respectively. The corresponding 2 K data after subtracting 14 K data are similarly
Figure 5.19: Constant-Q scans of NaFe$_{0.98}$Cu$_{0.02}$As. Constant-Q scans at $Q = (1, 0, L)$ for (a) $L = 0$, (c) $L = 0.5$ and (e) $L = 1$. The difference of magnetic intensity in the superconducting state and the normal state for (b) $L = 0$, (d) $L = 0.5$ and (f) $L = 1$. The solid lines are fits to Gaussian peaks, which provide a rough estimate of the peak center of the resonance mode. The fits in (b) and (f) are constrained to have the same center.
shown in Fig. 5.19(b), (d) and (f). A clear resonance mode that displays a weak c-axis dispersion can be clearly seen. For $L = 0.5$ [Fig. 5.19(d)], corresponding to the magnetic zone center in magnetically ordered NaFeAs, the resonance is centered at around $E \approx 5.5$ meV. Similarly for $L = 0$ and 1 [Fig. 5.19(b), (f)], corresponding to the magnetic zone boundary along c-axis in magnetically ordered NaFeAs, the resonance is centered at $E \approx 6.5$ meV.

$H$-scans at the peak of the resonance mode for $L = 0.5$ ($E = 5.5$ meV) is shown in Fig. 5.20. At both 2 K and 14 K, a clear peak is observed, with the peak at 2 K only slightly stronger than the one at 14 K, meaning the resonance is weak compared to the normal state excitations in contrast to slightly overdoped NaFe$_{1-x}$Co$_x$As [126] in which the resonance mode dominates the magnetic excitations in the superconducting state. Given the normal state spin fluctuations have indistinguishable intensities in Co- and Cu-doped BaFe$_2$As$_2$ [192], it is reasonable to assume the normal state intensities in Co- and Cu-doped NaFeAs are also similar. Therefore, compared to NaFe$_{0.955}$Co$_{0.045}$As [126], the resonance mode in NaFe$_{0.98}$Cu$_{0.02}$As is also quantitatively much weaker. The width of the magnetic peak for $E = 5.5$ meV at 2 K [FWHM = 0.228(8) (r.l.u.)] and 14 K [FWHM = 0.25(1) (r.l.u.)] are similar with the peak in the superconducting state slightly narrower, similar to slightly overdoped NaFe$_{1-x}$Co$_x$As [126]. The change in peak width can be seen more clearly by comparing the difference of 2 K and 14 K data [Fig. 5.20(b)], as can be seen the difference is significantly narrower than the 14 K data itself [Gaussian peak in red dashed line], fitting the difference results in a much smaller peak width [FWHM = 0.17(3) (r.l.u.)]. This suggests the effect of superconductivity is not only to enhance intensity at the energy of the resonance mode, but also to increase the correlation length of magnetic excitations. A weak neutron spin resonance mode is seen in Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ near
Figure 5.20: $H$ scans of NaFe$_{0.98}$Cu$_{0.02}$As. (a) $H$-scans at $E = 5.5$ meV centered at $Q = (1,0,0.5)$. Solid lines are fits to Gaussian peaks with the linear background restrained to be the same for 2 K and 14 K. The two positions marked by arrows are contaminated by spurious scattering and are not used in the fits. (b) The difference between 2 K and 14 scans in (a), the solid line is the difference between the fits at 2 K and 14 K. The red dashed line is a Gaussian peak with width of the data at 14 K, shown for comparison. Fitting the difference to a Gaussian peak [not shown] results in a much narrower peak [FWHM = 0.17(3) (r.l.u.)] compared to the 14 K data [FWHM = 0.25(1) (r.l.u.)].
optimal doping and ascribed to weakened electronic correlations [193]. In comparison, the weak resonance in NaFe$_{0.98}$Cu$_{0.02}$As is likely due to impurity effects given electronic correlations in superconducting NaFe$_{1-x}$Co$_x$As and NaFe$_{1-x}$Cu$_x$As should be similar.

Our results are further substantiated by data obtained using HYSPEC in Figure 5.21 and 5.22. Constant-energy maps of the $[H, 0, L]$ scattering plane are shown in Figure 5.21 at $T = 1.6$ K and 12 K, as can be clearly seen magnetic excitations form rods along $L$ with little $L$-dependence in both the normal and the superconducting state. In magnetically ordered NaFeAs, $c$-axis polarized spin waves exhibit a spin gap of $E_g \approx 4.5$ meV at $Q = (1, 0, 0.5)$ and $E_g \approx 7$ meV at $Q = (1, 0, 1)$ [90]. Upon Co-doping into the slightly overdoped regime, magnetic excitations become $L$-independent [126]. Therefore, the reduction of effective $c$-axis magnetic coupling by doping Cu doping into NaFeAs is similar to doping Co, such behavior is also seen in Ni-doped BaFe$_2$As$_2$ [194]. By comparing the maps in Fig. 5.21(a) and (b) or Fig. 5.21(c) and (d), which are plotted to the same color scale, it is clear that the intensities differ little in the superconducting and normal state, consistent with the resonance mode being weak. In Fig. 5.22(a) we show the 1.6 K data subtracted by 12 K data for $L = 0 \pm 0.2$. Similar to Fig. 5.19(b) and (f), a resonance that is rather broad in energy is seen. The temperature dependence of the resonance mode is shown in Fig. 5.22(b), an superconducting-order-parameter-like increase below $T_c$ is observed.

The weak resonance mode in NaFe$_{1-x}$Cu$_x$As is likely a result of the stronger impurity potential of Cu, which is also likely responsible for the lower optimal $T_c$ in NaFe$_{1-x}$Cu$_x$As [167] compared to NaFe$_{1-x}$Co$_x$As [121, 195] and the near-absence of superconductivity in Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ [175]. Compared to Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ in
Figure 5.21: Maps of magnetic excitations in NaFe$_{0.98}$Cu$_{0.02}$As. Constant-energy maps in $[H, 0, L]$ scattering plane at $T = 1.6$ K for (a) $E = 5.5 \pm 0.5$ meV, (c) $E = 6.5 \pm 0.5$ meV, (e) $E = 7.5 \pm 0.5$ meV and (g) $E = 8.5 \pm 0.5$ meV. The corresponding results at $T = 12$ K are shown in panels (b), (d), (f) and (h). The streak of signal marked by the dashed line in (a) is spurious, as are similar signals in other panels.
Figure 5.22: **Resonance mode in NaFe$_{0.98}$Cu$_{0.02}$As.** (a) $H$-energy map of 1.6 K data subtract by 12 K data obtained by binning data with $-0.2 \leq L \leq 0.2$. (b) Temperature dependence of the resonance mode, obtained by binning data with $4.5 \leq E \leq 6.5$ meV, $0.87 \leq H \leq 1.13$ and $-0.2 \leq L \leq 0.2$. The arrow marks $T_c$, and the solid line is a guide-to-the-eye.
which superconductivity is nearly absent, the presence of a superconducting dome in NaFe$_{1-x}$Cu$_x$As may be related to the lower Cu concentration needed to suppress the magnetic order. The impurity potential and concentration of dopants therefore has significant effects on the physical properties of iron pnictide superconductors.

The resonance mode in slightly overdoped NaFe$_{0.98}$Cu$_{0.02}$As with $T_c = 11.8$ K is at $E \approx 5.5$ meV for $L = 0.5$, corresponding to $E_r \approx 5.5 k_B T_c$. This is higher than $E_r \approx 4.3 k_B T_c$ suggested for doped BaFe$_2$As$_2$ [174] and $E_r \approx 4.5 k_B T_c$ in slightly overdoped NaFe$_{0.955}$Co$_{0.045}$As [126] but lower than $E_r \approx 7.1 k_B T_c$ in heavily overdoped NaFe$_{0.92}$Co$_{0.08}$As [120]. Therefore, due to multi-orbital physics and impurity effects, there appears to be no simple relationship between $E_r$ and $T_c$ in doped NaFeAs. Specifically, both the concentration of dopants [slightly overdoped and heavily overdoped NaFe$_{1-x}$Co$_x$As] and impurity potential of dopants [slightly overdoped NaFe$_{1-x}$Co$_x$As and NaFe$_{1-x}$Cu$_x$As] seem to increase the ratio $E_r/k_B T_c$.

The superconducting phase in NaFe$_{1-x}$Cu$_x$As near $x \approx 0.02$ can be continuously tuned to the antiferromagnetically ordered insulating phase with significant electronic correlations near $x \approx 0.5$ through a region of short-range cation and magnetic order, pointing to the possibility of the generic phase diagram of iron pnictides to be anchored around a Mott-insulating state [159, 168]. The observation of a spin resonance mode in superconducting NaFe$_{1-x}$Cu$_x$As demonstrates that the superconducting state is similar to other iron pnictide superconductors, and therefore electronic correlations should be an integral part of the physics of iron pnictide superconductors.
Chapter 6

Robust Upward-Dispersing Resonance Mode in \( \text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5 \)

In this chapter the resonance mode in \( \text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5 \) will be discussed [196]. The background will be briefly introduced, followed by neutron scattering results on \( \text{Ce}_{1-x}\text{Yb}_x\text{CoIn}_5 \) samples with nominal compositions \( x = 0, 0.05 \) and 0.3.

6.1 Introduction

The neutron spin resonance is a collective magnetic excitation coupled to superconductivity with a temperature dependence similar to the superconducting order parameter [197, 44]. It is located near the antiferromagnetic (AF) ordering wave vector \( Q_{\text{AF}} \) of the undoped parent compound and its energy \( E_r \) at \( Q_{\text{AF}} \) is related to either \( T_c \) [47] or the superconducting energy gap \( \Delta \) [46]. Although it is generally accepted that the resonance is a signature of unconventional superconductivity [45], there is no consensus on its microscopic origin. A common interpretation of the resonance is that it is a spin-exciton, arising from particle-hole excitations involving momentum states near the Fermi surfaces that possess opposite signs of the \( d \) (or \( s^\pm \))-wave superconducting order parameter [44, 160].

In hole-doped copper oxide superconductors, the magnetic excitations has an hourglass dispersion with a downward dispersion at energies below \( E_r \) and an upward spin-wave-like dispersion at energies above \( E_r \) [54]. The resonance on the other hand, obtained by subtracting the normal state magnetic excitations, displays predomi-
Figure 6.1: Crystal Structure of Ce$_{1-x}$Yb$_x$CoIn$_5$. The structure is tetragonal for all compositions with $a = b$, the Ce/Yb ions form a square lattice in the $ab$-plane similar to the cuprates.

nantly a downward dispersion [198, 199]. In the case of Ni-underdoped BaFe$_2$As$_2$ with coexisting AF order and superconductivity [26], the resonance only reveals an upward magnon-like dispersion [49]. In both cases the resonance is well described by the spin-exciton scenario, the opposite dispersions being a result of $d_{x^2-y^2}$ or $s\pm$ symmetry of the superconducting order parameter [48, 49].

For the heavy fermion superconductor CeCoIn$_5$ ($T_c = 2.3$ K) with a tetragonal crystal structure [20] and Ce$^{3+}$ ions forming a square lattice in the $ab$-plane like the cuprates (Fig. 6.1), the resonance appears below $T_c$ at $E_r = 0.60 \pm 0.03$ meV and the commensurate AF wave vector $Q_{AF} = (1/2, 1/2, 1/2)$ in reciprocal space [43]. Since CeCoIn$_5$ has a superconducting gap with $d_{x^2-y^2}$-wave symmetry as determined from scanning tunneling microscopy (STM) experiments [200, 201], the resonance is expected to show a downward dispersion similar to the cuprates within the spin-
exciton picture [202, 203]. Alternatively, the resonance, with its three-dimensional character [43], could be a magnon-like excitation of $f$ electrons that becomes visible due to its reduced decay rate in the superconducting state [52, 53]. In this case, the resonance is not a signature of $d_{x^2−y^2}$-wave superconductivity, but a measure of the hybridization between $f$ electrons and conduction electrons and its associated pairing-sensitive Landau damping [53].

When La is substituted for Ce in Ce$_{1−x}$La$_x$CoIn$_5$ [204, 205], superconductivity and the energy of the resonance are both rapidly suppressed while $E_r/k_BT_c$ remains approximately constant, where $k_B$ is the Boltzmann constant [206, 207]. At the same time, the energy width of the resonance broadens with increasing La-doping [206, 207].

When Yb is doped into CeCoIn$_5$ to form Ce$_{1−x}$Yb$_x$CoIn$_5$, superconductivity is suppressed much slower compared to La [208]. This is true despite actual doping is $\sim 1/3$ of the nominal doping [209] (nominal doping is adopted in this chapter to be consistent with published works). With increasing Yb, de Haas-van Alphen and angle resolved photo emission studies find a change in the Fermi-surface topology between Yb nominal doping levels of $x = 0.1$ and 0.2 [210, 211]. In addition, London penetration depth measurements suggest that the superconducting gap changes from nodal to nodeless around a similar Yb doping level [212] (the change of pairing symmetry is controversial as recent thermal conductivity experiments suggest superconductivity remains nodal for all Yb dopings [213], but the London penetration depth results nonetheless attest to the dramatic change of Fermi surface with Yb doping), arising possibly from composite electron pairing in a fully gapped superconductor for $x > 0.2$ [214]. If the resonance in CeCoIn$_5$ is a spin-exciton, it should be dramatically affected by the Yb-doping induced changes in Fermi surface topology and superconducting gap. On the other hand, if the resonance is a magnon-like excitation, it should
be much less sensitive to Yb-doping across $x = 0.2$ and display a upward dispersion similar to spin waves in antiferromagnetically ordered nonsuperconducting CeRhIn$_5$ characteristic of a robust effective nearest-neighbor exchange coupling, regardless of its itinerant electron or local moment origin [44, 39, 40].

Previous neutron scattering results suggested the resonance in CeCoIn$_5$ is strongly $Q$-dependent [43], and its strong $L$-dependence led to the proposal that the resonance could be a magnon-like excitation [53]. It has also been proposed that the resonance is an excitation from the superconducting condensate to Ce$^{3+}$ crystal field states, this proposal is based on the observation that the resonance splits into a doublet with applied magnetic field and the intensity of the resonance being consistent with the matrix element for crystal field transitions [215]. It has also been proposed that the resonance is in fact incommensurate and is a dynamic precursor to the field-induced incommensurate magnetic order that appears just below $H_{c2}$ and disappears above $H_{c2}$ [216, 217]. These results beg an understanding of resonance mode that has the potential to explain these observed phenomena in a single framework, moreover understanding the resonance mode in CeCoIn$_5$ can shed light on similar modes found in cuprates and iron pnictides.

## 6.2 Resonance mode in Ce$_{1-x}$Yb$_x$CoIn$_5$

Single crystals of Ce$_{1-x}$Yb$_x$CoIn$_5$ ($x = 0, 0.05, 0.3$) were prepared by indium self-flux method. Details of sample preparation and characterizations have been previously reported, lattice parameters for Ce$_{1-x}$Yb$_x$CoIn$_5$ remain similar to pure CeCoIn$_5$ for all reported doping levels [208]. We use the nominal doping throughout the chapter to be consistent with earlier work [208], while the actual doping is $\sim 1/3$ of the nominal doping [209]. Fig. 6.2 (a) shows the out-of-phase AC magnetic susceptibility (15.9
Figure 6.2: AC magnetic susceptibility and alignment of Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals. (a) AC magnetic susceptibility measured on Ce$_{1-x}$Yb$_x$CoIn$_5$ ($x = 0.05$ and $0.3$), with $T_c = 2.25$ K and 1.5 K. (b) Several aluminum plates with hundreds of co-aligned Ce$_{1-x}$Yb$_x$CoIn$_5$ ($x = 0.05$) single crystals. The crystallographic axes are marked by red arrows. (c) Co-aligned plates in the [$H,H,L$] scattering plane. (d) Co-aligned plates in the [$H,K,H$] scattering plane. The angle between $[1,0,1]$ and $[1,0,0]$ is $\approx 31^\circ$.

Hz) measured on Ce$_{1-x}$Yb$_x$CoIn$_5$ samples with $x = 0.05$ and 0.3 from the same growth batches used for neutron scattering experiments. Bulk superconductivity appear at $T_c = 2.25$ K and $T_c = 1.5$ K respectively, whereas $T_c = 2.3$ K in pure CeCoIn$_5$ [208].

Hundreds of Ce$_{1-x}$Yb$_x$CoIn$_5$ single crystals with total masses of 0.8 g, 2.5 g and 1.4 g respectively for $x = 0, 0.05$ and 0.3 were co-aligned on several aluminum plates using CYTOP as hydrogen-free glue [Fig. 6.2(b)]. The plates are then mounted...
in either the \([H, H, 0] \times [0, 0, L] ([H, H, L])\) [Fig. 6.2(c)] or the \([H, 0, H] \times [0, K, 0] ([H, K, H])\) scattering plane [Fig. 6.2(d)]. The total thickness of samples on co-aligned plates is 1-2 mm, minimizing neutron absorption due to indium. Absorption becomes most significant when the incident or the scattered neutron beam becomes perpendicular to \([0,0,1]\), which does not occur for reciprocal space regions probed in this work.

Neutron scattering experiments were carried out on the PANDA cold three-axes spectrometer at Heinz Maier-Leibnitz Zentrum and the Multi-Axis Crystal Spectrometer (MACS) at the NIST Center for Neutron Research. The experiments on PANDA used a Be filter 180 mm in length after the sample which is highly effective in removing contamination from higher order neutrons, both the analyzer and the monochromator are doubly focused to maximize neutron flux at the sample. Vertical focusing of the analyzer is fixed whereas horizontal focusing is variable. Both the horizontal and vertical focusing of the monochromator are variable. The variable focusings are adjusted depending on the neutron wavelength based on empirically optimized values. The PANDA experiment in the \([H, H, L]\) scattering plane used fixed \(k_f = 1.3 \text{ Å}^{-1} (E_f \approx 3.5 \text{ meV})\) and the experiment in the \([H, K, H]\) scattering plane used fixed \(k_f = 1.57 \text{ Å}^{-1} (E_f \approx 5.1 \text{ meV})\). The MACS experiments in the \([H, H, L]\) scattering plane used Be filters both before and after the sample with fixed \(E_t = 3.7 \text{ meV}\). MACS consists of 20 spectroscopic detectors each separated by 8°. By rotating the sample and shifting all of the detectors to bridge the 8° gaps, a map in terms of sample rotation angle and scattering angle at a fixed energy transfer can be efficiently constructed. A significant portion of the reciprocal space in the scattering plane can be covered, which further allows cuts along the high symmetry directions. 90° collimators are used between the sample and each individual analyzers. The analyzers
are vertically focused while the monochromator is doubly focused.

For the neutron scattering results on PANDA, a linear background is assumed for all measured constant-energy scans while no background is used for scans obtained by subtraction data above $T_c$ from those obtained below $T_c$. The constant energy scans are then simply fit to either one or two Gaussian peaks.

For the neutron scattering results obtained on MACS, maps of large portions of the scattering plane for several energies transfers were collected both below and above $T_c$. A $|Q|$-dependent background is obtained by masking the signal near $Q = (0.5, 0.5, 0.5)$ and is then fit to a polynomial. The signal with $|Q| < 0.5$ Å$^{-1}$ is masked throughout the analysis. The fit background is then subtracted from the map and the data is folded into the first quadrant of the scattering plane to improve statistics.

6.2.1 PANDA and MACS results on Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$ in $[H,H,L]$ scattering plane

Compared to undoped CeCoIn$_5$, $T_c$ in Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$ is mildly suppressed from 2.3 K to 2.25 K, this means the resonance mode in Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$ should be similar to CeCoIn$_5$, although likely broader in energy and momentum. The results on PANDA measured in the $[H,H,L]$ scattering plane are shown in Fig. 6.3. For $E = 0.7$ meV at 2.3 K ($T > T_c$), magnetic excitations are broad and centered at $Q_{AF} = (0.5, 0.5, 0.5)$, whereas at 0.6 K ($T < T_c$) a resonance mode appears and is incommensurate along the $[H,H,0]$ direction [Fig. 6.3(b)]. Carrying out similar scans at several different energies reveals a clear dispersive mode [Fig. 6.3(c)], with the dispersion being magnon-like as can be seen in the color-coded plot in Fig. 6.3 (a). The present results are consistent with earlier measurement of CeCoIn$_5$ as can be seen in Fig. 6.3 (d), for a constant-$Q$ scan at $Q_{AF} = (0.5, 0.5, 0.5)$ the resonance
vanishes above $\sim 0.8$ meV, but as our results show the resonance actually still persists up till at least 1 meV away from $Q_{AF} = (0.5, 0.5, 0.5)$.

Having seen the resonance in $\text{Ce}_{0.95}\text{Yb}_{0.05}\text{CoIn}_5$ displays an upwards dispersion along the $[H, H, 0]$ direction, it becomes interesting to study how the mode evolves along the $[0, 0, L]$ direction. To answer this question we carried out measurements at MACS to map the entire $[H, H, L]$ scattering plane. The results are shown in Fig. 6.4 and Fig. 6.5. For the neutron scattering results obtained on MACS, maps of large portions of the scattering plane for several energies transfers were collected both below and above $T_c$. A $|Q|$-dependent background is obtained by masking the signal near $Q_{AF} = (0.5, 0.5, 0.5)$ and is then fit to a polynomial. The signal with $|Q| < 0.5$ Å$^{-1}$ is masked throughout the analysis. The fit background is then subtracted from the map and the data is folded into the first quadrant of the scattering plane to improve statistics. Cuts along the $[1, 1, 0]$ direction are obtained by binning data with $0.45 \leq L \leq 0.55$ and fit with a single or two Gaussian peaks. Cuts along the $[0, 0, 1]$ direction are obtained by binning data with $0.45 \leq H \leq 0.55$ and fit by a sum of Lorentzian peaks, accounting for the $\text{Ce}^{3+}$ magnetic form factor $f(Q)$ and the polarization factor assuming excitations are dominantly polarized along the $c$-axis similar to previous work [43]. The function used to fit scans along $[0, 0, 1]$ can be written as

$$I(Q) \propto f(Q)^2 (1 - (\hat{Q} \cdot \hat{c})^2) \sum_{n=-\infty}^{\infty} F(n + L),$$  \hspace{1cm} (6.1)$$

where $F(L)$ is either a single Lorentzian peak centered at $L = 0.5$ or two Lorentzian peaks equally displaced from $L = 0.5$. The peaks along the $[0, 0, 1]$ direction are significantly broader compared to those along the $[1, 1, 0]$ direction, and remains non-zero even for $L = 0$ [Fig. 6.5 (c)]. This contrasts with similar scans along the $[1, 1, 0]$ direc-
Figure 6.3: Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$ results on PANDA in $[H, H, L]$ scattering plane. (a) Color-coded intensity of magnetic excitations along the [1,1,0] direction centered at $Q_{AF}$ at 0.6 K obtained from fits to data in (c). (b) Constant-energy scans along the [1,1,0] direction centered at $Q_{AF}$ with $E = 0.7$ meV. The solid symbols are data well below $T_c$ (0.6 K) where two peaks can be resolved, while empty symbols are obtained above $T_c$ (2.3 K) showing a single peak centered at $Q_{AF}$. The solid line is a fit to the data at 0.6 K with two Gaussian functions whereas the dashed line is a fit to a single Gaussian function for the data at 2.3 K. Data at the two temperatures are fit simultaneously to have the same linear background. (c) Constant-energy scans along the [1,1,0] direction at 0.6 K. For clarity, scans with $E = 0.55, 0.75, 0.75$ and 1 meV are respectively shifted upwards by 5, 13, 18 and 22. The solid lines are fits to either one or two Gaussian functions with linear backgrounds. (d) Constant-$Q$ scans at $Q_{AF}$. The arrows represent energies at which constant-energy scans are shown in (c).
tion in Fig. 6.4 (c) where the intensity drops to zero away from \( Q_{AF} \). The magnetic excitations in the normal state are commensurate at all measured energies above \( T_c \) but becomes dispersive in the superconducting state [Fig. 6.4]. The results on MACS reveals that the resonance also disperses along the \((0,0,L)\) direction, although the line shape of the excitations along \( L \) is better described by Lorentzian functions.

6.2.2 PANDA results on Ce\(_{0.95}\)Yb\(_{0.05}\)CoIn\(_5\) in \([H,K,H]\) scattering plane

Having shown that the resonance mode displays an upward dispersion in Ce\(_{0.95}\)Yb\(_{0.05}\)CoIn\(_5\), we aligned the sample in \([H,K,H]\) scattering plane to carry out scans along the \([0,K,0]\) direction centered at \( Q_{AF} = (0.5, 0.5, 0.5) \). The \([H,H,L]\) and the \([H,K,H]\) scattering planes are schematically shown in Fig. 6.6 to illustrate the scans that were done in these scattering planes. As can be seen, while scans along the \([H,H,0]\) and \([0,0,L]\) directions can be carried out in the \([H,H,L]\) scattering plane, it is not possible to carry out scans along other in-plane directions. It is important to study whether the dispersion observed along the \([H,H,0]\) direction is ring-like in the \(ab\)-plane or highly anisotropic, since previously observed incommensurate excitations [216] along the \([H,H,0]\) direction in CeCoIn\(_5\) was linked to the field-induced magnetic order [217] that only occurs along the \([H,H,0]\) direction.

In the \([H,K,H]\) scattering plane scans along the \([0,K,0]\) direction which is at 45\(^\circ\) with the \([H,H,0]\) direction can be carried out. Such scans serve as ideal tests for whether the dispersion is ring-like or highly anisotropic. The results from this experiment are shown in Fig. 6.7. From Fig. 6.7(a)-(f) with increasing energy a clear upwards dispersion can be seen. A constant-Q scan at \( Q_{AF} = (0.5, 0.5, 0.5) \) reveals a clear resonance mode obtained by subtracting 2.3 K data from 0.5 K data as shown in Fig. 6.7(g). These results are similar to the results obtained in the \([H,H,L]\) scattering
Figure 6.4: MACS results on Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$. Constant-energy map at $E = 0.40$ meV at (a) 1 K and (b) 2.4 K. A $|Q|$-dependent background has been subtracted. (c) Cuts obtained from (a) and (b) by binning data with $0.45 \leq L \leq 0.55$; solid lines are fits to the data using either a single or two Gaussian functions. Since a background has already been subtracted in maps in (a) and (b), no background is assumed in the fits. Similarly, (d), (e) and (f) are for $E = 0.55$ meV, (g), (h) and (i) are for $E = 0.70$ meV, (j), (k) and (l) are for $E = 1.00$ meV and (m), (n) and (o) are for $E = 1.20$ meV.
Figure 6.5: More MACS results on Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$. (a) Constant-energy map for Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$ at $E = 0.4$ meV and 1 K after subtracting data from 2.4 K. (b) Cut along the [1,1,0] direction for the map in (a) at $E = 0.4$ meV, the solid line is a fit assuming zero background. (c) Cuts along the [0,0,1] direction at both 1 K and 2.4 K obtained from maps in Fig. 6.4 (a) and (b). (d) Cut along the [0,0,1] direction for the map in (a) at 1K after subtracting data from 2.4 K. The solid lines in (c) and (d) are sums of Lorentzian peaks polarized along $\hat{c}$. Similarly (e), (f), (g) and (h) are for $E = 0.55$ meV, (i), (j), (k) and (l) are for $E = 0.7$ meV, (m), (n), (o) and (p) are for $E = 1.00$ meV and (q), (r), (s) and (t) are for $E = 1.20$ meV. For cuts along the [0,0,1] direction at 2.3 K and $E = 0.40$ and 0.55 meV, $F(L)$ is a single Lorentzian peak centered at $L = 0.5$. For 1 K and 1 K-2.4 K cuts with $E = 0.7, 1.0$ and 1.20 meV, $F(L)$ is two Lorentzian peaks equally displaced from $L = 0.5$. 
Figure 6.6: Scattering planes used for studying Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$. [H, H, L] scattering plane is shown on the left, with the red arrow representing a scan along the [0, 0, L] direction and the green arrow representing a scan along the [H, H, 0] direction, both centered at $Q_{AF}$. The measured wave vector is $Q = Q_{AF} + q$. Similarly the [H, K, H] scattering plane is shown on the right side with the blue arrow representing a scan along the [0, K, 0] direction. The purple circles in both plots represent the antiferromagnetic wave vector $Q_{AF}$.

plane and suggest the dispersion is ring-like in the ab-plane. To verify the dispersive feature also respond to $T_c$, a critical criterion for designating it as a resonance mode, a temperature scan was carried out away from $Q_{AF}$ at $Q = (0.5, 0.35, 0.5)$ with $E = 0.85$ meV shown in Fig. 6.7(h). As can be seen, the scan shows a clear response to superconductivity with a temperature dependence following the superconducting order parameter.

From the above results on Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$, dispersions of the resonance mode along the [H, H, 0], [0, K, 0] and [0, 0, L] directions are summarized in Fig. 6.8. An isotropic dispersion along all three measured directions describe the data well. It should be noted that below $E \sim 0.6$ meV the resolution in our experiment cannot resolve splittings found in previous work at $E = 0.5$ meV in CeCoIn$_5$ [216], and the phenomenological magnon gap may be smaller than what is shown in Fig. 6.8. It
Figure 6.7: Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$ results on PANDA in the $[H, K, H]$ scattering plane. Neutron scattering results on Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$ in the $[H,K,H]$ scattering plane. (a) Constant-energy scan along the $[0, 1, 0]$ direction centered at $Q_{AF}$ at 0.5 K for $E = 0.35$ meV. The solid line is a fit to a single Gaussian with a linear background. (b) Similar to (a) but for $E = 0.45$ meV. (c) Constant-energy scan along the $[0, 1, 0]$ direction centered at $Q_{AF}$, obtained by subtracting data at 2.3 K from data at 0.5 K for $E = 0.55$ meV. The solid line is a fit to a Gaussian function with zero background. (d) Similar to (c), but for $E = 0.7$ meV and the solid line is a fit to two Gaussian functions. (e) Similar to (d), but for $E = 0.85$ meV. The arrow points to $Q = (0.5, 0.35, 0.5)$, where measurement of the temperature dependence was carried out, shown in (h). (f) Similar to (d) and (e), but for $E = 1.00$ meV. (g) Constant-Q scan at $Q_{AF}$ obtained by subtracting the 2.3 K data from the 0.5 K data. The solid line is a Gaussian function centered at $E = 0.57(1)$ meV with zero background. Arrows represent energies at which constant-energy scans are shown in (a)-(f). (h) Temperature dependence of scattering intensity at $Q = (0.5, 0.35, 0.5)$ for $E = 0.85$ meV. The solid line is a fit to $d$-wave superconductivity order parameter with constant background. The superconducting critical temperature $T_c$ obtained from the fit is 2.0(1) K.
Figure 6.8: Summary of dispersion of the resonance mode in Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$. (a) Dispersion of the resonance along the [1,1,0] direction. The axis above the figure is $Q$ in reciprocal lattice units (r.l.u.) whereas the axis at the bottom is $q$ in Å$^{-1}$. An isotropic dispersion $E = \sqrt{\Delta^2 + (c|q|)^2}$ [$\Delta = 0.55(1)$ meV, $c = 3.2(1)$ meV·Å] is shown in cyan, where $\Delta$ represents a phenomenological spin gap and $c$ is the dispersing velocity. The horizontal bars represent experimentally observed peak full-width-at-half-maximums (FWHM). The dashed lines indicate the ordering wave vector of the so-called $Q$ phase at $Q = Q_{AF} \pm (\delta, \delta, 0)$ with $\delta = 0.05 [217]$. (b) and (c) are similar to (a) but are for dispersions along the [0,1,0] and [0,0,1] directions, respectively.

should be noted the dispersion plotted in Fig. 6.8 is obtained by subtracting data in the normal state from data well in the superconducting state. The dispersion of the magnetic excitations in the superconducting state alone, which can be thought of as the resonance plus the normal state response, will have a faster dispersion. This is illustrated in Fig. 6.9, together with spin waves in CeRhIn$_5$. As can be seen, the dispersion of the resonance clearly resembles the ‘acoustic’ branch of the spin waves in CeRhIn$_5$, suggesting a similar nearest-neighbor coupling causing the dispersion in both cases. Comparison of the dispersion of the magnetic excitations in the superconducting state (resonance plus normal state) shows it is even more similar to the spin waves in CeRhIn$_5$ [Fig. 6.9(c)].
Figure 6.9: Dispersion of the resonance mode in $\text{Ce}_{0.95}\text{Yb}_{0.05}\text{CoIn}_5$ and comparison with spin waves in $\text{CeRhIn}_5$. (a) Comparison of dispersions of the resonance in $\text{Ce}_{0.95}\text{Yb}_{0.05}\text{CoIn}_5$ (solid cyan line) and spin waves in $\text{CeRhIn}_5$ (dashed purple [40] and orange lines [39]). (b) Dispersion of magnetic excitations along the [1,1,0] direction in $\text{Ce}_{0.95}\text{Yb}_{0.05}\text{CoIn}_5$ in the superconducting state obtained at 0.6 K on PANDA and 1 K on MACS. The solid red curve is the fit to $E = \sqrt{\Delta^2 + (cq)^2}$ with $\Delta = 0.55(1)$ meV and $c = 4.0(1)$ meV·Å. (c) Comparison of dispersion of magnetic excitations in $\text{CeRhIn}_5$ and $\text{Ce}_{0.95}\text{Yb}_{0.05}\text{CoIn}_5$, similar to (a) but with the red curve from (b) also added in for comparison. The response in the superconducting state can be thought of as the sum of the resonance mode and normal state excitations and since the normal state response are broad peaks centered at $Q_{\text{AF}}$, the dispersion of the magnetic excitations in the superconducting state has a larger velocity than the resonance itself.
6.2.3 MACS results on CeCoIn$_5$ and Ce$_{0.7}$Yb$_{0.3}$CoIn$_5$

The observation that the resonance mode in Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$ displays isotropic upwards dispersion is quite surprising since earlier work on CeCoIn$_5$ [43] and Ce$_{1-x}$La$_x$CoIn$_5$ [206, 207] did not report such behavior. It therefore raises the possibility that the dispersive behavior may be related to Yb that are doped into CeCoIn$_5$. To investigate if this is the case, we measured the magnetic excitations in CeCoIn$_5$ on MACS using the same setup as we used for Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$. The results are shown in Fig. 6.10. As can be seen, the resonance in CeCoIn$_5$ also displays an upward dispersion similar to Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$ and the dispersive mode is in fact better defined in CeCoIn$_5$. We have therefore established the upward dispersing resonance is not due to Yb doping.

Since it has been reported the Fermi surface is modified dramatically with Yb doping (between nominal doping levels 0.1 < $x$ < 0.2) [212, 211, 210], it would interesting to know how the resonance is affected. To study how increasing Yb doping would affect the upward dispersing resonance in CeCoIn$_5$ and Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$, we measured the resonance mode in Ce$_{0.7}$Yb$_{0.3}$CoIn$_5$ on MACS. The results are shown in Fig. 6.11. As can be seen the upward dispersion is still clearly seen in Ce$_{0.7}$Yb$_{0.3}$CoIn$_5$ despite the transformation of the Fermi surface implied by quantum oscillations, ARPES and London penetration depths measurements [210, 211, 212]. Compared to samples with lower Yb concentration, the resonance becomes weaker and broader in Ce$_{0.7}$Yb$_{0.3}$CoIn$_5$ but the resonance can still nevertheless be seen. How does the apparent results compare with previous results on Ce$_{1-x}$La$_x$CoIn$_5$ where the resonance mode at $Q_{AF} = (0.5, 0.5, 0.5)$ was found to scale with $T_c$ [206, 207]? We also carried out constant-$Q$ scans at $Q_{AF}$ for Ce$_{0.7}$Yb$_{0.3}$CoIn$_5$ to directly compare our results with Ce$_{1-x}$La$_x$CoIn$_5$. As can be seen in Fig. 6.12 (a), the resonance mode in Ce$_{0.7}$Yb$_{0.3}$CoIn$_5$ is lowered to $\sim 0.4$ meV in Ce$_{0.7}$Yb$_{0.3}$CoIn$_5$ from $\sim 0.6$ meV in
Figure 6.10: **MACS results on CeCoIn$_5$.** (a) Constant-energy map for CeCoIn$_5$ at $E = 0.5$ meV and 0.1 K after subtracting the data at 2.5 K. (b) Cut along the [1,1,0] direction for the map in (a), the solid line is a fit assuming zero background. (c) Cut along the [0,0,1] direction for the map in (a), the solid line is a sum of Lorentzian peaks polarized along $\hat{c}$. Similarly (d), (e) and (f) are for $E = 0.6$ meV, (g), (h) and (i) are for $E = 0.8$ meV and (j), (k) and (l) are for $E = 1.00$ meV. For cuts along the [0,0,1] direction for $E = 0.50$ and 0.60 meV, $F(L)$ is a single Lorentzian peak centered at $L = 0.5$. For $E = 0.8$ and 1.0 meV, $F(L)$ is two Lorentzian peaks equally displaced from $L = 0.5$. 
CeCoIn$_5$ [43]. We also carried out temperature dependence scan at $E = 0.45$ meV and $Q_{AF} = (0.5, 0.5, 0.5)$ and found the resonance also displays a clear anomaly at $T_c$ and has an intensity that tracks the superconducting order parameter [Fig. 6.12 (b)]. Energy of the resonance at $Q_{AF}$ as a function of Yb doping is plotted in Fig. 6.12 (c), as can be seen the ratio $E_r/k_B T_c$ is roughly constant as a function of Yb doping, consistent with what was found in Ce$_{1-x}$La$_x$CoIn$_5$ [206, 207].

The dispersion of the resonance in CeCoIn$_5$ are summarized in Fig. 6.13, plotted together with the fit for the dispersing resonance in Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$. As can be seen although the resonance extends to lower energies in Ce$_{0.7}$Yb$_{0.3}$CoIn$_5$, the dispersive features remain similar to samples with lower doping levels. These results demonstrate that the upward-dispersing resonance mode in Ce$_{1-x}$Yb$_x$CoIn$_5$ is robust against Yb doping, through the doping level at which dramatic changes of the Fermi surface has been reported [212, 211, 210]. The bottom of the dispersion, which is measured by constant-Q scans at $Q_{AF} = (0.5, 0.5, 0.5)$ scales with $T_c$ similar to previous reports. However, since we are unable to resolve any splitting below $\sim 0.6$ meV, we are limited by the resolution to determine where the resonance starts to disperse. While we obtain $\sim 0.55$ meV to be the value at which the resonance starts to disperse in Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$, the actual value may be lower in energy, which would be more consistent with incommensurate excitations observed at $E = 0.5$ meV previously reported [216].

### 6.3 Incommensurate excitations near $E = 0.5$ meV

We have uncovered the resonance mode in CeCoIn$_5$ displays a ring-like upward dispersion, which persists with Yb doping. In contrast to previous results that linked incommensurate magnetic excitations at $E = 0.5$ meV with the field-induced mag-
Figure 6.11: MACS results on Ce$_{0.7}$Yb$_{0.3}$CoIn$_5$. (a) Constant-energy map for Ce$_{0.7}$Yb$_{0.3}$CoIn$_5$ at $E = 0.3$ meV and 0.3 K after subtracting data from 2.0 K. (b) Cut along the [1,1,0] direction for the map in (a), the solid line is a fit assuming zero background. (c) Cut along the [0,0,1] direction for the map in (a), the solid line is a sum of Lorentzian peaks polarized along $\hat{c}$. Similarly (d), (e) and (f) are for $E = 0.4$ meV, (g), (h) and (i) are for $E = 0.55$ meV, (j), (k) and (l) are for $E = 0.7$ meV, (m), (n) and (o) are for $E = 0.85$ meV and (p), (q) and (r) are for $E = 1.0$ meV. For cuts along the [0,0,1] direction for $E = 0.3$, 0.4 and 0.55 meV, $F(L)$ is a single Lorentzian peak centered at $L = 0.5$. For $E = 0.7$, 0.85 and 1.0 meV, $F(L)$ is two Lorentzian peaks equally displaced from $L = 0.5$. 

Ce$_{0.7}$Yb$_{0.3}$CoIn$_5$  0.3 K - 2.0 K
Figure 6.12: **Resonance at Q\textsubscript{AF} in Ce\textsubscript{1-x}Yb\textsubscript{x}CoIn\textsubscript{5}**. (a) Difference of constant-Q scans at Q\textsubscript{AF} for 0.3 K and 2 K displaying a resonance mode at E\textsubscript{r} \approx 0.4 meV for Ce\textsubscript{0.7}Yb\textsubscript{0.3}CoIn\textsubscript{5}. Filled symbols are obtained with E\textsubscript{f} = 3.7 meV and empty symbols are for E\textsubscript{f} = 2.5 meV scaled up by 4 times. All of the data in the rest of the figure are obtained with E\textsubscript{f} = 3.7 meV. The solid line is a guide to the eye. (b) Temperature dependence of the resonance mode in Ce\textsubscript{0.7}Yb\textsubscript{0.3}CoIn\textsubscript{5} for E = 0.45 meV and Q\textsubscript{AF}, the solid line is a fit to d-wave superconducting gap, with T\textsubscript{c} = 1.5(1) K. (c) Yb-doping dependence of the resonance energy E\textsubscript{r} divided by k\textsubscript{B}T\textsubscript{c} for the three samples studied in the present work.

Figure 6.13: **Summary of resonance dispersion in CeCoIn\textsubscript{5} and Ce\textsubscript{0.7}Yb\textsubscript{0.3}CoIn\textsubscript{5}**. Dispersion of the resonance along the (a) [1, 1, 0] and (b) [0, 0, 1] directions for Ce\textsubscript{0.7}Yb\textsubscript{0.3}CoIn\textsubscript{5}. Dispersions of the resonance for CeCoIn\textsubscript{5} along the (c) [1, 1, 0] and (d) [0, 0, 1] directions, respectively. The solid lines are dispersions of Ce\textsubscript{0.95}Yb\textsubscript{0.05}CoIn\textsubscript{5}. 
netic order [216], we do not resolve the incommensurate peaks at $E = 0.5$ meV in the present work. We have attempted to fit two peaks to our $E = 0.5$ meV data as shown in Fig. 6.14(a). A splitting of $\delta = 0.042$ previously reported does not result in a good fit while a smaller splitting of $\delta = 0.033$ agrees better with our data. It should be noted that $\delta = 0.33$ is not obtained from fitting, since we do not resolve two peaks from our present data, but our data points the splitting should be smaller than $\delta = 0.042$ previously reported [216]. Since the splitting of the field-induced incommensurate magnetic order is $\delta = 0.05(1)$ which is significantly larger than $\delta = 0.033$, our result does not support the scenario proposed in previous work [216].

There are two possibilities that can reconcile the differences between our results and previous work. One possible scenario is the incommensurate magnetic excitations seen at $E = 0.5$ meV previously is part of the upward dispersion that we observe. Because our resolution is not as good as previous work, we do not resolve two peaks but rather a single peak. Another possibility is there is an incommensurate mode that forms the dynamic precursor to the field-induced magnetic order, in addition to the ring-like upward dispersing mode we observe. In this case the upward-dispersing mode dominate the overall spectra, so when the resolution is poor the obtained peak is dominated by the commensurate peak (in this case this would be why our $E = 0.5$ meV cannot be fit with $\delta = 0.042$). It should also be noted that whereas our data along $[H, H, 0]$ direction is well described by Guassian peaks, Lorentzian functions were employed in previous work [216] which may also in part account for the subtle experimental differences. It is currently not possible to differentiate between these two cases, due to the limitation of our experimental resolution. More work using finer resolution would be desirable to distinguish the two possibilities.

It is instructive to examine the doping and energy dependence of $Q$-widths of the
Figure 6.14: **Widths of the resonance mode in Ce$_{1-x}$Yb$_x$CoIn$_5$**. (a) Cut along [$H, H, 0$] at $E = 0.5$ meV for CeCoIn$_5$ measured on MACS, the dashed ($\delta = 0.033$) and solid lines ($\delta = 0.042$) are fits to two Gaussian peaks with fixed splitting $2\delta$ from each other. (b) Full width at half maximum (FWHM) along the [$H, H, 0$] direction for Ce$_{1-x}$Yb$_x$CoIn$_5$ from fits using Gaussian functions. The open symbols are from a single Gaussian function at $Q_{AF}$, and closed symbols are from two Gaussian functions equally split from $Q_{AF}$. (c) Full width at half maximum (FWHM) along the [0, 0, $L$] direction for Ce$_{1-x}$Yb$_x$CoIn$_5$ from fits using sums of Lorentzian functions. The open symbols are from sum of Lorentzian functions centered at half-integer $L$ positions, and closed symbols are from sum of double Lorentzian functions equally split from half-integer $L$ positions.

resonance, as shown in Fig. 6.14(b) and (c). Open symbols are for fits of a single Gaussian/Lorentzian centered at $Q_{AF}$ while closed symbols are fits of double Gaussian/Lorentzian functions equally split from $Q_{AF}$. The single peak fits with highest energy has the largest width for all measured samples, this suggest the resonance is already incommensurate at these energies although we are unable to resolve two peaks. These results imply for all measured samples it is possible the excitations are already incommensurate at $E = 0.55$ meV, and even at $E = 0.4$ meV for Ce$_{0.7}$Yb$_{0.3}$CoIn$_5$. The spin gap $\Delta$ employed in our fit $E = \sqrt{\Delta^2 + (c|q|^2)}$ therefore appears to decrease with increasing Yb doping, although we cannot extract how much it decreases. This is consistent with the decrease of $E_r$ with Yb doping that scales with $T_r$ shown in Fig. 6.12. It is also clear from the measured widths that Yb broadens the resonance mode, this is expected since Yb atoms would reduce the correlation lengths for Ce$^{3+}$ atoms.
To resolve these issues, we have further carried additional measurements using the cold triple-axis spectrometer PANDA on CeCoIn$_5$, for energy transfers close to $E = 0.5$ meV. Fixed $k_f = 1.3$ Å$^{-1}$ was used for all measurements, monochromator and analyzer were doubly-focused. Most of the data were taken with a Be filter before the sample, the data with $E = 0.6$ meV further had a BeO filter placed after the sample. Constant-energy scans for $E = 0.4$, 0.425, 0.45, 0.5, 0.55 and 0.6 meV at $T = 0.45$ K are shown in Fig. 6.15, these scans are fit with both two Gaussian peaks (orange solid lines) and two Lorentzian peaks (red dashed lines) on linear backgrounds. These results indeed reveal two peaks as found in previous work [216] for all measured energies, although the data at $E = 0.4$ meV [Fig. 6.15(a)] can also be fit using a single peak due to poor statistics. Our detailed studies further allows us to extract the energy dependence of the splitting, as shown in Fig. 6.16(a). The obtained splitting is similar whether the data is fit with two Gaussian or Lorentzian peaks, strikingly a trend of decreasing splitting $\delta$ is seen as energy is decreased. A comparison with similar data previously reported is shown in Fig. 6.16(b), as can be seen our data are consistent with previous results, although a slightly smaller splitting is suggested by our data.

These results indicate incommensurate resonance mode peaks are observed in CeCoIn$_5$ down to $E = 0.425$ meV, exhibiting a splitting that decreases with energy. The picture that links this incommensurate feature to the field-induced magnetically ordered $Q$-phase [217] appears to contradict the present results. Our data suggests two possible scenarios, one is that the feature is a continuation of the upward dispersing resonance mode discussed in previous section, however the intensity is maximum not at the bottom of the dispersing mode at $Q_{AF} = (0.5, 0.5, 0.5)$, but near $E = 0.5$ meV with $\delta \approx 0.04$. Alternatively, there are two contributions to the resonance near
Figure 6.15: **Constant-energy scans near $E = 0.5$ meV in CeCoIn$_5$.** Constant-energy scans on CeCoIn$_5$ for (a) $E = 0.4$ meV, (b) $E = 0.425$ meV, (c) $E = 0.45$ meV, (d) $E = 0.5$ meV, (e) $E = 0.55$ meV and (f) $E = 0.6$ meV. The orange solid lines are fits to data using a model of two Gaussian peaks on a linear background, the center of the two peaks are not restrained to be 0.5. Similarly, the red dashed lines are fits using two Lorentzian peaks.
$E = 0.5$ meV, one is the magnon-like mode discussed in previous sections, another is soft mode for the field-induced $Q$-phase at $\mathbf{Q} = (0.5 \pm \delta, 0.5 \pm \delta, 0.5)$ with $\delta \approx 0.05$. In this case the data in Fig. 6.15 should be fit with a single peak at $\mathbf{Q}_{\text{AF}}$ in addition to two split peaks to account for these two contributions. $\delta$ obtained from such fits are larger than the ones presented in Fig. 6.16(a), and clusters close to $\delta \approx 0.05$ which is consistent with such a scenario, as shown in Fig. 6.17. Unfortunately, such fitting requires very high data quality to obtain good estimates of $\delta$, more experiments are needed to fully resolve this issue.

6.4 Discussion of results

Previous works suggested that the resonance is entirely polarized along the $c$-axis [43, 216], this conclusion is based on two experimental observations. The first observation is the resonance has a strong $L$-dependence, which implies the resonance being polarized along $c$-axis due to the polarization factor $\sum_{\alpha,\beta} (\delta_{\alpha,\beta} - \hat{Q}_\alpha \hat{Q}_\beta)$. However as noted in another study [216], even such an assumption cannot account for the suppression of intensity at $L = 1.5$ compared to $L = 0.5$. The problem is In absorbs neutron strongly and absorption depends on the scattering geometry realized at various energies and wave vectors, for $E_f = 3.7$ meV the scattering geometry is shown for $E = 0.55$ meV in Fig. 6.18. The gray slabs in the figure represent the sample with $c$-axis perpendicular to the slabs. As can be seen for $L = 1.5$ either $k_i$ or $k_f$ is close to the $[1,1,0]$ direction, which results in strong absorption of neutrons since the beam has to travel through a large part of the sample. On the other hand, for $L = 0.5$ neither $k_i$ nor $k_f$ is close to $[1,1,0]$ so that absorption is much less significant. The strong absorption for $L = 1.5$ is difficult to correct and accounts for the weak intensity at $L = 1.5$ in previous work [43] that even purely $c$-axis magnetic excitations
Figure 6.16: **Energy-dependence of peak splitting near** $E = 0.5$ meV in CeCoIn$_5$. (a) Energy dependence of obtained peak splitting $\delta$ in obtained from fits in Fig. 6.15, using two Gaussian and two Lorentzian peaks. (b) Comparison of data from PANDA measured at $T = 0.45$ K with those from previous work [216] measured at $T = 1.45$ K. The data are fit with two Lorentzian peaks in both cases. The data from PANDA have been scaled and adjusted to have the same background and peak height.
cannot account for. Given the strong absorption that is present at $L = 1.5$ but not at $L = 0.5$, the conclusion that the resonance is $c$-axis polarized based on $L$-scans is not fully warranted.

Another evidence used to argue for the resonance being entirely polarized along $c$-axis comes from polarized neutron scattering [216]. The experiment was carried out in the geometry as shown in Fig. 6.19(a), similar to our work on iron pnictides this geometry allows one to extract $M_y$ and $M_z$. In the polarized neutron scattering results [216], spin-flip (SF) neutron scattering cross sections $\sigma_x^{SF}$, $\sigma_y^{SF}$, and $\sigma_z^{SF}$ as shown in Fig. 6.19(a) were measured where $x$ is parallel to $Q$, $y$ is perpendicular to $Q$ but within the scattering plane (the $[H,H,L]$ plane), and $z$ is perpendicular to the scattering plane. Since $\sigma_x^{SF}$, $\sigma_y^{SF}$, and $\sigma_z^{SF}$ measures magnetic excitations perpendicular to both $Q$ and the neutron polarization direction, $\sigma_x^{SF} \propto M_y + M_z$, $\sigma_y^{SF} \propto M_z$, and $\sigma_z^{SF} \propto M_y$. 

Figure 6.17: Energy-dependence of peak splitting near $E = 0.5$ meV in CeCoIn$_5$ using single+double Gaussian fit. The results in Fig. 6.15 are fit with a single Gaussian peak plus two symmetrically displaced Gaussian peaks on either side, the resulting splitting of the double Gaussian peaks are shown. The dashed line is $\delta = 0.05$ corresponding to the position of the magnetic Bragg peaks of the field-induced $Q$-phase [217].
$E_f = 3.7 \text{ meV, } E = 0.55 \text{ meV}$

Figure 6.18: **Scattering triangles for Q = (0.5,0.5,0.5) and Q = (0.5,0.5,1.5).**

(a) Scattering triangle for $Q = (0.5,0.5,1.5)$ for $E_f = 3.7 \text{ meV}$ and $E = 0.55 \text{ meV}$, the slab represents the sample array which is much longer along [1, 1, 0] than [0, 0, 1].

(b), (c) and (d) show similar scattering triangles for $Q = (0.5,0.5,-1.5)$, (0.5,0.5,0.5) and (0.5,0.5,-0.5).
At $Q_{AF} = (0.5, 0.5, 0.5)$, $M_y$ and $M_z$ can be related to magnetic excitations along crystallographic axes by $M_y = M_{110} \sin^2 \theta + M_{001} \cos^2 \theta$ and $M_z = M_{110}$, with $\theta$ being the angle between $Q_{AF}$ and $[1, 1, 0]$ (Fig. 6.19). Previous polarized neutron scattering measurements [216] conclusively demonstrated vanishing intensity of $M_z$ compared to $M_y$, or $M_{110} \approx 0$. It was then argued that due to tetragonal symmetry of CeCoIn$_5$, $M_{110} = M_{110}$ and so only $M_{001}$ is present [216]. However given that the system is close to a field-induced $Q$-phase that breaks the four-fold rotation of the lattice [217, 218], it is possible dynamic in-plane spin anisotropy [between $[1, 1, 0]$ direction at $Q_{AF} = (0.5, 0.5, 0.5)$ and transverse $[1, \bar{1}, 0]$ direction at $Q_{AF} = (0.5, 0.5, 0.5)$] is already present in CeCoIn$_5$ at zero field as shown in Fig. 6.19(b). When such is the case, the polarized neutron scattering experiment [216] only ruled out the excitations polarized along the in-plane transverse direction.

Moreover $M_{110}$ contributes little to intensity at $Q_{AF} = (0.5, 0.5, 0.5)$ due to the polarization factor compared to $M_{001}$, making it difficult to observe in either previous [43, 216] or our work (this is why while our data are fit assuming excitations are polarized along the $c$-axis, they do not rule out $M_{110}$). This is illustrated in Fig. 6.19(c), with $M_{110}$ and $M_{001}$ being intrinsically equal and the measured difference solely due to the polarization factor. Compounded with the strong absorption near $L = 1.5$ this makes $M_{110}$ very hard to experimentally observe. In summary, in addition to $c$-axis polarized contribution to the resonance, there could also be a contribution from the in-plane longitudinal direction [$M_{110}$ for $Q_{AF} = (0.5, 0.5, 0.5)$].

To understand if the observed resonance mode can be understood as a spin-exciton, we used RPA to calculate the dynamic magnetic susceptibility using the band structure obtained for CeCoIn$_5$ from STM [200, 203]. The results are shown in Fig. 6.20 along $[H, H]$ and $[0, K]$ directions plotted together with the experimentally obtained
Figure 6.19: Possible $M_{110}$ in CeCoIn$_5$. (a) Scattering geometry of polarized neutron scattering experiment used in previous work [216]. (b) Schematic of the reciprocal space for CeCoIn$_5$ with tetragonal symmetry. The green box indicates the first Brillouin zone, dynamic spin anisotropy at $Q_{AF} = (0.5,0.5)$ between the longitudinal direction ([1, 1, 0], red solid line) and the transverse direction ([1, 1, 0], blue solid line) may be possible in light of the proximate $Q$-phase which breaks four-fold rotational symmetry [217, 218]. (c) Comparison of $M_{110}$ and $M_{001}$ at $Q_{AF} = (0.5,0.5,0.5)$. In unpolarized neutron scattering measurements, $M_{110}$ contributes little to the overall intensity near $L = 0.5$ but becomes significant near $L = 1.5$.

upward dispersion for Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$. As can be seen the spin-exciton scenario as obtained from RPA displays a clear downward dispersion and rather weak modes above the central mode at $Q_{AF} = (0.5,0.5)$, these results qualitatively agree with similar calculations for the cuprates [48] where an hour-glass dispersion of the resonance was seen (the downward-dispersing branch being much more prominent than the upper branch) [198, 199]. Therefore while the superconducting order parameter is believed to be $d_{x^2-y^2}$ for both cuprates and CeCoIn$_5$ [200, 201], the resonance mode displays opposite dispersion. Moreover the maximum gap for CeCoIn$_5$ is $\Delta \approx 0.6$ meV [200], given that positions on the Fermi level connected by $Q_{AF}$ do not have maximum $\Delta$, this means the resonance mode within the spin-exciton picture has to be $E < 2\Delta \approx 1.2$ meV. Our observation of the resonance at 1.2 meV in Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$ (Fig. 6.4) also suggests that the resonance in Ce$_{1-x}$Yb$_x$CoIn$_5$ cannot be interpreted as a spin-exciton. In addition the upper branch in RPA calculations is very differ-
Figure 6.20: **RPA calculation for spin exciton in CeCoIn$_5$.** (a) The dynamic magnetic susceptibility calculated within RPA along $[0, K]$ and $[H, H]$ directions are shown in (a) and (b), respectively. The blue curve is the experimental fit obtained from Ce$_{0.95}$Yb$_{0.05}$CoIn$_5$.

Our experimental results therefore indicate the resonance in Ce$_{1-x}$Yb$_x$CoIn$_5$ cannot be understood as a weak coupling spin-exciton mode, in contrast to the case of iron pnictides and cuprates. Given the similar dispersion of the resonance compared to spin waves in CeRhIn$_5$ (Fig. 6.9), it is more likely to be a magnon-like mode [202, 52].
Chapter 7

Conclusion and Outlook

While the intimate connection between magnetism and unconventional superconductivity is well established, the precise pairing mechanism remains elusive in compounds such as cuprates, iron-based superconductors and heavy fermion superconductors. Dedicated neutron scattering efforts have been devoted towards unraveling such a connection from an experimental perspective, and this work forms an integral part of this large effort.

The work on the effect of uniaxial pressure on iron pnictides suggested the Ising-nematic phase in iron pnictides is likely driven by magnetism. Detailed measurements of the doping dependence of magnetic excitations under uniaxial pressure using time-of-flight neutron spectroscopy in future work (as first done for BaFe$_{1.9}$Ni$_{0.1}$As$_2$ by me) are needed to fully resolve this question.

Using polarized neutron scattering we have shown spin anisotropy resulting from spin-orbit coupling is a common occurrence in iron pnictides, and points to this interaction being important for superconductivity in this system. Comparison of NaFeAs and BaFe$_2$As$_2$ derived compounds suggests a similar evolution of behavior with doping, although near optimal superconductivity NaFe$_{1-x}$Co$_x$As does not exhibit the anisotropic resonance mode seen in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$. On this front future work should focus on elucidating the relationship between the normal state spin anisotropy and the anisotropic resonance mode, by carrying out more detailed measurements on the well studied compounds. Importantly, spin-orbit should also be incorporated into
theoretical models to understand these systems.

The case of NaFe$_{1-x}$Cu$_x$As provides evidence that electron correlations are significant in iron pnictides, similar to the copper-based superconductors. Moreover, by measuring magnetic excitations in NaFe$_{0.53}$Cu$_{0.47}$As it is shown the fluctuation spectrum is easily understood from a local moment perspective while revealing striking similarities to iron pnictide superconductivity - longitudinally elongated excitations in [H, K] plane. This led to my hypothesis of (fluctuating) antiferromagnetic spin stripes to be the structural motif to understand iron pnictides. I look forward to theories and calculations from such a starting point. From an experimental perspective, NaFe$_{1-x}$Cu$_x$As should be more thoroughly investigated to understand its behavior and attempts should be made to dope NaFe$_{1-x}$Cu$_x$As with $x \approx 0.5$ to search for superconductivity. BaFe$_{2-x}$Cu$_x$As$_2$ and similar systems should be investigated for comparison.

For Ce$_{1-x}$Yb$_x$CoIn$_5$, I have clearly demonstrated the resonance exhibits a clear upward dispersion. This is inconsistent with the predominant view in the field that it can be described as a spin-exciton due to itinerant electrons. One cautionary note is that my conclusion is based on the assumption that CeCoIn$_5$ has $d_{x^2-y^2}$ pairing symmetry, although this has been well established, conclusive phase-sensitive experiment is still lacking. Furthermore, the relationship of my observations to the field-induced magnetic order (this phase likely has spatially modulated superconductivity and is highly interesting) is still unclear. Future work in this system should be dedicated to clarifying this relationship and examining the possibility that the resonance mode has two contributions with different polarizations.
Bibliography


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BaFe$_{2-x}$Ni$_x$As$_2$,” *Science*, 2014.


and N. J. Curro, “Coexistence of Cluster Spin Glass and Superconductivity in \( \text{Ba}(\text{Fe}_{1-x}\text{Co}_x)\text{As}_2 \) for \( 0.060 \leq x \leq 0.071 \),” *Phys. Rev. Lett.*, vol. 111, p. 207201, Nov 2013.


T. Egami, and P. Dai, “Magnetic anisotropy in hole-doped superconducting $\text{Ba}_{0.67}\text{K}_{0.33}\text{Fe}_2\text{As}_2$ probed by polarized inelastic neutron scattering,” *Phys. Rev. B*, vol. 87, p. 081101, Feb 2013.


anisotropy in Fe-based superconductors due to static and fluctuating antiferro-

[118] Q. Q. Ge, Z. R. Ye, M. Xu, Y. Zhang, J. Jiang, B. P. Xie, Y. Song, C. L. 
Zhang, P. Dai, and D. L. Feng, “Anisotropic but Nodeless Superconducting 
Gap in the Presence of Spin-Density Wave in Iron-Pnictide Superconductor 

anisotropy, and spin resonance excitations in a multiorbital $t$-$J_1$-$J_2$ model for 

[120] C. Zhang, W. Lv, G. Tan, Y. Song, S. V. Carr, S. Chi, M. Matsuda, A. D. 
doping evolution of the neutron spin resonance in NaFe$_{1-x}$Co$_x$As,” *Phys. Rev. 
B*, vol. 93, p. 174522, May 2016.

[121] G. Tan, Y. Song, C. Zhang, L. Lin, Z. Xu, T. Hou, W. Tian, H. Cao, S. Li, 
S. Feng, and P. Dai, “Electron doping evolution of structural and antiferromag-
netic phase transitions in NaFe$_{1-x}$Co$_x$As iron pnictides,” *Phys. Rev. B*, vol. 94, 

[122] S. V. Carr, C. Zhang, Y. Song, G. Tan, Y. Li, D. L. Abernathy, M. B. Stone, 
magnetic excitations in NaFe$_{1-x}$Co$_x$As,” *Phys. Rev. B*, vol. 93, p. 214506, Jun 
2016.

[123] K. Terashima, Y. Sekiba, J. H. Bowen, K. Nakayama, T. Kawahara, T. Sato,


[154] Z. P. Yin, K. Haule, and G. Kotliar, “Kinetic frustration and the nature of the


for Ba(Fe$_{1-x}$TM$_x$)$_2$As$_2$ (TM = Ni, Cu, Cu/Co) single crystals,” *Phys. Rev. B*, vol. 82, p. 024519, Jul 2010.


[180] A. J. Williams, T. M. McQueen, V. Ksenofontov, C. Felser, and R. J. Cava,


