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Studies of Magnetism and Strain Tuning in Detwinned Iron Pnictides and Chalcogenides and Other Unconventional Systems

by

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ABSTRACT

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Uniaxial pressure can be used as a “clean” tuning parameter to smoothly change the atomic spacings and bond angles in a crystal lattice, induce phase transitions, or to break the rotational lattice symmetry and thereby provide access to underlying symmetries such as electron nematic phases. I present experiments (transport, neutron diffraction, inelastic neutron scattering, and muon spin rotation) that use uniaxial pressure as a platform for tuning iron-based superconductors and other unconventional magnetic systems. Simple clamps were used to break the in-plane symmetry of iron-based superconductors, enabling investigations of the magnetic ground state of a single domain. In the ground state of Fe$_{1+y}$Te, anisotropy of spin fluctuations stemming from the magnetically ordered positions was observed to rapidly relax at an energy scale near $E = 30$ meV, which can be understood as the result of a competing quasi-degenerate magnetic ground state. Detwinning of NaFeAs, on the other hand, reveals orbital-selective spin fluctuations that are dominated by $d_{yz} - d_{yz}$ spin fluctuations at low energy, while $d_{xy} - d_{xy}$ scattering processes control the overall magnetic bandwidth. To study the uniaxial pressure dependence of materials with transport and scattering experiments, I developed a compressed air-based instrument which exerts controlled and repeatable uniaxial pressure on large samples, which we
first used to show that in-plane pressure in Co- and Ni- doped BaFe$_2$As$_2$ increases the magnetic ordering temperature and ordered moment, while decreasing the superconducting $T_c$. Experiments with this instrument on many other systems are also reported here, including the uniaxial pressure dependence of Fe$_{1+y}$(Se,Te), BaFe$_2$As$_2$ and SrFe$_2$As$_2$ and their derivatives, Sr$_3$Ru$_2$O$_7$, and other materials along various crystallographic directions. For example, comparing the transport properties of BaFe$_2$As$_2$ and SrFe$_2$As$_2$ under finely tuned in-plane uniaxial pressure reveals subtle differences that connect resistivity anisotropy to low-energy spin fluctuations, adding evidence for a spin-driven nematic phase in iron-based superconductors. In addition to uniaxial pressure experiments, I present theoretical calculations on the LiFeAs and BaFe$_2$As$_2$ systems and neutron scattering experiments on UPt$_3$ that elucidate key aspects of the mechanism of magnetically-driven superconductivity in these systems. Finally, I discuss other experimental progress in magnetic systems such as the spin liquid candidate Ce$_2$Zr$_2$O$_7$. 
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Chapter 1

Introduction: Uniaxial pressure, iron superconductors, and experimental techniques

1.1 Uniaxial pressure experiments and devices

Uniaxial pressure, the application of compressive stress along one axis, has been used as an experimental probe in a wide variety of materials. In some cases, one can simply take a single crystal, cut two parallel faces or use existing crystal facets, and put it in a clamp or in a diamond anvil of the type commonly used for hydrostatic pressure. For low pressures, the material will deform linearly according to the stress-strain relation along that axis, and for high pressures some nonlinear response is expected. Most uniaxial pressure experiments are, in this spirit, strain tuning experiments, where the pressure may be considered a small perturbation to the electronic structure and the response may be seen as a linear susceptibility to the resulting strain. To interpret the meaning of the strain response in such experiments, no microscopic details are required.

In practice, more complicated instruments have been designed and used, and the answers to more detailed scientific questions have been produced. Pfleiderer and coworkers designed in 1997 an instrument containing an inflatable bellows containing helium gas, in which the gas was able to be controlled in situ from outside the sample environment [1]. The force could be measured in this instrument using a piezoelectric crystal below the sample, where the slow decay of charge in the piezo
could be measured and accounted for in order to produce accurate results, although the temperature dependence of the stress-strain relation of the piezo was not explicitly taken into account. This instrument was used to study, for instance, the uniaxial pressure dependence of MnSi where it was found that uniaxial pressure expands the phase boundaries of the well-known skyrmion phase [2]. Other instruments have been developed essentially operating on the same principle of a helium bellows with in situ tunability, including an instrument to measure resistivity and AC magnetic susceptibility [3, 4], an instrument to measure heat capacity using a piezo as a pressure sensor [5, 6], an instrument for small-angle neutron scattering which was used to study the vortex lattice also in MnSi [7], and an instrument for finely controlled uniaxial strain for NMR [8], among others.

The method of using a piezo to measure strain overcomes a problem with the manometer technique commonly used in hydrostatic pressure experiments, where the pressure is measured using the superconducting transition temperature of a metal such as tin. Such a calibration method would only be strictly applicable at low temperatures close to the superconducting temperature of tin, for at higher temperatures the flexibility and other mechanical properties of the pressure apparatus would change. This is of little consequence in most hydrostatic pressure experiments, since one is focused on a regime of large pressure, and often low temperature, and the apparatus itself is very rigid. However, in uniaxial pressure experiments the consequences of thermal expansion of the apparatus can be significant.

A significant development in strain tuning instrumentation was published by Hicks et al. in 2014 [9], in which piezoelectric actuators were arranged in a special yoke configuration in order to cancel out the effects of thermal expansion of the apparatus. Moreover, when samples were firmly attached to the moving parts by clamps filled
with epoxy, the device could apply strain without the sample pulling out of the jaws of the clamps. In a seminal paper, the device was used to show that the superconducting transition temperature in $\text{Sr}_2\text{RuO}_4$ increased under both compression and tension, which was thought to be a strong indicator of chiral superconductivity, although this conclusion is now doubted. The piezo-based yoke instrument was patented and is now distributed through Razorbill Instruments, and the design has also been adapted for use in $\mu$SR experiments [10]. However, while the methodology provides clean results on the uniaxial strain dependence of materials, this instrument lacks a way to measure stress. In the $\text{Sr}_2\text{RuO}_4$ experiments, the amount of strain applied in the material was enormous - nearly 3% - undoubtedly corresponding to thousands of MPa. However, without a measure of stress it is difficult to know how to re-create the same conditions using a method that applies fixed stress.

For experiments requiring neutron scattering, the instrument design must incorporate two crucial elements: (1) the sample holder must be made of a material suitable for neutron scattering, such as aluminum, and (2) since neutron scattering is a weakly interacting probe and one wants as large a sample mass as possible in the beam, the apparatus must be able to apply a large force on large samples. Most of the designs mentioned above, and notably those involving the use of piezoelectric actuators, are therefore unsuitable for this purpose under element (1). Even if some separation is given between the sample and the piezo, the piece of material used for this purpose will inevitably have its own temperature dependent properties, leading to uncertainty. Moreover, since the absolute magnitude of strain in a piezo is also small, its use would present additional difficulties under element (2) given that the overall size of piezo elements cannot be made arbitrarily large, and so the strain applied to large samples decreases as the sample size increases. One could in principle measure the strain of
the piezo or of the sample in real time during the experiment using an independent
method, but this has not yet been implemented in practice.

For good control of the uniaxial pressure in a neutron scattering experiment, we
found it is far easier to control the uniaxial stress, measuring the applied force in
real time using a calibrated commercial load cell held at room temperature. The
apparatus is described in Chapter 3, and it has been used to study the uniaxial
pressure dependence of materials in a variety of experimental conditions, which are
described in Chapters 3 and 4. For simple experiments requiring some uniaxial
pressure, with no need to calibrate it, we have used several clamp-type devices, as
described in Chapters 2 and 5.

1.2 Iron superconductors

Iron superconductors, or iron-based superconductors (with emphasis on the “basal”
planes which are composed of iron), are layered materials that predominantly adopt
tetragonal symmetry at high temperature, with a structural transition \( T_s \) lowering
the in-plane symmetry to an orthorhombic phase below room temperature, quickly
followed in many cases by a transition to an antiferromagnetic state \( T_N \) [11]. Above
the (magneto-)structural transition, spin fluctuations spontaneously break the fourfold
rotational symmetry of the tetragonal lattice. As these fluctuations do not break
translational symmetry above \( T_N \), they are described as an electron nematic phase,
which is discussed in Chapter 4. Magnetism is believed to play a central role in
the mechanism of high-temperature (high-\( T_c \)) superconductivity [12, 13], although
somewhat counterintuitively, both antiferromagnetic order and nematic fluctuations
have been observed to compete with superconductivity [14–18]. Magnetic fluctuations,
in the form of spin waves, are observed universally in iron superconductors. The
superconducting phase is considered unconventional because it is strongly momentum dependent.

Large samples can be grown with the self-flux method [19] and tend to have a plate-like habit with an orientation within the crucible that is different depending on the material as well as the furnace used. Due to the layered structure with \( c > a \), the short axis in the macroscopic crystal is the tetragonal \( c \)-axis. In reciprocal space, the electronic structure is highly two-dimensional with mostly weak variations along the \( c \) (\( L \)) direction except in certain cases such as for very low energy dynamical fluctuations, or for materials in the vicinity of a Lifshitz transition. In the undoped (parent) materials, typically there are mostly two-dimensional (cylindrical) hole sheets at \((0,0,L)\), and electron sheets at the \((1,0,L)\) and \((0,1,L)\) positions in the one-Fe Brillouin zone. Fermi surface nesting between these two pockets gives rise to metallic behavior and leads to some itinerant characteristics of spin fluctuations, which also display characteristics of local moment physics [14, 20]. The crystal growth and structure, and momentum space information, are shown in Fig. 1.1 and Fig. 1.2.

Early in the study of iron superconductors it was realized that the orthorhombic phase consists of crystal twin domains, specifically, merohedral twins [21] that share one single plane of atoms at the twin boundaries. Tanatar and coworkers found in 2009-10 that the twins could be removed by the application of a weak uniaxial pressure at room temperature, the strain field creating a preferred direction for rotational symmetry breaking which polarized light transmission showed was highly effective [22]. Other small clamps were then designed and used by several groups to further study detwinning effect using resistivity anisotropy, ARPES and other experimental techniques [23–25]. This was similar to the results of uniaxial pressure application in the cuprates at temperatures well above room temperature, which was found to be
Figure 1.1 : Crystal growth and structure of layered iron-based superconductor BaFe$_2$As$_2$. (a) The crystal lies along bottom edge in the photo, and the rest is flux. (b) Arrangement of ions along the orthorhombic directions of BaFe$_2$As$_2$ with lattice parameters in Å.

very effective for removing twin domains and creating large, perfectly orthorhombic crystals [26, 27], which required no special apparatus during the measurements since $T_s$ sits above room temperature. In 2012, uniaxial pressure was used in a neutron scattering experiment on an iron superconductor by Dhital and coworkers, in which small values of pressure on the order of 1 MPa were applied to BaFe$_2$As$_2$ along the tetragonal (1,1,0) axis, and the regime near the magnetic ordering temperature of nearly 140 K was studied [28]. In that experiment, a simple clamp was placed around the crystal and a belleville washer was used to maintain roughly constant force on the sample when the clamp and sample both thermally contracted in the sample environment. This experiment was groundbreaking because it showed that uniaxial
Figure 1.2: Momentum-space picture of BaFe$_2$As$_2$ in the 1-Fe Brillouin zone from a 5-orbital model. (a) The band structure of tetragonal BaFe$_2$As$_2$ along the $k_x$ direction. Different bands are shown in different colors. The width of the blue bar at the Fermi level ($E = 0$) shows the region of mobile charge carriers at a temperature $T = 250$ K. (b) Fermi surface of BaFe$_2$As$_2$ in three dimensions. The sheets at (0,0) are hole-like, while the sheets at (1,0) and (0,1) are electron-like.

Pressure could be applied \textit{in situ} in a neutron diffraction experiment, and that it could have a measurable effect despite little control over the actual value of the pressure and some unknown degree of nonuniformity of the stress (and strain) over the sample volume.

The use of uniaxial pressure for detwinning is a crucial tool for examining the magnetic ground state of iron superconductors, and in Chapters 2, 3, 4, and 5, I discuss experiments that make use of this technique [29–31]. With the crystal detwinned, the rotational symmetry of spin excitations can be determined unambiguously, which is not possible in the twinned case because the overlapping domains necessarily result in an artificial fourfold symmetry. In some cases, the energy and temperature
scales of the in-plane anisotropy directly associated with uniaxial pressure-induced symmetry breaking beyond the detwinning effect have also been directly measured [29, 31–35]. Unfortunately, it took many years for this method to be applied systematically in neutron scattering experiments, especially time of flight neutron experiments which probe higher energy scales and are the only choice for fully determining the momentum and energy dependence of spin excitations in this family of materials [11].

Under in-plane uniaxial pressure, one generally presumes that the unit cell volume is conserved, and more specifically that in-plane uniaxial pressure should distort the in-plane lattice parameters without appreciably affecting $c$, although by applying pressure along $c$ directly we have observed some consequences on the in-plane lattice parameter in the case of optimally-doped $\text{BaFe}_2(\text{As},\text{P})_2$. Microscopically, neutron Larmor diffraction measurements show that the application of uniaxial pressure on iron superconductors causes in-plane distortion of less than 0.1% near room temperature, which increases as $T_s$ is approached, and that below $T_s$ the splitting reaches values essentially identical to the unstrained case [36]. Thus, uniaxial pressure broadens the phase transition region into a kind of crossover rather than a sharp phase boundary, which is also consistent with the rotational symmetry breaking of the nematic low-energy dynamical spin fluctuations. Recent work suggests that in this region, a magnetic moment also develops along the $c$-axis, indicating the highly interconnected nature of the electronic degrees of freedom is still a very open question [Dai et al., submitted].

As discussed in Chapters 3 and 4, uniaxial pressure is observed to have a strain tuning effect on the lattice of iron superconductors; indeed, even the original neutron diffraction experiments by Dhital et al. show that $T_N$ increases with pressure in $\text{BaFe}_2\text{As}_2$, a result that requires a microscopic mechanism to explain [28]. However,
clamps are accurate enough for simple detwinning in most cases, and in general we have used a spring or spring washer with a known force constant and estimated the pressure by the length compression of the spring, which carries a systematic error of 10% or more. For well-studied materials such as BaFe$_2$As$_2$, the clamp-induced pressure has sometimes determined more accurately based on the observed increase of $T_N$, since this effect has now been studied several times using more precise methods. Moreover, since $T_N$ in the iron superconductors is often not close to either room temperature or zero temperature, the thermal expansion or deformation of the clamp relative to the sample in the temperature range of interest can be problematic if the applied force at room temperature is reduced as the temperature is lowered such that the sample does not become detwinned. Conversely, in the case of BaFe$_{1.9}$Ni$_{0.1}$As$_2$, Y. Song in our group designed an all-aluminum clamp (no spring) to specifically take advantage of thermal effects: since the thermal contraction of aluminum is larger than that of the sample along the orthorhombic (1,0,0) direction, the clamps were tightened very minimally and the pressure required for detwinning was applied naturally as the sample cooled [32]. For BaFe$_2$As$_2$, the thermal contraction is actually smaller than aluminum and this principle would not work. In other all-aluminum clamp designs, the aluminum itself was stretched with screws and therefore acted as its own spring at all temperatures.

The detwinning ratio $\eta = (S - W)/(S + W)$, with “strong” majority-domain as $S$ and “weak” minority-domain as $W$, varies between 0 and 1, with 1 corresponding to complete detwinning. Experiments can be designed to measure the structural and/or magnetic peaks corresponding to the majority and minority domain populations, and the detwinning ratio can be calculated. At a thermal neutron triple-axis spectrometer, the momentum resolution of the beam is not good enough to resolve the splitting
between structural Bragg peaks and thus the magnetic intensity has been used. In
time of flight experiments, we have often used the integrated magnetic peak intensity
off the elastic line and just above the spin gap (energies of approximately 10 meV),
although this method is not entirely reliable and thus we have used it to derive a
lower bound for the detwinning ratio.

The high-temperature tetragonal lattice of iron superconductors consists of a unit
cell with two Fe ions in one plane and a lattice parameter \( a \approx 3.8 \, \text{Å} \), and sometimes
with four Fe ions in two planes such as in the case of BaFe\(_2\)As\(_2\) which contains an
inversion center in the unit cell, thus \( c \) is either near 6-7 Å, or near 13 Å. In the low-
temperature orthorhombic phase, the distortion is along the diagonal direction to the
high-temperature lattice, lengthening \( a \) by a factor \( \sqrt{2} \) and rotating by 45 degrees to
accommodate four Fe ions per layer. The magnetic unit cell depends on the material
but due to the twinning effect it is customary to retain orthorhombic lattice units,
since this results in a coordinate system that can be used to describe both twin
orientations [11]. Locally, the electronic wavefunctions of the unfilled \( d \) shell of iron
may be projected into the usual basis of energy eigenstates, with the crystal field at the
Fe sites lowering the energy in the \( e_g \) submanifold, containing \( d_{x^2} \) and \( d_{x^2-y^2} \), relative
to that of \( t_{2g} \) orbitals \( d_{xz}, d_{yz}, \) and \( d_{xy} \) [37]. Since the ground state configuration
is \( d^6 \), magnetic electrons inhabit the \( t_{2g} \) orbitals. The real-space projections of the
\( d_{xz} \) and \( d_{yz} \) orbital eigenstates have lobes pointed in the direction of neighboring
Fe ions and have natural twofold rotational symmetry in the basal place, although
they are degenerate in the tetragonal phase; \( d_{xy} \) has manifest fourfold rotational
symmetry in the plane. The role of the orbital degree of freedom is relatively poorly
understood, but recent ARPES experiments have made great progress in describing
systematic trends, such as band renormalization factors as a function of electron
filling, which can naturally explain the electron-hole asymmetry in the phase diagrams of iron pnictides in terms of proximity to a Mott insulating state arising from a $d^5$ configuration [38]. Whether spin waves arise from Fermi surface nesting of itinerant electrons, or via local moment superexchange across the As anions analogously to the cuprate superconductors, is an open question. Initially, spin fluctuations were often modeled with effective Heisenberg exchange interactions [14], although the numerical values of the exchange coupling parameters are not particularly instructive in most cases, save for the observation that the next-nearest neighbor exchange coupling seems to be similar across many materials [14]. Many properties of BaFe$_2$As$_2$ have been successfully understood within a purely weak-coupling picture, such as an emergent energy scale for rotational symmetry breaking [32, 34] and predictions for a leading $s^\pm$-wave superconducting pairing state in RPA calculations under both hole [39, 40] and electron doping [41]. In Chapters 5 and 6, I will explore some of the issues and energy scales associated with both itinerant and local moment behaviors and draw connections between spin fluctuations and the orbital degree of freedom.

### 1.3 Neutron scattering and $\mu$SR

Neutron scattering is a natural choice for investigating the structural and magnetic effects of uniaxial pressure in bulk systems. Many good references exist on the basic experimental techniques of neutron scattering [42, 43], and here I will only briefly overview the particular elements relevant to the experiments reported in this work. For experimental purposes, neutrons can interact with atomic nuclei or with the magnetic moments of free electrons. In both cases, the interaction strength is weak and the scattering formalism of the Born approximation is used to derive cross-sections for various processes.
In general in a neutron scattering experiment we utilize the wavelike properties of a single neutron scattering event, which is sensitive to the reciprocal space structure of the interacting material; this is termed coherent scattering and can either be elastic (energy conserving, probing static structure) or inelastic (non-energy-conserving, probing dynamical fluctuations). For magnetic coherent scattering, we write

$$\frac{d^2\sigma}{d\Omega_f dE_f} = \frac{k_f}{k_i} \sum_{i,f} P(\lambda_i) |\langle \lambda_f | \sum_l e^{iQ \cdot r_l} U_{i}^{s_i s_f} | \lambda_i \rangle|^2 \delta(h\omega + E_i - E_f) \quad , \quad (1.1)$$

which is Fermi’s golden rule where \(P\) is the probability of the initial state with wavelength \(\lambda_i\), \(Q\) and \(r_l\) are the vector momentum transfer and atomic positions at index \(l\), and the interaction matrix element \(U_i\) is given for initial and final spin states as

$$U_{i}^{s_i s_f} = \langle s_f | b_i + B_i \hat{I} \cdot \sigma - \left( \frac{\gamma r_0}{2} g f(Q) \right) S_{\perp} \cdot \sigma | s_i \rangle \quad , \quad (1.2)$$

where the term \(b_i\) is the nuclear scattering length, \(B_i \hat{I} \cdot \sigma\) represents the spin-dependent nuclear operator with Pauli matrices \(\sigma\), and the magnetic scattering term is expressed in terms of the gyromagnetic ratio \(\gamma\) and g-factor, the classical electron radius \(r_0\), the magnetic form factor of the scattering ion \(f(Q)\), and the quantity \(S_{\perp} = \hat{Q} \times (S \times \hat{Q})\) which reflects the fact that neutrons only scatter magnetically from magnetic moments perpendicular to \(Q\). In this thesis, I drop the boldface vector notation for \(Q\) and write it in terms of reciprocal lattice units \((H,K,L)\). In the case of inelastic magnetic scattering, which comprises a large percentage of the work here, the principle of detailed balance implies that the dynamical structure factor \(S(Q,\omega)\) is related to the linear response function in the material with the relationship

$$S(Q,\omega) = \frac{\chi''(Q,\omega)}{1 - e^{-\hbar \omega/k_BT}} = \frac{\chi''(Q,\omega)}{1 - e^{-E/0.0862T}} \quad , \quad (1.3)$$
for $E$ in meV and $T$ in K in neutron-energy-loss mode. We typically measure in neutron-energy-loss mode because it provides a higher cross-section in most cases: the neutron can more easily create an excitation with definite energy rather than relying on an existing excitation with that energy to already exist at the moment of interaction.

In a triple axis instrument, one selects the wavelength of neutrons incident on a sample using a monochromator, typically a nuclear reflection from a crystal with a desirable degree of mosaicity that balances flux and resolution, relying the angle of the Bragg reflection to select the wavelength of interest. Wavelength filters are used before or after scattering from the sample to eliminate neutrons that have passed through the monochromator at the correct angle due to a higher-order Bragg process; these are typically made of polycrystalline Be or BeO, which reject nearly all neutrons above a certain wavelength, or pyrolitic graphite (PG) oriented along the $c$ axis which strongly scatters neutrons as a function of wavelength and certain wavelengths can be found with a high transmission at $\lambda$ and low transmission at $\lambda/2$ and $\lambda/3$. The energy scale of the dynamical fluctuations probed in the material is related to the energy loss (or energy gain) of the neutron, as selected by tuning the angle between an analyzer crystal and the detector, which is typically a high-voltage wire. Many other aspects of the beam may also be tuned, such as the collimations lengths of the focusing elements which affect the beam divergence, typically tens of arcminutes, and the careful selection of slits in various positions made of neutron-absorbing material such as boron nitride, to block spurious scattering from other equipment such as the sample environment. The experimental setup is sketched in Fig. 1.3(a), where the monochromator and analyzer have been ignored for simplicity. Scattering resulting from a magnetic interaction in an itinerant system with an appreciable density of
states at the Fermi level, such as an iron superconductor, may result in an interaction like the one depicted in (b), where an electron receives momentum $Q$ from the neutron in order to scatter elastically between two states connected at $Q$ on the Fermi surface.

Since all elements of a triple axis spectrometer are in a parallel plane, the sample must also be studied in a single two-dimensional plane, termed the scattering plane. The sample or sample + sample environment is often mounted on the combination of a translation stage and a two-axis goniometer, which can correct the position and orientation of the sample by typically 10-20 mm and 5-10 degrees in two dimensions after setting up the experiment. In some cases, one wants to align the sample in an unconventional scattering plane in order to access a certain set of positions. In Fig. 1.4, two unconventional choices of scattering plane are shown in green, which were both used to study $\text{BaFe}_2\text{As}_2$ under uniaxial pressure with neutron diffraction. The choice of scattering plane is reflected in the conventional label $HKL$ where the values...
Figure 1.4: Two unconventional choices of scattering plane that were used to study BaFe₂As₂. In (a), the scattering plane shown in green can access the magnetically ordered positions (1,0,1) and (0,1,1), whereas in (b) the scattering plane is (1,0,5) × (0,1,5) or, equivalently, (1,-1,0) × (1,1,10). The dimensions are exaggerated for clarity.

of $H$, $K$, and $L$ are given in such a way to specify the plane by express a constraint along one direction. For instance, $HK0$ refers to the scattering plane containing (1,0,0) and (0,1,0), while $H0L$ refers to the plane with (1,0,0) and (0,0,1).

In a triple-axis experiment with only one detector, since one can specify all four quantities $H$, $K$, $L$, and $E$ independently, experiments mainly consist of scans of one parameter, such as $H$, or of an external parameter such as temperature or field. In this case, the data analysis largely proceeds by fitting the scans taken with various
forms such as a single Gaussian, two Gaussians, Lorentzian, etc., typically by a least-squares algorithm. In some approaches the error estimate when performing these fits is typically given in terms of the standard error of a single parameter. However, when computing the integrated area of a fitted peak over the background, using the standard error of the fitted peak height ignores the fitted error coming from orthogonal parameters such as peak width, or the slope of a linear background. To avoid underestimating the error in these cases, I developed an algorithm that finds confidence intervals of parameters including integrated area based on varying all the individual fit parameters to their confidence limits, in all possible combinations, and accepts the largest deviations above and below the best fit result as the more likely confidence interval. An example of this algorithm is shown in Fig. 1.5.

Figure 1.5 : Two peaks fitted with the 1-dimensional peak fitting algorithm for estimating the integrated area and thereby the total scattered neutron intensity. The background is assumed to be linear and the slope and intercept are fitting parameters, and the results are shown in orange. The dotted purple lines show the curves generated at the boundaries of the confidence interval of the integrated area, as determined by the algorithm.

Neutron spherical polarization analysis may be carried out in a triple axis setting
by implementing spin polarizers before and after the sample. The scattering cross section for coherent magnetic neutron spin flip scattering (where the neutron interacts with unpaired electrons in the sample) is only sensitive to the components of the magnetic moment perpendicular to the neutron spin. For neutron spin polarization along the direction of momentum transfer $Q$ (termed $S_{xx}$), the neutron spin flip scattering channel will consist of magnetic cross sections both in the scattering plane and perpendicular to $Q$, and perpendicular to the scattering plane. For neutron spin polarization in the scattering plane and perpendicular to $Q$ ($S_{yy}$), only the cross section of out of the scattering plane will contribute. Likewise, for neutron spin polarization out of the scattering plane ($S_{zz}$), only the cross section in the scattering plane and perpendicular to $Q$ will contribute. By analyzing either all three spin flip cross sections and three non-spin flip cross sections at a single $Q$, one may in principle extract the information about the magnetic moment direction, but in practice this is difficult since non-spin flip scattering contains contributions from nonmagnetic channels and therefore the background level is higher, making it difficult to extract the moment information simply because of counting statistics. In practice, a better method is to analyze the three spin flip scattering cross sections at two equivalent $Q$, after taking into account the known magnetic form factor in case the two values of $Q$ have different values of $|Q|$, and an overall instrument-specific intensity ratio between the two $Q$ which may be simply computed from the intensity ratio of scattering in any channel. This information has low background and may be used to determine the three directional components of the magnetic moment or magnetic fluctuations, as has been done previously in experiments in our group [44–47]. In such case, there is still a background scattering contribution at each $Q$, arising from spin-incoherent nuclear scattering and scattering from unknown sources, but by measuring six cross sections
(three polarization directions at two \( Q \)) for only five unknowns (three polarization components and two background contributions), the system is overdetermined and may be solved by least squares at each point of equivalent \((Q, E)\). Practically, in a triple axis experiment with neutron polarization analysis, one expects the background to vary rather slowly with energy, and thus the background may be fitted or smoothed for each scattering channel and the system reduced to solving for three polarizations from six unknowns, creating even more accurate results. In this work, polarized neutron scattering experiments were conducted on the ground state of \( \text{Fe}_{1+y}\text{Te} \), discussed in Chapter 2, and in \( \text{Fe}_{1+y}\text{Te} \) above the magnetic ordering temperature and under uniaxial pressure, as discussed in Chapter 4.

Finally, the remainder of the neutron scattering scattering experiments presented in this work were performed at time of flight spectrometers. This class of spectrometer contains many detector tubes and time-sensitive electronics, thus it can essentially multiplex the neutron scattering signals received at many different \( Q \) and \( E \) simultaneously. To accomplish this, the detector tubes are typically arranged in a semicircle around the sample position, with different choices of areal coverage at different spectrometers creating different sets of capabilities such as momentum resolution or the useful range of available energies. At ORNL and ISIS, which are spallation sources, an incident beam of neutrons is generated by pulsing high-energy protons from an accelerator source onto a target that releases neutrons such as liquid mercury or solid tungsten fins. Each spectrometer then contains a flywheel ("chopper") rotating at the same frequency as the pulses and contains a slit that lets a pulse of neutrons through it and eventually onto the sample. In this work all experiments were performed on "direct geometry" spectrometers, which contain an additional chopper that is used to select parts of the neutron pulse with definite momentum/energy. At MERLIN,
one chopper that may be used contains multiple slits which allow neutrons through at different times, which have different energy and reach the sample and finally the detectors at different times, which offers a great advantage in efficiency since one can effectively measure in different energy ranges simultaneously. The neutron events are recorded individually and later reduced into bins using software, after which a user can project these in various ways for analysis. One such projection is shown in Fig. 1.6, which shows the projection of a constant-energy slice into orthogonal planes to show how the neutrons at this energy are scattered onto the semicircular detector bank. In case a measurement is made using the same spectrometer configuration but with a piece of vanadium in place of the sample, which is a strong incoherent scatterer of neutrons, one can obtain a normalization factor that can be used to convert the data into absolute units.

In certain cases where the data analysis leads to confusion, it can be useful to project cuts along the third direction in momentum space rather than along energy. In Fig. 1.7, it is clear that by projecting along $L$ leads to the identification of the feature at 6-8 meV as the $(1/2, 0, 1/2)$ magnetic peak while the feature near 18 meV is around $(H, 0, 2)$.

Finally, fitting time of flight data to expected models, analogously to the one-dimensional fit algorithm for triple axis data, is in general quite difficult because the background scattering could be large and anisotropic. This issue will be addressed in this work for each material separately. However, awareness of the three-dimensional nature of the two-dimensional slices due to the coupling of $E$ and $L$ can be helpful in identifying background features. For example, phonons in the sample holder material, often aluminum, presents as powder rings, which in three dimensions are spheres with well-known momentum $Q$ and energy $E$. By projecting data into three
Figure 1.6: (a) Diagram of time-of-flight neutron scattering data within a narrow energy window, projected onto orthogonal planes. The detector tubes are oriented along the $H$ axis in this diagram, and the semicircular arrangement of the detectors allows data to be projected into two planes (in this case $HK$ and $HL$). Along the radial direction of the circle, the momentum of the neutron is coupled to energy. Thus, choosing a larger (smaller) energy range for this projection would cause the “radius” of the semicircle in the $KL$ plane to become smaller (larger). (b) Using software, narrow regions of momentum $Q$ and energy $E$ can be selected, such as in this figure which contains $-1.2 < H < 1.2$ and $-1.2 < K < 1.2$ with values in reciprocal lattice units of the chemical unit cell, $6 < E < 8$ meV, and all available values of $L$ collected on the detector banks. The data in this figure was collected on Fe$_{1+y}$Te at ARCS, with data reduction performed in Mantid and the final slices made using Mslice for Matlab.
Figure 1.7: (a) Projection of Fe\textsubscript{1+y} data along the $H$ axis, with $K$ integrated around 0, and the vertical axis as energy. (b) Projection of Fe\textsubscript{1+y} data along the $H$ axis, with $K$ integrated around 0, and the vertical axis as $L$.

Dimensions in momentum space, one can identify where the aluminum phonons exist and those features can be removed or ignored, such as in the Fe\textsubscript{1+y}Te experiment discussed in Chapter 2. This method has proven very useful in identifying where the problematic regions exist in the background of certain figures, even when a blind “radial” background subtraction algorithm may have removed them. For datasets with different neutron incident energies $E_i$, projections with fixed energy transfer will occupy different ranges along the direction in momentum space that is coupled to energy, such as the four surfaces in Fig. 1.8. In this case the background phonon from aluminum appears closer to $(H, K) = (0, 0)$ for the data with lower $E_i$, possibly intersecting a feature under study, and it is for this reason that neutron scattering experiments are often performed with multiple incident neutron energies. It is also useful to observe that, for increasing energy transfer at fixed $E_i$, one observes the background phonon feature moving toward the center $(H, K) = (0, 0)$ because the
energy window is crossing out of range of the acoustic aluminum phonon “sphere”. Without the benefit of multiple datasets at different $E_i$, it would be easy to confuse this feature with an optical phonon.

![Surfaces for 34<E<40](image)

Figure 1.8: Phonons in the sample holder contribute to the background. In the case of materials like aluminum, the phonons are identifiable because their momentum and energy dependence are well known. In three dimensions, they appear at spheres centered at $(H, K, L) = (0, 0, 0)$, shown in green. In two-dimensional projections at constant energy with $L \parallel k_i$, they appear at different apparent in-plane $Q$, shown in orange compared to the blue background in these slices.

In addition to neutron scattering, muon spin rotation experiments ($\mu$SR) are presented in this work. As with neutron scattering, many useful resources already exist [48, 49] and my aim is merely to provide an overview of the methodology used here. Proton accelerators create a beam of positively charged (anti-)muons by
bombarding a target, similar to the case of a spallation neutron source. Since muons are magnetic, the $\mu$SR technique can be used to study magnetism by embedding muons into a sample, where they rapidly thermalize and come to rest in a favorable position within the lattice. The magnetic moment precesses according to the direction and magnitude of the local magnetic field at the muon site until it undergoes spontaneous decay after a mean lifetime of about 2.2 $\mu$s, decaying into a positron and two neutrinos, which conserves lepton number. Parity violation results in an outgoing direction for the positron that is preferential in the direction of the muon spin at the time of decay, thus the time dependence of the positron decay direction encodes information about the local magnetic field direction and magnitude at the muon stopping site. Scintillators (dyed plastic) are arranged around the cryostat to detect the outgoing positrons by Cerenkov light, which is collected in an optical fiber and passed on to pulse shaping electronics which record the events. At TRIUMF and PSI, which are continuous muon sources, the scintillators consist of pairs of panels placed on opposite sides of the sample, for instance above and below or to the left and right. At continuous sources, the muon beam intensity is stopped down with slits so that the beam flux is so low that muons are implanted one at a time in the material, a surprising fact to those familiar with neutron scattering where the beam flux is always being maximized. In this case, a clock is started when a very thin scintillator at the entrance to the sample area records an incoming muon, and if a second muon enters before a positron is detected the entire event is discarded. At other facilities such as ISIS and JPARC, silicon detectors are placed in many positions so that more radial resolution can be achieved. This is especially useful at pulsed sources, which can count many muon events simultaneously since the time of incoming muons is always known, thus the silicon detectors can also measure multiple outgoing positrons simultaneously.
Crucially, since in both situations muons are implanted at one or a few unique muon sites within the crystalline matrix that have identical internal magnetic fields, $\mu$SR has been called a local probe.

Decay events are recorded as a function of delay time between muon implantation and detection of a positron. The quantity of interest is the asymmetry between the detectors as a function of time, $A(t) = (N^\uparrow - N^\downarrow)/(N^\uparrow + N^\downarrow)$, out of which the exponential decay of the muon naturally falls out. In an experiment, since one records different curves $A(t)$ at different temperatures or fields, or uniaxial pressure, certain quantities like the asymmetry at $t = 0$ should remain constant throughout the experiment. In practice, the software MUSRFIT developed by A. Suter [50] is an extremely useful tool for refining fits with certain parameters and functional forms held constant, and all of the analysis in this work has used it.

In the case of zero static internal field and zero field applied externally, one expects the only change in $A(t)$ will be due to random fluctuations. In the case of a well-defined and constant field applied externally, often by Helmholtz coils around the sample, the expected result depends on the field direction with respect to the initial muon spin polarization. For fields oriented transversely to the muon spin direction (TF), $A(t)$ exhibits sinusoidal oscillations at the frequency $\omega = \gamma_\mu B$ where $\gamma_\mu = 2\pi \times 135.5$ MHz/T is the muon gyromagnetic ratio. At low fields of $\sim 30$ G (0.003 T), one expects a few oscillations within the useful window of 0.02 to about 8 $\mu$s. These “weak” TF measurements can then be fitted to a functional form to determine volume fraction information: if parts of the sample exhibit fast depolarization due to the onset of a magnetic field, weak TF can easily distinguish the muons landing in the two regions because the oscillating part of $A(t)$ will have an amplitude less than the starting asymmetry at $t = 0$. On the other hand, for large external fields applied in
the same direction as the incoming muon polarization (LF, for longitudinal field), the
muon sees little depolarization effect, since even random fluctuations of the local field
are small compared to the overall field which tends to keep the muon spin aligned.
The experimental quantity to measure in this situation is the field strength below
which random fluctuations begin to depolarize the muon spins, thus quantifying such
dynamical fluctuations.

In zero applied field (ZF), the relaxation of $A(t)$ can be modeled with a variety
of functional forms depending on the dynamical and statistical properties of the
fluctuations that lead to depolarization. For example, we modeled BaFe$_{1.915}$Ni$_{0.085}$As$_2$
with a function containing Gaussian depolarization from the paramagnetic regions of
the sample as well as the paramagnetic background holder, and exponential depolarization
from regions with disordered magnetism [29]:

$$A_{ZF}(t) = A_b e^{-\frac{1}{2}(\sigma_b t)^2} + A_s \left[ (1 - F) e^{-\frac{1}{2}(\sigma_{param} t)^2} + F e^{-\lambda t} \right] ,$$

where $A_b$ denotes the fraction of background muons landing outside the sample and
$A_s = 1 - A_b$ represents the fraction of muons landing in the sample, with $F$ the fraction
of those muons landing in magnetically ordered regions. In the analysis, $A_b$ can be
globally constrained across all runs, while the other parameters are individually fitted
at each temperature. Similarly, for Ba(Fe$_{0.95}$Co$_{0.05}$)$_2$As$_2$ we found less disorder of the
internal magnetic field, leading to some coherent oscillations, and we used

$$A_{ZF}(t) = +(1 - A_b) \left[ F_1 e^{-\lambda t} \cos(\omega_1 t + \phi_1)/\cos(\phi_1) \right.$$

$$+(1 - F_1) e^{-\lambda t} \cos(\omega_2 t + \phi_2)/\cos(\phi_2) \right] .$$

A variety of neutron and muon spectrometers were used for the experiments
reported in this work. Information about these spectrometers is given in Table 1.1.
The facilities operating these spectrometers are: Oak Ridge National Lab in Oak Ridge, Tennessee (ORNL); the NIST Center for Neutron Research in Gaithersburg, Maryland (NCNR); the ISIS Pulsed Neutron and Muon Source in Didcot, Oxfordshire, UK (ISIS); the Institut Laue-Langevin in Grenoble, France (ILL); the Research Neutron Source Heinz Maier-Leibnitz in Garching, Germany (FRMII); the Tri-University Meson Facility in Vancouver, BC, Canada (TRIUMF); the Paul Scherrer Institut in Villigen, Aargau, Switzerland (PSI); the Materials and Life Science Experimental Facility at the Japan Proton Accelerator Research Complex in Tokai, Ibaraki, Japan (JPARC).
Table 1.1: Particle scattering spectrometers and experiments described in this work

<table>
<thead>
<tr>
<th>Name</th>
<th>Type</th>
<th>Facility</th>
<th>Experiment &amp; year</th>
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</thead>
<tbody>
<tr>
<td>HB-1A</td>
<td>Triple axis</td>
<td>ORNL</td>
<td>BaFe$_2$As$_2$ (2015)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>BaFe$<em>{1.915}$Ni$</em>{0.085}$As$_2$ (2015)</td>
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<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>Sr$_3$Ru$_2$O$_7$ (2018)</td>
</tr>
<tr>
<td>HB-1</td>
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<td>ORNL</td>
<td>Fe$_{1+y}$Te$^\ast$ (2014,2015)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe$_{1+y}$Te$^\delta$ (2018)</td>
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<tr>
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<td></td>
<td>FeSe$<em>{0.35}$Te$</em>{0.65}$ (2015)</td>
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<tr>
<td>BT-7</td>
<td>Triple axis</td>
<td>NCNR</td>
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<td>Multiple triple axis</td>
<td>NCNR</td>
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<td>IN20</td>
<td>Triple axis</td>
<td>ILL</td>
<td>Fe$_{1+y}$Te$^\delta$ (2018)</td>
</tr>
<tr>
<td>MIRA</td>
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<td>FRMII</td>
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<td>Time of flight</td>
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<td>Fe$_{1+y}$Te$^\ast$ (2015)</td>
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<tr>
<td>SEQUOIA</td>
<td>Time of flight</td>
<td>ORNL</td>
<td>NaFeAs$^*$ (2017)</td>
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<td>UPt$_3$ (2017)</td>
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<tr>
<td>MERLIN</td>
<td>Time of flight</td>
<td>ISIS</td>
<td>BaFe$_2$As$_2$ (2015)</td>
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<td>Fe$_{1+y}$Te$^*$ (2016)</td>
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<td>NaFeAs$^*$ (2018)</td>
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<td>4SEASONS</td>
<td>Time of flight</td>
<td>JPARC</td>
<td>NaFeAs (2017)</td>
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<td>Muon</td>
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</tr>
<tr>
<td>GPS</td>
<td>Muon</td>
<td>PSI</td>
<td>Ce$_2$Zr$_2$O$_7$ (2018)</td>
</tr>
</tbody>
</table>

$^\ast$ with clamp  $^\dagger$ with uniaxial pressure instrument  $^\ddagger$ with uniaxial pressure instrument and high magnetic field  $^\S$ with uniaxial pressure instrument and spherical polarization analysis  $^\|$ with spherical polarization analysis
1.4 RPA calculations

To investigate iron superconductors theoretically, many approaches have been employed, from simple Ginzburg-Landau analysis to very complicated microscopic models. In this thesis, I present the results of various types of theoretical calculations that were performed to support the experimental work. My contribution to this area was in the form of calculations of the static and dynamic “RPA” magnetic susceptibility, and of the superconducting gaps induced by this susceptibility, through a linearized formalism. Results of this work is presented in Chapters 3, 6, and 7.

The random-phase approximation (“RPA”) is a generic method in physics that deals with simple scattering processes. In materials, the eigenstates corresponding to quasiparticle excitations are, in the simplest form, simply single-particle excitations dressed by interactions with other single-particle excitations. The RPA reduces these complicated interactions to simple forms that can be represented by numbers which describe the vertex amplitudes for scattering processes in the spin and charge channels. Thus, the RPA is a way to meaningfully transform a calculation of the noninteracting magnetic susceptibility at a given momentum and energy \((Q, E)\) into a good approximation of the real value. This information is very valuable in understanding the iron superconductors because they are metallic and have single-particle excitations involving itinerant electrons, and therefore the noninteracting magnetic susceptibility at \((Q, E)\) can be calculated from models of the electronic structure where the necessary information is given by the geometry of the electronic bands at and nearby the Fermi surface. Indeed, works by our collaborators and others have shown that the RPA spin susceptibility, and the concomitant superconducting pairing states it generates in a linearized model, have been very successful at predicting the form of the superconducting pairing that is actually observed experimentally.
The methodology for these calculations is fully described in my work \[41\] and elsewhere [51–57]. Beginning from electronic structure models produced with density functional theory within the local density approximation, one has all the ingredients necessary to perform the calculations since the electronic bandstructure is known, as are the eigenstates of electronic orbitals that comprise these bands, which is different for different values of electronic momentum $k$ and energy. Calculations of the “bare” (noninteracting) electronic susceptibility at $(Q, E)$ can be computed by summing over all bands and all orbital eigenstates via the tensor

$$
\chi^0_{\ell_1 \ell_2 \ell_3 \ell_4}(q, \omega = 0) = -\frac{1}{N_{Fe}} \sum_{k, \mu \nu} \frac{a^{\ell_4}_\mu(k) a^{\ell_2 \ast}_{\mu}(k) a^{\ell_3}_\nu(k+q) a^{\ell_1 \ast}_{\nu}(k+q)}{E_\mu(k) - E_\nu(k+q) + i\delta} (f[E_\mu(k), kT] - f[E_\nu(k+q), kT])
$$

(1.6)

with $N_{Fe}=2$ the number of iron sites per unit cell, $N_k$ the number of grid points in momentum $(k)$ space, band indices $\mu$ and $\nu$, and orbital indices $\ell$. The matrix elements are represented by the orbital projection of the Bloch state, $a^\ell_\mu = \langle \ell | \mu k \rangle$, $f[E, kT]$ is the Fermi function at temperature $T$, and the small parameter $\delta \approx 0.01$ enforces analyticity in the sum.

In other words, states with definite $Q$ are fluctuations in the electronic structure stemming from each possible value of $k$ and its partner at $k+Q$. As such, $Q$ represents a two-particle state, and it is precisely these fluctuations at $Q$, which correspond to a change in the system where the momentum and energy is lost or gained, that are probed by neutron scattering experiments in which momentum and energy is lost and gained to or from the neutron.

The noninteracting susceptibility may then be transformed into the RPA spin susceptibility by applying the vertex coefficients and summing over all orders at which
the interactions process can occur:

\[ \chi_{\text{RPA}} = \chi_0/(1 - U\chi_0) \quad , \]  

which is the Dyson equation involving the matrix of interaction vertices in orbital space, \( U \). This matrix contains numbers representing the interaction strengths for intra- and inter-orbital Coulomb repulsion \( U \) and \( U' \) as well as Hund’s rule and pair-hopping couplings \( J \) and \( J' \), as described more fully in the references. While the actual interaction strength is a complicated number to calculate for a real material, these four parameters are constrained if we assume spin rotational invariance [58], so that we often choose \( U' = U/2, J = J' = U/4 \) although we find small changes in these ratios generally have only a very slight effect on the final spin susceptibility. The remaining free parameter \( U \) is determined empirically by increasing its value until Eq. 1.7 diverges, then reducing it by perhaps 5%, which gives good results and is again not very sensitive to the exact value. Finally, the physical susceptibility at a given \((Q,E)\) is computed by tracing over the diagonal terms in \( \chi_{\text{RPA}} \), i.e. those with \( \ell_1 = \ell_3 \) and \( \ell_2 = \ell_4 \).

We carry out calculations of the RPA spin susceptibility in the paramagnetic state of iron superconductors. Specifically, we study how it explains the condensation of magnetic order from the paramagnetic system in electron-doped \( \text{BaFe}_2\text{As}_2 \) (Chapter 3) and the effect of different orbitals on spin fluctuations in parent compound and electron-doped \( \text{LiFeAs} \) (Chapter 5). The inclusion of magnetic order in these calculations, which reconstructs the Fermi surface and introduces other features in the magnetic susceptibility [34], is beyond the scope of this work.

The RPA spin susceptibility, as well as the charge susceptibility, which is similar computed from the noninteracting susceptibility, may be used to calculate the superconducting
pairing states via

\[ -\sum_j \oint_{C_j} \frac{dk'}{2\pi v_F(k'\parallel)} \Gamma_{ij}(k, k') g_\alpha(k') = \lambda_\alpha g_\alpha(k) \]

in which \( \Gamma_{ij} \) in this expression represents the pairing vertex between bands \( i \) and \( j \), \( g(k) \) is the projection of the \( \alpha \)th pairing state onto the Fermi surface states, and the sum is over closed Fermi arcs involving band \( j \) while weighting each interacting state at \( k' \) by its Fermi velocity \( v_F \) along the parallel direction \( k'\parallel \). Hence, this expression linearizes the pairing interactions between bands \( i \) and \( j \), creating an eigenvalue problem to which the solutions are the pairing states, or superconducting gaps, with corresponding strength given by the eigenvalues. For a larger magnitude of eigenvalue, the solution is more stable and there will be a larger energy associated with the gapping out of unpaired electrons from these states. The approach is described in more detail in [41]. In Chapter 6, I study the RPA superconducting pairing states in parent compound and electron-doped LiFeAs and electron-doped BaFe\(_2\)As\(_2\).

1.5 Miscellaneous

Transport measurements described in this thesis were collected in a 9 T Quantum Design Dynacool Physical Property Measurement System (PPMS) with all measurements collected on warming. The samples were cut into square-like shapes with the leads placed at the corners of the sample to measure resistance using the Montgomery method with \( V \) and \( I \) in parallel directions [33, 59]. With the uniaxial pressure instrument described in Chapter 3, independent wires are run up the sample stick in a twisted pair arrangement, so that the sample holder does not necessary mate with the puck holder in the PPMS. In neutron scattering data, error bars represent the statistical (counting) error unless otherwise specified. Where a background subtraction
was used involving an independent measurement, the error was combined in quadarature. For background subtraction from a fitted model, no modification was made to the statistical error or to the error bars. For derived quantities from fitted model parameters, the error was estimated using the best and worst solutions obtained by varying all the parameters of the model to within one confidence interval, as determined by the fit. For $\mu$SR, error bars in the raw asymmetry data also represent the statistical error, which increases with increasing decay time since fewer muons live long enough to contribute to the signal for $t \gtrsim 8\mu s$. I also note that in certain figures, extra letters appear in the plots that originate from the original context from which the figure was clipped. In these cases, the LaTex lettering system should be considered superior, and in cases where the subplots are referred to directly, a reference is made to both letters in hierarchical order, with a notation like Fig. 2.1(a)(a). Finally, the notation of momentum space coordinates uses various conventions due to the differences in worldviews between the specific areas of study to which they belong. For instance, in sections describing RPA calculations, the units are often given in terms of $\pi$, a factor from the Fourier transform between real and reciprocal space that is usually taken inside the unit when reporting neutron scattering results. In this text, I hope to have clarified the units in all cases where ambiguity may arise.
Chapter 2

Clamp-based experiments to determine the magnetic ground state of iron-based superconductors

2.1 Uniaxial pressure and the magnetic ground state

As described in Chapter 1, iron superconductors with a structural transition can be detwinned with uniaxial pressure applied in the basal plane along one orthorhombic lattice direction, [1,0,0] in orthorhombic notation or [1,1,0] in tetragonal notation. Microscopically, the uniaxial stress creates enough lattice distortion (strain) at room temperature that when the material undergoes a structural transition at temperature $T_s$ below room temperature, orthorhombic domains with a short axis along the pressure direction are favored. Across several families of iron superconductors, nearly 100% detwinning of the undoped (parent) compounds is achieved for weak uniaxial pressure of $\sim$10-15 MPa, which would be 50-75 N (11-17 lbf) on the edge of a plate-like crystal measuring 5 x 1 mm$^2$. In addition to the detwinning effect, $T_s$ and $T_N$ are promoted to higher temperature, which needs to be understood microscopically and which is presented in Chapter 3.

In this section, I describe the result of uniaxial pressure experiments with clamps on the low-temperature magnetic ground state of BaFe$_2$As$_2$ [34] and BaFe$_{1.9}$Ni$_{0.1}$As$_2$ [32], Fe$_{1+y}$Te [30], and Fe$_{1+y}$(Se,Te). This is the simpliest type of uniaxial pressure experiment, in the sense that the actual value of pressure is considered a small and
ignorable perturbation on the spin fluctuation spectrum: the only relevant fact is that the sample is detwinned and/or that the rotational symmetry is broken by the applied pressure. In BaFe$_2$As$_2$ and Fe$_{1+y}$Te, which have structural transitions, we found the samples were detwinned well using clamp-based methods. The detwinning has a profound effect on neutron scattering measurements because the intrinsic spin fluctuation spectrum of the antiferromagnetic orthorhombic domains has twofold rotational symmetry, whereas in a twinned sample the domains are oriented at 90 degrees and overlap in momentum space, and therefore the contributions from each domain cannot be distinguished. This situation is shown in Fig. 2.1 for two samples studied here, Fe$_{1+y}$Te (this chapter), and NaFeAs (Chapter 5). In BaFe$_2$As$_2$, Ba(Fe,Ni)$_2$As$_2$, and Fe$_{1+y}$Te, the pressure-induced anisotropy was directly measured for the first time and energy scales were found in all three compounds at which the fourfold symmetry was spontaneously restored. For the Fe$_{1+y}$(Se,Te) samples, there is no structural transition resulting in twin domains, and we expect uniaxial pressure to generate measurable symmetry breaking through the induced lattice distortion, but at this time the results are inconclusive and future experiments will be necessary to determine whether the spin fluctuation spectrum is altered by uniaxial pressure.

Neutron scattering, and in particular time of flight neutron scattering, is the only choice for measurements of the complete inelastic spin fluctuation spectrum up to the magnetic band top of 200-300 meV, since inelastic xray experiments do not have the momentum space coverage to reach the Brillouin zone boundary of iron superconductors [11]. Triple axis neutron scattering was also employed to investigate the magnetic anisotropy at lower energies in the range 1-40 meV. Fig. 2.2 shows several aluminum clamps used for these experiments, which were designed by X. Lu and Y. Song in our group.
Figure 2.1: (a) Magnetic unit cell and corresponding momentum space diagram of Fe$_{1+y}$Te, from [30]. The spin arrangement shows double stripes, ordering at $Q = (1/2, 0, 1/2)$ in the notation of the chemical unit cell, which is shown in green. For the spin arrangement shown, magnetic Bragg peaks occur at the positions of the red dots, and the same peaks from the extinguished “weak” domain are shown in blue. The black hexagon shows a position that is insensitive to the detwinning and at which polarized neutron measurements were collected to demonstrate the existence of a competing plaquette ground state. (b) Two chemical unit cells of NaFeAs with magnetic Bragg positions for the strong and weak domains shown in the momentum space diagram.
Figure 2.2: Clamp-based detwinning: (a) Single crystal detwinning clamp with spring, shown mounted for a displex can and containing the BaFe$_2$As$_2$ crystal measured at HB-1A and described in Chapter 2; (b) Single crystal detwinning clamp using a stack of aluminum spacers as a spring, shown with the 530 mg FeSe$_{0.35}$Te$_{0.65}$ crystal measured at SPINS; (c) 16-sample manifold of detwinning clamps, shown with Fe$_{1+y}$Te measured at MERLIN.
2.2 BaFe$_2$As$_2$ and BaFe$_{1.9}$Ni$_{0.1}$As$_2$

BaFe$_2$As$_2$ was studied at the HB-1A spectrometer at Oak Ridge National Lab in a detwinning experiment with five values of unaixial pressure. The low-temperature region was found to be fully detwinned, and the magnetic ordering temperature $T_N$ also systematically increased with pressure, consistent with the idea that the pressure-induced splitting promotes the antiferromagnetic ordering. The results of this experiment are more completely described in Chapter 3 in context with measurements on doped Ba(Fe,Ni)$_2$As$_2$ samples.

To fully understand the magnetic ground state of BaFe$_2$As$_2$, clamp-based detwinning was carried out on a manifold of 16 samples similar to the setup shown in Fig. 2.2(c) and the spin fluctuation spectrum was measured at MERLIN, in an experiment designed by X. Lu. Surprisingly, the spin fluctuation spectrum was found to be highly anisotropic but only up to an energy scale of $\sim$150 meV, whereas the spectrum at the highest energies (up to $\sim$300 meV) was found to have restored fourfold symmetry [34]. The restoration of symmetry was explained using a weak-coupling model.

Similar to the BaFe$_2$As$_2$ experiments, BaFe$_{1.9}$Ni$_{0.1}$As$_2$ was studied using the same technique at ARCS and HB-1A, in experiments designed by Y. Song. This compound is optimally doped and has a superconducting transition at $T_c \approx 20$ K and simultaneous $T_s/T_N$ near 30 K. The spin fluctuation spectrum is nearly the same as in the undoped parent compound, but the energy scale at which the fourfold rotational symmetry is restored is lowered to near 60 meV [32], compared with 150 meV for BaFe$_2$As$_2$. These results were understood in the context of orbital selectivity: electronic bands in BaFe$_2$As$_2$ and doped BaFe$_2$As$_2$ are connected by Fermi surface nesting near the antiferromagnetic ordering wavevector, and under unaixial pressure the rotational symmetry is broken and the bands along the (1,0) and (0,1) directions are split.
apart in energy. However, since the spin fluctuation anisotropy was observed in BaFe$_{1.9}$Ni$_{0.1}$As$_2$ to persist at temperatures well above $T_N$, whereas the band splitting was not, we argued that intrinsically anisotropic spin fluctuations were likely the cause of rotational symmetry breaking in both the high-temperature and low-temperature phases. It is noteworthy that the spin fluctuations in the BaFe$_2$As$_2$ system and other iron pnictides such as NaFeAs [60] have approximately the same form even when the temperature is raised and static magnetic order disappears, such that only the low-energy part of the spectrum is sensitive to the Fermi surface restructuring generated by antiferromagnetic order. This observation is strong evidence that spin fluctuations in the iron superconductors are not classical spin waves originating from an ordered spin system.

2.3 Fe$_{1+y}$Te: neutron time of flight spectroscopy

The magnetic ground state of iron chalcogenide Fe$_{1+y}$Te differs from other iron superconductors in a very significant way: antiferromagnetic order appears at a wavevector completely unrelated to the Fermi surface nesting of its low energy bandstructure. Moreover, the magnetostructural phase transitions occur simultaneously and are considered strongly first-order due to the very sharp onset at $T_s = T_N \approx 60 - 70$ K [61–63]. It has been argued that this evidence supports an antiferromagnetic ground state in Fe$_{1+y}$Te arising from localized electronic moments on the Fe sites, which is backed up by measurements of the large magnetic moment of about $2\mu_B$ [61, 64] and by theoretical calculations demonstrating a high degree of electronic correlations compared to other iron pnictides and chalcogenides [65]. As such, if magnetism in Fe$_{1+y}$Te arises from local moment correlations, it is natural to expect that in a detwinning experiment, the spin fluctuation spectrum of Fe$_{1+y}$Te in the
low-temperature ground state should maintain strict twofold rotational symmetry across the magnetic bandwidth. Moreover, since magnetic order occurs in a region unconnected to the Fermi surface nesting wavevector, one would not necessarily expect to observe the same behaviors of nematic spin correlations that are ubiquitous in superconducting iron-based materials.

To shed light on the rotational symmetry of spin fluctuations in Fe$_{1+y}$Te, I conducted clamp-based detwinnings experiments at HB-1, ARCS, and MERLIN. The experiments at HB-1 focused on the region around the magnetic ordering temperature $T_N$, where it was found that the transition remains strongly first order, yet low-energy spin fluctuations do exist at the magnetic ordering position and remain anisotropic to temperatures well above $T_N$. These results are fully described in Chapter 4.

The value $y$ in Fe$_{1+y}$Te represents excess “interstitial” Fe ions that sit between the layers and are necessary for the growth of large crystals: only a range of compositions with $0.04 < y < 0.17$ have been reported to be successfully synthesized [64]. The low-temperature antiferromagnetic phase exists on a monoclinic lattice, but the angle of repose of the monoclinic distortion is small, as is the orthorhombic distortion, and for the purposes of the magnetic properties the material is described with respect to the tetragonal unit cell for convenience. For values of $y$ below about 0.10, the system crosses directly from the high-temperature paramagnetic tetragonal phase into the low-temperature antiferromagnetic orthorhombic phase, while for larger values the system first enters a “mixed” phase with complex spin arrangement that may be elliptical or helical [63, 64, 66]. We note that the values of $y$ reported in the literature are somewhat confusing in that Fe deficiencies within the iron layers also exist [64, 67, 68], so it is important to distinguish between experiments measuring Fe content with a real-space probe like lattice distortion, and those using compositional
analysis like energy dispersive x-rays (EDX) and inductively coupled plasma (ICP). We use the phase diagram of Ref. [63] and determine the interstitial iron content from the transition temperature(s) observed in our samples. In general, the existence of interstitial iron up to about 0.12 is acceptable since it presents a negligible effect on the magnetic fluctuation spectrum at low temperature.

I grew large single crystals in our lab using the self-flux method, while additional crystals were grown by X. Lu at IOP Beijing and by J. Hu at Tulane University. In our lab, a tube furnace was used with a temperature gradient carefully measured and is shown in Fig. 2.3, along with three of the large Fe$_{1+y}$Te crystals that were produced. The furnace growth schedule used roughly followed the procedure outlined in [69], with the furnace angled between vertical and about 45 degrees during different trials. To prepare the samples for the neutron scattering experiments, they were aligned using the Laue method of x-ray diffraction in order to find the (1,0,0) tetragonal direction, and cut with a high precision wire saw in our lab.

Time of flight neutron experiments were carried out at ARCS and MERLIN. In both experiments, it was observed, surprisingly, that the anisotropy associated with twofold rotational symmetry breaking in the low-temperature phase quickly relaxes to fourfold symmetry at an energy scale near 20-30 meV, well below the values observed for BaFe$_2$As$_2$ (150 meV) and BaFe$_{1.9}$Ni$_{0.1}$As$_2$ (60 meV). Our triple axis neutron scattering experiments with polarization analysis, described below, later gave a more precise estimate of 26 meV. We understand the results within a theoretical model of magnetic frustration between the observed bicollinear antiferromagnetic ground state and a state consisting of four-iron block-like “plaquettes” with internal ferromagnetic correlations, similar to the state proposed in S-doped FeTe in Ref. [70]. The anisotropy was also observed to decrease with increasing temperature, quickly
Figure 2.3: (a) Heat gradient measured at two temperatures along the axial direction of the tube, used to grow FeTe crystals. The quartz tube containing the powdered starting materials was placed 0-1.5 inches below the center position. (b-d) Three crystals of FeTe. The first sample weighed 4.4 g and was dissected into many smaller pieces used successfully for several experiments. The latter two were made using similar growths but yielded different physical properties. The squares on the paper are 0.25x0.25 inches.
dropping to near zero in a first-order-like fashion at $T_N$ for the entire spin fluctuation spectrum except those at quasielastic energy scales, as discussed in Chapter 4.

Data analysis for both experiments on Fe$_{1+y}$Te proved challenging, and I describe some of the methodology here before describing the experimental conclusions. In Chapter 1, the neutron scattering cross section was discussed along with the influence of the so-called bose factor arising from detailed balance in the transition probabilities for creating or annihilating an excitation. To make an accurate assessment of the properties of the magnetic fluctuation spectrum, it is important to correct for the influence of the bose factor on spin fluctuations, which artificially enhances the linear response function for fluctuations at low energy and high temperature. To successfully rescale these fluctuations, it is important to first subtract the background. The background can arise from various sources, including spurious scattering from the sample, and incoherent scattering that is largely flat or only weakly momentum dependent. Different spectrometers and sample environments exhibit more or less background scattering overall, and sometimes also a characteristic shape to the background. At ARCS, there is always a linear gradient from the bottom to top of the detector tubes, which the instrument scientists have ascribed to fast neutrons escaping the spallation target and scattering off the concrete floor of the instrument hall. Additionally, the background at any spectrometer almost always begins to increase toward the edges of the detector array, which can be due to the contribution from multi-phonon processes from e.g. the sample holder, which give an expected $\sim Q^4$ dependence with spherical symmetry ($Q^{2n}$ where $n$ is the order of the multiphonon process) [71]. In the UPt$_3$ experiment described in Chapter 6, strong features in the background were observed at specific sample rotation angles, and we attribute this to a multiple scattering process of neutrons off a strong Bragg peak in the UPt$_3$ sample and then
off the sample environment and onto the detectors.

With a multitude of origins for the scattering processes contributing to the background, it is important to subtract these systematically. The initial methodology developed for background subtraction developed in our group, largely by S. Carr, is illustrated in Fig. 2.4(a-c). After reducing the data (binning every recorded neutron event into predefined momentum and energy bins and optionally normalizing to a vanadium standard), and projecting the data into slices with constant energy, the algorithm consists of the subtraction of a linear gradient along the horizontal and vertical directions, followed by a “radial” subtraction of the lowest pixel in every ring of given $|Q|$. While this method is generally effective for many experiments, and easily eliminates the background resulting from aluminum phonon rings, during the time of flight experiments on Fe$_{1+y}$Te it was found that this method was problematic for three reasons. First, this method eliminates regions of interest for Fe$_{1+y}$Te, since the plaquette phase contains broad rings of scattering, including rings centered around the origin $(H, K) = (0, 0)$. Second, the phonon rings from the aluminum sample holder were found in the expected places, but the intensity was found to be highly nonuniform around each ring, similar to what W. Wang reported in the appendix to his thesis [72]. We attribute this issue either to large domains in the crystal structure of the aluminum pieces, possibly formed during periods of intense heat when the manifold was machined, or possibly to to small pockets of residual hydrogen-containing oil which could have been insufficiently removed after the pieces were cut under oil using the wire saw. Third, this method suffers from an additional methodological issue, namely that to obtain good fitting it is sometimes important to eliminate the neutron scattering features of interest, but no method was developed for this other than identifying these regions by eye and eliminating them by hand.
To solve these problems, I developed a background subtraction algorithm which makes the assumption that the background can be expanded about the origin in powers of $|Q|$. To make this method effective, all regions that may plausibly contribute to the desired neutron scattering signal must be first removed. Two assumptions are made at this stage: (1) the neutron scattering features of interest will always have higher intensity than the background that one is trying to eliminate; and (2) the features of interest will also have a significantly smaller footprint in momentum space compared to the broadly changing background. (Note that assumption (2) usually fails to hold for constant-energy slices with high energy transfer near the magnetic band top, where spin fluctuations are as broad as half a Brillouin zone; luckily, in this region no background subtraction is usually necessary.) Under these assumptions, three filters were applied: (1) a filter which discards pixels of high intensity, (2) a filter which discards pixels with high statistical error (such as would be found near the edge of a detector tube where few neutrons would be counted), and (3) a filter which scans along each one-dimensional row or column of pixels, smooths the intensities into broad features, and eliminates pixels which lie far from the smoothed curve. Various ways of implementing the filters have been tried, and I prefer to apply the filters in the order 1, 2, 3, and let each filter operate in a loop until about 60-90% of the pixels remain, which leaves about 50% of the initial pixels after all three filters. Finally, one obtains a two-dimensional array of pixels that only contain background scattering, and these are fitted with a two-dimensional polynomial of the lowest order that is practical, which I found to often be satisfied at order 2 (paraboloid), and otherwise at order 4. The fitted paraboloid is then subtracted, leaving a background-subtracted array. The result of this method is shown in Fig. 2.4(d). To successfully implement this background subtraction algorithm for different experiments, it was found to be quite convenient
to simply tune the parameters by hand for each experiment (such as the width of the filter applied along the one-dimensional rows and columns, and the fraction of pixels eliminated by each filter), making small adjustments until the algorithm produces plausible results for all the constant-energy slices in an experiment. For instance, in the NaFeAs experiments described in Chapter 5, which took place at 5 temperatures and over a broad range of energies between 5 and 150 meV, it was found that one set of parameters was able to produce clean, background-subtracted slices for the entire experiment. It should also be noted that this method has also proven successful in subtracting the background from other types of two-dimensional slices, and even for $Q - E$ slices, as shown for UPt$_3$ in Chapter 6.

The results of performing this background subtraction on the time of flight data on Fe$_{1+y}$Te succeeded in clarifying the curious behavior in this material. On the elastic line ($E = 0$), magnetic order exists in the form of Bragg peaks at the double-stripe antiferromagnetic ordering position $Q = (1/2, 0, 1/2)$ in the single detwinned domain. With increasing energy, no fluctuations are observed in the material until $E = 4$-7 meV (depending on $L$) [47], which corresponds to the energy associated with the single-ion anisotropy of the magnetic iron ions. Above this energy, spin excitations take the familiar form of cones of dispersion emanating from the Bragg peak positions, reminiscent of a classical spin wave. Upon increasing energy through the range 20-30 meV, spin fluctuations quickly relax to a fourfold symmetric pattern, which was unanticipated. Finally, near 250 meV, spin fluctuations reach their band top [73].

For the detwinning experiments in Fe$_{1+y}$Te at both ARCS and MERLIN, stainless steel spring washers were used within the aluminum detwinning manifold to maintain force on the samples at all temperatures, and the springs were covered with neutron absorbing material on the incident neutron side (Cd foil at ARCS and B$_4$C at MERLIN).
Figure 2.4: Background subtraction for neutron time of flight data projected into two dimensional slices with constant energy. (a) Data before background subtraction; (b) Data after a linear filter; (c) Data after a linear and radial filter, which artificially removes the ring-like feature around the origin; (d) Background subtraction using a parabolic fit after statistically removing regions of interest, which preserves the central ring-like feature.
The sample was held in a fixed orientation with the c axis parallel to the incident neutron direction \( \mathbf{k}_i \), leading to a coupling of \( L \) and neutron energy transfer as discussed in Chapter 1. The detwinning ratio of the Fe\(_{1+y}\)Te experiment at MERLIN was at least 75\%, or a 7:1 domain ratio, and 3:1 at ARCS. Because we find the measurements at the elastic line to be somewhat unreliable for the purposes of determining the detwinning ratio exactly, we calculate this number based on the lowest possible energy slice above the spin anisotropy gap that also gives a half-integer value of \( L \), which in this case is \( 13 < E < 16 \) meV at \( L = \frac{3}{2} \), as shown in Fig. 2.5.

![Graph showing detwinning ratio in Fe\(_{1+y}\)Te at MERLIN](image)

**Figure 2.5**: Detwinning ratio in Fe\(_{1+y}\)Te at MERLIN, computed by taking transverse cuts through narrow spin wave dispersion cones at \( 13 < E < 16 \) meV and \( L = \frac{3}{2} \), where appreciable magnetic intensity is found. The detwinning ratio is found to be 75\%, or a 7:1 domain population, and is a lower bound.

Data analysis was carried out by projecting the data into two-dimensional slices at constant energy, and performing background subtraction using the algorithm described
above. The results for various energies across the $E \approx 26$ threshold are shown and described in Figs. 2.6 and 2.7.

The results of these experiments are summarized in Fig. 2.8. We find that the anisotropy between strong and weak domains, which encompass the red and blue diamonds in Fig. 2.1, respectively, falls off dramatically with increasing energy, or with increasing temperature above $T_N$.

To understand the neutron scattering results theoretically, we compare our patterns to those generated within a bilinear biquadratic model by H.-H. Lai and described in detail in [30]. The results show that the pattern emanating from bicollinear order matches the experimental observations at low energy, while the pattern from the plaquette phase matches the observations at an energy scale of 50-60 meV and above. In principle the two magnetic ground states found theoretically would be energetically degenerate in the Hamiltonian at the level considered in this model, but higher-order ring exchange terms should break this degeneracy, as discussed in [74]. We find, then, that the inelastic spin fluctuation spectrum of Fe_{1+y}Te exhibits a sharp crossover near 30 meV between a spin wave-like dispersion at low energies to a bicollinear + plaquette phase with most spectral weight existing in the plaquette phase, consisting of broad ring-like features in momentum space. We note that, significantly, our model and interpretation does not rely on the existence of interstitial iron to polarize neighboring Fe ions in order to stabilize the plaquette phase. Rather, the plaquette phase is shown to be macroscopically competing with the bicollinear ground state above 30 meV.

In terms of the absolute magnitude of the magnetic fluctuations and the size of the fluctuating magnetic moment, previous results on twinned Fe_{1+y}Te showed two components in the dynamical fluctuation spectrum, distinguished by the shape of
Figure 2.6: Time of flight neutron scattering slices with constant energy, from Fe$_{1+y}$Te at MERLIN: 5 K data (at left), 100 K (second from left), 5 - 100 K (second from right), and 100 - 5 K (at right), shown for raw data (top row) and background-subtracted data that has also been smoothed (bottom row). At far left, the projection of this slice through the third $Q$ dimension, in this case $L$, while holding $H = 0$ or $K = 0$. The values of constant energy are (a) $16 < E < 20$ meV and (b) $26 < E < 31$ meV.
Figure 2.7: Similar to Fig. 2.6, with values of constant energy (a) $30 < E < 36$ meV and (b) $45 < E < 55$ meV.
Figure 2.8: Summary of time of flight results in detwinned Fe$_{1+y}$Te, from [30]. (c) Anisotropy of the integrated intensity in the four diamond-shaped zones at $T = 5$ K, from time-of-flight neutron scattering, demonstrating a complete relaxation to fourfold symmetry by $E = 40$ meV. (d) Magnetic fluctuation spectrum for the plaquette position $Q_{PL} = (1/4, 1/4, 0)$ shown as a black hexagon in (b). Fluctuations become nearly isotropic above $E \approx 26$ meV, where the magnetic moment projections along the $a$ and $b$ crystallographic directions become nearly equal. (e) Temperature dependence of the anisotropy between strong and weak zones, as a function of energy. The anisotropy drops off rapidly above 22 meV.
Figure 2.9: Comparison of neutron scattering and bicollinear/plaquette Hamiltonian for Fe$_{1+y}$Te, from [30]. (a-b) Neutron scattering data at $E = 14$ ($E_i = 30$) and $E = 50$ meV ($E_i = 80$), with the central magnetic zone from Fig. 2.1(a) shown in black. (c-d) $S(Q,E)$ calculated with the bicollinear/plaquette biquadratic Hamiltonian, at (c) $\omega=1.7$ (corresponding to approximately 20 meV) and (d) $\omega=7.5$ (approximately 90 meV), showing the correspondence with (a-b). The correspondence between $\omega$, the energy parameter in the calculations, and experimental energy is made by identifying $\omega=20$ as the magnetic band top which lies near 250 meV [73]. (e-f) $S(Q,E)$ calculated with the bicollinear biquadratic Hamiltonian only, at (e) $\omega=1.7$ and (f) $\omega=7.5$, showing a disagreement with (a-b).
their momentum-integrated intensity as a function of energy [16, 75]. By integrating a similar region, our data also exhibits this trend as shown in Fig. 2.10, although we identify the low-energy component with the bicollinear spin fluctuations and the component with higher energy to be associated with the plaquette fluctuations.

![Figure 2.10](image)

Figure 2.10: Total integrated intensity of Fe$_{1+y}$Te from MERLIN data at 5 and 100 K. Since no background subtraction was performed, the lowest pixel was subtracted from each constant energy slice. The data are consistent with previous measurements demonstrating a rapid decay of intensity at $E = 20 - 30$ meV [16, 75]. The difference between 5 K and 100 K data at energies below $\sim 10$ meV is due to the bose factor.

### 2.4 Fe$_{1+y}$Te: neutron triple axis spectroscopy with polarization analysis

To further show consistency between the time of flight neutron scattering results on Fe$_{1+y}$Te and the proposed theoretical model, we conducted triple axis neutron scattering experiments on detwinned Fe$_{1+y}$Te with three-dimensional neutron polarization analysis, producing the results in Fig. 2.1(d). These experiments were carried out at IN20 in the HK0 scattering plane using an array of eight samples in an aluminum...
clamp manifold, and the detwinning ratio was estimated to be at least 3:1 using the inelastic method described above for the time of flight measurements, which was necessary because the HK0 plane does not intersect any magnetic Bragg peaks. Neutron polarization analysis was carried out by measuring neutron spin flip and non-spin flip cross sections at different positions in reciprocal space. As described in Chapter 1, measuring the spin flip cross section in all three polarization channels at multiple equivalent $Q$ can be used to extract the polarization directions of the magnetic moment in the material.

In this experiment, we carry out such measurements at several positions that capture the bicollinear spin wave dispersion at finite energy, revealing the polarization of the dynamical spin fluctuations. Spin wave dispersion, which is gapped up to $E = 4.5$ meV for $L = \frac{1}{2}$, is sufficiently two-dimensional that intensity is observed at $L = 0$ by 7 meV [47]. We observe the expected result that spin fluctuations exist only at the “strong” majority domain, and that they peak at the expected energy of 10 meV and are primarily polarized along the $c$ axis [30]. In addition, we observe that for larger energies, the spin waves stemming from the bicollinear ordered positions become more isotropic and decay in intensity, as shown in Fig. 2.11, which is consistent with the MERLIN data. Near $E = 26$ meV, the intensity of spin fluctuations at the bicollinear position approaches zero. A full determination of the intensity of spin fluctuations in all three polarization dimensions was only carried out below 12 meV, and is not possible from the data in Fig. 2.11 because these two $Q$ represent the bicollinear positions for the majority and minority domains, which are made unequal by the application of uniaxial pressure, and are therefore not equivalent $Q$. More details about the methodology of this experiment, and how the data in Fig. 2.11 was corrected for imperfect detwinning, are described in [30].
Figure 2.11: Polarized neutron scattering from bicollinear positions in Fe$_{1+y}$Te, from [30]. Magnetic fluctuations at the BC positions in the second Brillouin zone, from smoothed-background-subtracted spin flip channel data. Due to the different Q positions, the projections onto the neutron spin coordinate systems in the lower row, based on the smoothed raw data in the upper row, have a different projection onto the crystallographic axes $a$, $b$, and $c$ as noted in the panel titles. In this figure, the data in all panels has been rescaled for the ideal case of 100% detwinning, and therefore shows slightly $c$-axis polarized spin waves emanating from the majority-domain “strong” bicollinear order position $Q_s = (1/2, 1, 0)$ only, and vanishing intensity above $E \sim 25$ meV.
In addition, we carry out measurements at positions equivalent to the plaquette position $Q = (\frac{1}{4}, \frac{1}{4}, 0)$, shown as a black hexagon in Fig. 2.1(a). In this case, the values of $Q$ shown in Fig. 2.12 are equivalent and a resolution of the spin fluctuation intensities along all three crystallographic axes is possible, after smoothing and subtracting the background as described in Chapter 1. We find that the spin fluctuations below $E = 26$ meV are polarized primarily along the $c$ axis, similar to the measurements in the bicollinear positions, and also exhibits stronger fluctuations along the $a$ axis than the $b$ axis. Moreover, at $E = 26$ the fluctuations along the $b$ axis suddenly increase and equal in intensity to fluctuations along $a$. This data confirms that, as seen in scattering patterns in the MERLIN and ARCS time of flight experiments, at the energy scale of $E = 26$ meV spin fluctuations in Fe$_{1+y}$Te quickly relax from spin wave-like cones stemming from the bicollinear ordered positions to broad rings of scattering that are spin-isotropic.

### 2.5 FeSe$_{0.2}$Te$_{0.8}$ and FeSe$_{0.35}$Te$_{0.65}$

Uniaxial pressure experiments were also conducted on two Se-doped members of the FeTe material. These materials do not exhibit a structural transition, but they may exhibit superconductivity with $T_c$ near 10-15 K, and at low Se doping they exhibit a spin glass with short-range ordering [76–78]. Uniaxial pressure was applied using simple clamps in order investigate the influence of breaking lattice symmetry on the spin excitations.

In FeSe$_{0.2}$Te$_{0.8}$, neither magnetic order nor superconductivity exist, but the material shows evidence of a short-range spin glass at $Q = (\frac{1}{2}, 0, L)$. Spin fluctuations had been previously observed at the $Q = (\frac{1}{2}, \frac{1}{2}, L)$ position, which is crystallographically equivalent to the antiferromagnetic ordering wavevector at $Q = (1, 0)$ in the iron
Figure 2.12: Background subtraction process for spin flip channel data at the PL positions $Q_1 = (3/4, 3/4, 0)$ [light colors at left] and $Q_2 = (1/4, 7/4, 0)$ [dark colors at left]. Center and right panels show the calculated magnetic fluctuation projections $M_a$, $M_b$, and $M_c$ along the three crystallographic directions, and background values B1 and B2 at $Q_1$ and $Q_2$, respectively. At right, the solid lines show the assumed actual background from smoothing the raw values. The final values are shown in Fig. 2.8(d).

As such, our goal was to determine whether the uniaxial pressure effect could break the symmetry between the (1,0) and (0,1) directions as it does in BaFe$_2$As$_2$ above the magnetostructural transition. Alternatively, the glassy magnetic order at the Fe$_{1+y}$Te position $Q = (1/2, 0, L)$ could interfere with this mechanism, rendering the uniaxial pressure effect too small to be observed.

A FeSe$_{0.2}$Te$_{0.8}$ sample was cut and situated in an aluminum clamp with uniaxial pressure along the $Q = (1/2, 1/2)$ direction, and aligned in the MACS spectrometer in the $HK0$ scattering plane. The expectation based on iron pnictides is then that the intensity at $Q = (1/2, -1/2)$ and $(-1/2, 1/2)$ will be larger than those at $(1/2, 1/2)$ and $(-1/2, -1/2)$ due to the uniaxial pressure-induced lattice distortion. Measurements were taken such that a full two-dimensional map of spin excitations was collected at three energies $E = 3, 5.5, \text{ and } 8 \text{ meV}$ at base temperature under uniaxial pressure, and
also at 5.5 meV with pressure at 150 K and at base temperature without uniaxial pressure, shown in Fig. 2.13. At 3 meV, the scattering pattern shows peaks near the \((1/2, 0)\) ordering position which is expected from the glassy magnetism at this wavevector. At 5.5 meV, a scattering pattern was observed that is highly reminiscent of the pattern in \(\text{Fe}_{1+y}\)Te at 30-35 meV, as shown in Fig. 2.7. By subtracting the data without pressure from the data with pressure at base temperature, we observe an increase at the expected positions of \(Q = (1/2, -1/2)\) and \((-1/2, 1/2)\), although the statistics are on the border of reliability. Performing the subtraction using the 150 K data with pressure, on the other hand, results in no observed anisotropy. One possible conclusion is that uniaxial pressure induces anisotropy in the magnetic fluctuations at all temperatures, which would explain the observed anisotropy only in the case of changing from small to large uniaxial pressure. However, to prove this with certainty would require a much more systematic experiment, and we have not done so.

To further investigate the uniaxial pressure effect in \(\text{Fe}_{1+y}(\text{Se,Te})\), we carried out experiments on \(\text{FeSe}_{0.35}\)\(\text{Te}_{0.65}\), which does not exhibit a spin glass phase and does exhibit superconductivity. A sample was cut and aligned in the \(HK0\) scattering plane at HB-1, with uniaxial pressure along the \(Q = (1/2, 1/2)\) direction. Energy scans at constant \(Q\) were collected at the spin fluctuation positions \(Q = (1/2, -1/2)\) and \(Q = (1/2, 1/2)\) and anisotropy was observed, initially suggesting an increase of scattering at the expected position. However, constant-energy transverse \(Q\) scans collected at these positions showed no obvious pressure effect. In addition, the sample was found to exhibit some quasi-elastic scattering visible in constant-energy scans at \(E = 1\) meV, so further investigation of the quasi-elastic energy range was not carried out.

To more fully investigate possible symmetry breaking in \(\text{FeSe}_{0.35}\)\(\text{Te}_{0.65}\), we carried
Figure 2.13: Constant-energy scans of FeSe$_{0.2}$Te$_{0.8}$ at MACS with $E = 5.5$ meV, and the angular dependence of the ring passing through the $(\frac{1}{2}, \frac{1}{2})$ position at right.
Figure 2.14: Lack of a uniaxial pressure effect on low-energy spin fluctuations in FeSe$_{0.35}$Te$_{0.65}$ at HB-1 (a) Energy scans suggesting uniaxial pressure-induced symmetry breaking above $E = 6$ meV. (b) Constant-energy scans across the $Q = (-1/2, 1/2)$ (left side) and $Q = (1/2, 1/2)$ (right side) directions, measured in transverse directions along directions diagonal to the $H$ axis but shown here against the $H$ coordinate only. The uniaxial pressure direction is parallel to $(1/2, 1/2)$. The scans suggest no pressure effect.
out further experiments at SPINS. Similar to the HB-1 experiment, the sample was
cut and aligned in the $HK0$ plane and constant-energy scans at $E = 1$ and $E = 6$
meV were taken above and below $T_c \approx 14$ K. Uniaxial pressure was applied through
a stack of aluminum plates tightened very tightly by hand with a screw, and we
estimate a pressure on the order of 100 MPa at all temperatures. No obvious uniaxial
pressure effect was observed, either in the raw data or after subtracting the high
temperature data from the low temperature data, as shown in Fig. 2.15. While the
uniaxial pressure effect remains unresolved in Fe$_{1+y}$(Se,Te), we note that the intensity
gain observed at $E = 1$ meV is actually very different than previously published
results ([78], Fig. 2(c)), where an intensity gain was observed above $T_c \approx 14$ K.
The differences may be due to different interstitial iron content between the samples
studied, and as such presents an interesting opportunity for future experimental work
to relate the microscopic distribution of interstitial iron content to the quasi-elastic
fluctuation spectrum and superconductivity in Fe$_{1+y}$(Se,Te) materials.
Figure 2.15 : Lack of a uniaxial pressure effect on low-energy spin fluctuations in FeSe$_{0.35}$Te$_{0.65}$ at SPINS.
Chapter 3

Controlled uniaxial pressure experiments in iron-based superconductors

In 2015, a clamp-based detwinning experiment was carried out at BT-7 by Y. Song on BaFe$_{1.915}$Ni$_{0.085}$As$_2$, which lies in the underdoped part of the phase diagram and exhibits both antiferromagnetic order with $T_N \approx 45$ K and superconductivity below $T_c \approx 18$ K, in order to investigate the uniaxial pressure-induced effects in this material. What was found was very different from expectations: the detwinning was nearly perfect, but the total integrated intensity at the “strong” majority-domain position in the magnetically ordered state was much larger than the sum of intensities at both the “strong” and “weak” minority domain positions under zero-pressure conditions. This situation, depicted in Fig. 3.1, suggested that the tunability of magnetic order could be a possible new degree of freedom previously unknown in the iron superconductors. However, this particular experiment was somewhat unreliable, as it was carried out in the superconducting state, where the intensity of magnetic neutron scattering is known to change due to the formation of superconducting spin singlets because they are no longer unpaired electrons and thus do not participate in magnetic neutron scattering. In addition, this experiment was conducted at a single value of uniaxial pressure that was known only very approximately, so it was not known if the results could be reproduced. Finally, it could not be proved that uniaxial pressure was having an effect on the microscopic electronic structure, or simply increasing the magnetically ordered sample volume, perhaps by causing regions near defects or grain boundaries.
to condense into a magnetic ground state where under zero applied stress they could not.

Figure 3.1: Uniaxial pressure dependence of the magnetic peaks in BaFe$_{1.915}$Ni$_{0.085}$As$_2$ at BT-7, demonstrating an overall increase of the neutron scattering intensity under uniaxial pressure. The results were later shown to be due to a pressure-induced increase of the magnetic ordered moment.

To fully understand the uniaxial pressure dependence of BaFe$_{1.915}$Ni$_{0.085}$As$_2$, we carried out experiments under controlled unaxial pressure using several techniques. Firstly, a clamp and spring was used as a crude method of tuning the pressure in BaFe$_2$As$_2$, where we found the material can be detwinned near 10 MPa, and that for larger pressures $T_N$ continues to increase. For BaFe$_{1.915}$Ni$_{0.085}$As$_2$ we designed and built a compressed-air based instrument which could tune the applied pressure to better than 1 MPa and maintain constant stress for all temperatures. Crucially, this instrument was designed for use in transport measurements and neutron scattering, as well as $\mu$SR, which was necessary to address the volume fraction issues. This instrument was considerably successful in determining that the ordered magnetic moment does increase microscopically under uniaxial pressure, which was confirmed
by further $\mu$SR experiments on Ba(Fe$_{0.95}$Co$_{0.05}$)$_2$As$_2$. The instrument has subsequently been used to study the effects of controlled uniaxial pressure in other systems, and in this chapter, I report additional studies on the magnetic moment of several doped BaFe$_2$As$_2$ and SrFe$_2$As$_2$ compounds under in-plane pressure, as well as neutron and transport studies of BaFe$_2$(As,P)$_2$ and Sr$_3$Ru$_2$O$_7$. Additional experiments were carried out with this instrument on the effect of uniaxial pressure on the magnetostructural phase transitions and symmetry breaking in the high-temperature phases of BaFe$_2$As$_2$, SrFe$_2$As$_2$, and Fe$_{1+y}$Te, and are reported in Chapter 4. Finally, controlled uniaxial pressure experiments were also carried out on Ba(Fe,Ni)$_2$As$_2$ under $c$-axis uniaxial pressure at MIRA using their helium bellows uniaxial pressure instrument which was introduced in Chapter 1. I also discuss our ongoing development efforts for new methods to apply uniaxial pressure, including ideas for soft materials, detwinning devices for materials with $T_s$ above room temperature, and a new uniaxial instrument that will be capable of performing fixed-stress and fixed-strain experiments for large, neutron scattering sized samples, a development that may well unlock new degrees of freedom in iron superconductors and other unconventional systems.

### 3.1 BaFe$_2$As$_2$, P∥(100)$_O$

BaFe$_2$As$_2$ was studied at five values of uniaxial pressure in a neutron diffraction experiment at HB-1A. The values of the “strong” peaks, labeled $Q = (0,1,1)$ and $(0,-1,-1)$ with uniaxial pressure applied parallel to $(1,0,0)$, are shown in blue in Fig. 3.2(a). The temperature and pressure dependence of the nuclear $(2,-2,0)$ peak is also shown, which shows a decrease in intensity below $T_N \approx$ 140 K due to multiple scattering processes. This is understood to occur when the outgoing neutron momentum is in the direction of an allowed nuclear peak, as it is in the case of twinned BaFe$_2$As$_2$, ...
which allows the sample to easily re-scatter the neutron [43]. The methods for estimating the uniaxial pressure values and the associated error values are fully described in [29].

Figure 3.2: Uniaxial pressure dependence of the magnetic and structural peaks in BaFe$_2$As$_2$

3.2 $T_N$ shift of BaFe$_2$As$_2$ and BaFe$_{1.915}$Ni$_{0.085}$As$_2$, $P\parallel(100)_O$

We also found that the magnetic ordering temperature $T_N$ in BaFe$_2$As$_2$ is increased under uniaxial pressure by about 4 K under approximately 16 MPa, or 0.22 K/MPa.
when considering the best fit to several pressures. Since the lattice distortion is on the order of 0.1%, it is perhaps surprising that the system should become so much more susceptible to magnetic ordering so as to effect an increase at a temperature higher by 3%. The $T_N$ shift and methods for determining its value numerically are shown in Fig. 3.3, along with the very similar $T_N$ shift observed in BaFe$_{1.915}$Ni$_{0.085}$As$_2$ discussed below. The vertical error bars, representing the error of the measured $T_N$ shift, were computed by using four different methods to calculate the shift, and using the difference between the methods as the error. The methods are described in detail in the supplementary material of [29].

To understand how an increase in magnetic susceptibility can arise from the application of uniaxial pressure in the paramagnetic phase in BaFe$_2$As$_2$ and BaFe$_{1.915}$Ni$_{0.085}$As$_2$, I carried out calculations of the static RPA spin susceptibility according to the formalism discussed in Chapter 1. Models with and without lattice distortion were generated by T. Berlijn using density functional theory, with $\delta_{ab} \equiv (a - b)/(a + b) \approx 0.0013$ which is taken from neutron Larmor diffraction measurements [36]. To model BaFe$_{1.915}$Ni$_{0.085}$As$_2$, we use the model for BaFe$_2$As$_2$ and apply a rigid band shift of about 58 meV, which gives the expected electronic filling factor for this doping. We choose $U = 1.23$ eV for BaFe$_2$As$_2$ and $U = 1.32$ eV for BaFe$_{1.915}$Ni$_{0.085}$As$_2$, just below the divergence of $\chi_{\text{RPA}}$ in both cases. The calculations are performed at the experimentally observed values of $T_N$ for the two compounds. We found that the lattice distortion induced by uniaxial pressure creates a qualitative change in the Fermi surface geometry that is depicted, along with the change in RPA spin susceptibility, in Fig. 3.4.

A microscopic mechanism leading to a higher $T_N$ under uniaxial pressure must arise from either (a) better nesting between the Fermi surfaces connected at the
Figure 3.3: Uniaxial pressure dependence of $T_N$ in BaFe$_2$As$_2$ and BaFe$_{1.915}$Ni$_{0.085}$As$_2$, from [29]
Figure 3.4 : Fermi surfaces and RPA spin susceptibility in BaFe$_2$As$_2$ and BaFe$_{1.915}$Ni$_{0.085}$As$_2$ under uniaxial strain, with $x$ in BaFe$_{2-x}$Ni$_x$As$_2$ representing doping. (a-b) The Fermi surfaces are offset with a rigid band shift to achieve the stated doping. (c-d) RPA spin susceptibility under strain for both dopings, in orthorhombic units, and (e-f) the differences attributed to the strain effect through direct subtraction of tetragonal models, which in both cases shows at enhancement at (1,0) and (0,1) as well as a symmetry breaking preferring the (1,0) position.
antiferromagnetic $Q = (1, 0, 1)$, and/or (b) a redistribution of the orbital content contained within the Fermi surface states due to pressure, resulting in larger matrix elements connecting electronic states separated by $Q = (1, 0, 1)$. To investigate which of these scenarios is responsible, we make an adjustment to the calculation of the bare spin susceptibility wherein the matrix elements are simply removed, yielding (cf. Eq. 1.6 in Chapter 1):

$$\chi_{FS}^0(q, \omega = 0) = -\frac{1}{N_{Fe}N_k} \sum_{k, \mu\nu} \frac{1}{E_\mu(k) - E_\nu(k+q) + i\delta} \left( f[E_\mu(k), kT] - f[E_\nu(k+q), kT] \right).$$

(3.1)

For the calculations with orbital matrix elements removed (set to 1), we find a roughly equal enhancement of $\sim 1\%$ at both strong and weak Bragg positions, whereas with the matrix elements included, we find a symmetry breaking that is further enhanced by RPA interactions. The results are summarized in Table 3.1.

With this information, we conclude that the increase in $T_N$ in both compounds is mostly due to an enhancement of the Fermi surface nesting condition under uniaxial pressure, while the changes in the orbital weights due to uniaxial pressure account for the asymmetry between $Q_{\text{strong}}$ and $Q_{\text{weak}}$.

### 3.3 Pneumatic uniaxial pressure instrument

The uniaxial pressure dependence of BaFe$_{1.915}$Ni$_{0.085}$As$_2$ was further investigated at HB-1A using a compressed-air based uniaxial pressure instrument, to which a manual is appended at the end of this work. This instrument was developed in two “generations” with slightly different mechanical components and designs. The generation-1 instrument is described in Fig. 3.5, while the generation-2 instrument
Table 3.1: Peak values of bare and RPA susceptibility in uniaxially-strained BaFe$_2$As$_2$ and BaFe$_{1.915}$Ni$_{0.085}$As$_2$.

<table>
<thead>
<tr>
<th></th>
<th>AFM peak</th>
<th>Without $a(k)$</th>
<th>With $a(k)$</th>
<th>$\chi_{RPA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x=0$</td>
<td></td>
<td></td>
<td></td>
<td>(U=1.23)</td>
</tr>
<tr>
<td>P=0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{strong}}$</td>
<td>1.0063</td>
<td>1.8205</td>
<td></td>
<td>58.3</td>
</tr>
<tr>
<td>$Q_{\text{weak}}$</td>
<td>1.0155 (+0.9%)</td>
<td>1.8464 (+1.4%)</td>
<td>144 (+147%)</td>
<td></td>
</tr>
<tr>
<td>$x=0.085$</td>
<td></td>
<td></td>
<td></td>
<td>(U=1.32)</td>
</tr>
<tr>
<td>P=0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{strong}}$</td>
<td>0.9563</td>
<td>1.7174</td>
<td></td>
<td>55</td>
</tr>
<tr>
<td>$Q_{\text{weak}}$</td>
<td>0.9642 (+0.8%)</td>
<td>1.7362 (+1.1%)</td>
<td>95 (+73%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

is shown in Fig. 3.6 and following. The key operating principle is the same in both generations. Force is applied on the sample through concentric stainless steel tubes, using a compressed air linear thruster outside the cryostat that is controlled by an electronic gas regulator. As the gas pressure is increased, the inner tube gets pushed closer to the sample, with the force balanced by a large spring also outside the cryostat. Once in contact with the sample, the force in the inner tube is monitored in real time (with millisecond resolution) using a load cell, located outside the cryostat but inside the same vacuum space as the sample (to account for changes in vacuum pressure). By closing a negative feedback loop between the desired setpoint and the measured force, the system can maintain controlled constant force conditions at all temperatures, taking into account careful measurements of the sample under study to convert from force to effective pressure. At ORNL, we integrated the hardware with the beamline control systems so that users could change the setpoint automatically.
from within the same script used to control the spectrometer, while at TRIUMF, users could control the setpoint over the intranet using the local CAMP environment. This instrument can also be adapted for controlled uniaxial tension, although such experiments have not yet been performed in a particle scattering experiment. An operating manual for these instruments, including component specifications, drawings, operating principles, and other key information, is given in the Appendix.

One key difference between the designs involves the sample holder. In the generation-1 instrument, an attachment was installed on the end of the sample stick that allowed the overall length of the stick to be adjusted to coincide with the center of the neutron beam. In the second design, the sample is held in place against a plate that can itself be moved up and down the sample stick in discrete increments of 1/8 inch. This dramatically improves the efficiency of preparing the instrument for an experiment, while removing aluminum mass from the beam, which lowers the background.

3.4 Neutron diffraction on BaFe$_{1.915}$Ni$_{0.085}$As$_2$ with P$(\parallel$100)$_O$

The uniaxial pressure dependence of the elastic magnetic Bragg peaks in BaFe$_{1.915}$Ni$_{0.085}$As$_2$ was measured at HB-1A and the results were found to agree with the previous measurements at BT-7. To change the pressure, we first increase the temperature well above $T_s$ in order to take advantage of the natural structural phase transition in detwinning the material, rather than trying to force domains to switch orientation at low temperature. We fine the intensity of the strong peak increases to a value more than double its original intensity, in agreement with the BT-7 experiment. Since the sample is mounted in the $H0L$ scattering plane in order to apply top-down pressure in the cryostat along a sample edge, we cannot access the weak peak. The superconducting $T_c$ was also observed to decrease systematically with pressure. These
Figure 3.5: Drawings and photos of the generation-1 compressed air-based uniaxial pressure instrument used to investigate BaFe$_{1.915}$Ni$_{0.085}$As$_2$ at HB-1A and M20.
Figure 3.6: Drawings and photos of the generation-2 compressed air-based uniaxial pressure instrument used to investigate BaFe$_{1.915}$Ni$_{0.085}$As$_2$ at HB-1A and M20.
Figure 3.7: Generation-2 uniaxial instrument in PPMS and orange cryostat
results are summarized in Fig. 3.8.

Figure 3.8: Uniaxial pressure dependence of the (1,0,3) strong magnetic peak in BaFe$_{1.915}$Ni$_{0.085}$As$_2$ at HB-1A, from [29]. The left side shows rocking scans while the right side shows temperature scans.

We also experimented with applying stress within the low-temperature phase, where one may directly study the stress-strain relationship of this material. We find the modulus of this material becomes considerably harder within the superconducting state, as depicted in Fig. 3.9. At 22 K, above the superconducting phase, the sample appears to totally relax to the unstrained (but still likely detwinned) state. Interestingly, when the pressure is released from 40 MPa to nearly 0 at 2 K, scattering from the (1,0,3) magnetic Bragg peak only relaxes to its value under zero-stress conditions at 20 K above the superconducting $T_c$. This suggests that the temperature scale for superconductivity in the BaFe$_2$As$_2$ system is exactly correlated with a hardening of the lattice. I suggest this effect warrants further investigation to determine whether the inelastic phonon fluctuation spectrum has also changed.
Figure 3.9: In-situ measurements of the stress-strain relationship and the effect of releasing pressure at $T = 2$ K in BaFe$_{1.915}$Ni$_{0.085}$As$_2$. The temperature at which the lattice returns to its zero-pressure state appears to be exactly coincident with the superconducting $T_c$. 
3.5 $\mu$SR experiments on BaFe$_{1.915}$Ni$_{0.085}$As$_2$ and Ba(Fe$_{0.95}$Co$_{0.05}$)$_2$As$_2$

with $P \parallel (100)_O$

Figure 3.10: Sample stick with GaAs wafer behind the sample window, used to align the instrument at M20.

To investigate whether uniaxial pressure promotes magnetic order in BaFe$_{1.915}$Ni$_{0.085}$As$_2$ microscopically, or simply enlarges the volume of the sample that is magnetic, $\mu$SR experiments were conducted using the compressed air-based uniaxial pressure instrument at M20. The sample was mounted behind a mask made of unalloyed (1000 series) aluminum, which contributes a perfectly paramagnetic background that was found to be more than 50% of the signal. At the beginning of the experiment, the sample was aligned with the muon beam by temporarily covering the inside surface of the aluminum mask (on the side facing away from the beam) with a high-purity GaAs wafer, which quickly depolarizes the muons due to muonium formation. The setup
for alignment is shown in Fig. 3.10. The alignment was performed by moving the position of the entire cryostat.

Since magnetic order in BaFe$_{1.915}$Ni$_{0.085}$As$_2$ is highly disordered, a fast relaxation of the muon asymmetry was observed, as described in Chapter 1. The decay width constant $\lambda$ was shown to increase with uniaxial pressure, suggesting an increase in the internal magnetic field consistent with the neutron diffraction measurements. Crucially, weak transverse field measurements were also carried out, and demonstrate that the sample volume fraction is not changing with pressure, confirming that the neutron intensity gain is indeed due to an increase in the magnetic ordered moment. The volume fraction data also show that the distribution of $T_N$ in the sample is broadened with increasing pressure, consistent with a distribution of pressure. The results are summarized in Fig. 3.11(a).

To determine the robustness of the conclusion that uniaxial pressure increases the ordered magnetic moment in the electron-doped BaFe$_2$As$_2$ system, $\mu$SR experiments were also performed on the Co-doped material Ba(Fe$_{0.95}$Co$_{0.05}$)$_2$As$_2$, which is similar to BaFe$_{1.915}$Ni$_{0.085}$As$_2$ but closer to the parent compound, with higher $T_N$ and larger magnetic moment in the unstrained case [79]. The larger moment and smaller degree of disorder in this material qualitatively changes the shape of the $\mu$SR asymmetry such that a well-defined oscillation is observed, as shown in Fig. 3.11(b). This provides a platform for directly observing an increase in frequency which would be unambiguously tied to an increase of the internal magnetic field under strain.

The second-generation instrument was designed to fit inside the low-background insert for the MSPIGGY cryostat, which contains extra scintillators directly behind the sample to reject muons that pass through without being stopped. The narrow space inside this insert required a significant reduction in the tube diameter, which
Figure 3.11: $\mu$SR results for (a) $\text{BaFe}_{1.915}\text{Ni}_{0.085}\text{As}_2$ and (b) $\text{Ba(Fe}_{0.95}\text{Co}_{0.05})_2\text{As}_2$, demonstrating an increase of $T_N$ under pressure, as well as of the local internal field at the muon stopping site, as evidenced by the increase in relaxation rate in (a) or fast frequency component in (b). The small peak above the starting asymmetry at very short times in (b) represents the fact that the incident muon polarization is apparently not exactly parallel to the angle of the detectors and in fact at short times the muon spin rotates into the direction along the detector axis.
was found to be lighter and was adopted for all the sample sticks in the new design. In fact, the low-background port plug on the uniaxial stick did not fit exactly, due to a miscommunication about which face was the sealing surface which caused me to machine the curved edges too roughly. This issue was discovered when the sample space was evacuated and the helium reliquifier quickly indicated that atmospheric constituents were entering the loop. To overcome this issue, we added a thick o-ring, and we supported the heavy end of the instrument, containing the thruster and electronics equipment, with a jackstand to achieve an exact mating condition between the two parts, which fortunately was found to hold vacuum. We also monitored the liquifier carefully each time a new sample was loaded. Nevertheless, we found only a modest gain in signal fidelity of less than 50% using the low-background insert, since to be rejected a muon must “miss” the sample, but we require large jaws directly against the sample to apply uniform uniaxial pressure. We did our best to file off extraneous parts of the sample holder to allow muons to pass, but many were still landing in the paramagnetic aluminum sample holder.

The Ba(Fe$_{0.95}$Co$_{0.05}$)$_2$As$_2$ material was found to be doped strongly enough that the moment increase was indeed observed, and, as such, rejected the already implausible hypothesis that the moment increase could be particular to doping with Ni. The results and some raw data are shown in 3.11, with more details described in [29].

Finally, the overall summary of the BFA system is shown in Fig. 3.13. The phase diagram is captured by dynamical mean field theory (DMFT) calculations carried out by Z. P. Yin on the detwinned system, in which magnetism is modeled as an impurity problem in an average local field and the system is solved self-consistently. DMFT captures both the ordered moment increase (Fig. 3.13(a)(f) and (b)(g)) in Ba(Fe,Ni)$_2$As$_2$. Thus, DMFT is an excellent technique for elucidating and confirming
Figure 3.12: The author, Sky Cheung, and Donald Arseneau horsing around at M20 after inserting the first-generation compressed air-based uniaxial pressure instrument into the cryostat.

The plausibility of our experimental results. The upward $T_N$ shift is shown in Fig. 3.13(b)(h), and was explained by RPA calculations described above.

3.6 $\mu$SR experiments on BaFe$_{1.94}$Ni$_{0.06}$As$_2$ and Sr(Fe$_{0.93}$Co$_{0.07}$)$_2$As$_2$

with $P\parallel(100)_O$

The generation-2 compressed air-based uniaxial pressure instrument was also used to investigate the ordered magnetic moment and volume fraction of two other electron-doped iron pnictides at M20 using the same setup as with Ba(Fe$_{0.95}$Co$_{0.05}$)$_2$As$_2$. In BaFe$_{1.94}$Ni$_{0.06}$As$_2$, we found no statistically significant pressure dependence of the fast cosine frequency, the same parameter that was observed to change in Ba(Fe$_{0.95}$Co$_{0.05}$)$_2$As$_2$, although in this experiment the raw data does seem to suggest a frequency increase to the eye, which suggests the data analysis could still be refined. In Sr(Fe$_{0.93}$Co$_{0.07}$)$_2$As$_2$, 

Figure 3.13: Summary of uniaxial pressure effects on the phase diagram of the BaFe$_2$As$_2$ system, from [29], where $x$ represents the doping level in BaFe$_{2-x}$Ni$_x$As$_2$. 
a change was detected especially at the largest pressure (50 MPa), but more data would need to be taken to definitively confirm this result. These results are summarized in Fig. 3.14.

Figure 3.14 : μSR results for (a) BaFe$_{1.94}$Ni$_{0.06}$As$_2$ and (b) Sr(Fe$_{0.93}$Co$_{0.07}$)$_2$As$_2$

3.7 Neutron diffraction on Sr(Fe$_{0.945}$Co$_{0.055}$)$_2$As$_2$ with P$\parallel$(100)$_O$

The generation-2 uniaxial pressure instrument was used to study the detwinning ratio, magnetic moment, and $T_N$ shift of Sr(Fe$_{0.945}$Co$_{0.055}$)$_2$As$_2$ with neutron diffraction at HB-1A. This material is antiferromagnetic with $T_N \approx 115$ K, and does not appreciably superconduct, placing it in a regime analogous to a doping between the BaFe$_2$As$_2$ and Ba(Fe$_{0.95}$Co$_{0.05}$)$_2$As$_2$ samples studied earlier. As shown in Fig. 3.15(a), the $T_N$ shift was found to increase from 115 to 125 K under 50 MPa, which is a relative change of $\Delta T_N/T_N \approx 9\%$, similar to what was observed in parent compound BaFe$_2$As$_2$. However, since the samples were not annealed, we expect a broader distribution of domains and local doping levels in this sample compared to the BaFe$_2$As$_2$ samples studied, as well as the existence of internal stress lines between these micro-domains,
which could diminish the effects of externally-applied stress. The inefficacy of external stress is also demonstrated by the fact that we did not even observe full detwinning of the magnetic Bragg peaks at 50 MPa (Fig. 3.15(c)). However, releasing the pressure at base temperature pressure results in the material nearly holding the same Bragg peak intensity as the fully pressured state (Fig. 3.15(b)), much different from the case of BaFe$_{1.915}$Ni$_{0.085}$As$_2$.

Toward the end of this experiment we found sharp peaks in the order parameter near 65 K that we realized was due to the formation of nitrogen ice, the exact situation and sample (!) reported in Ref. [80]. Hence, the sample space was not fully sealed against the atmosphere outside and the buildup of ice could have conducted some of the applied stress around the sample (enlarging the area over which fixed stress was applied). Although this is not expected to have an effect on the detwinning ratio, since ice would not form until after the sample crossed $T_s$ into the low-temperature orthorhombic phase, a reduced force on the sample due to ice buildup might additionally explain the difficulty of applying perturbative stress on the lattice in this phase.

### 3.8 BaFe$_{1.915}$Ni$_{0.085}$As$_2$, $P\parallel(001)$

The effect of $c$-axis uniaxial pressure in BaFe$_{1.915}$Ni$_{0.085}$As$_2$ was investigated at MIRA using the helium bellows instrument installed at that spectrometer that was described at the beginning of Chapter 1. Since pressure along this axis does not break the tetragonal symmetry, we found it worthy to study the effect of changing the lattice shape without changing symmetry. We conducted temperature scans at the $Q = (1, 0, 1)$ antiferromagnetic ordering position, since the stronger peak at $(1,0,3)$ was not accessible with the limited range of inclination angle of the spectrometer, for uniaxial
Figure 3.15: Uniaxial pressure dependence of $T_N$ (upper panel in (a)) and the detwinning effect (lower panel in a and b) in Sr(Fe$_{0.945}$Co$_{0.055}$)$_2$As$_2$ from neutron diffraction at HB-1A. The values with $P < 0$ indicate pressure released at base temperature.
pressure values of 3, 10, 25, 50, and 80 MPa. We find no $T_N$ shift or detwinning effect, but rather what appears to be a strong suppression of superconductivity at 80 MPa, as shown in Fig. 3.16. Alternatively, one could state that we find an increase of the magnetic ordered moment in the superconducting phase. Whether this corresponds to a loss of superconductivity or a qualitative change in the relationship between magnetism and superconductivity could serve as a launching point for future experiments.

![Graph showing superconductivity data](image)

Figure 3.16: Total suppression of superconductivity under 80 MPa uniaxial pressure along (0,0,1) in BaFe$_{1.915}$Ni$_{0.085}$As$_2$ at MIRA, with no change in the magnetic intensity and no evidence for a detwinning effect or $T_N$ shift.

### 3.9 Metamagnetism under strain in Sr$_3$Ru$_2$O$_7$ with $P\parallel$(001):

resistivity and neutron scattering

The last neutron scattering experiment reported in this work concerns an incommensurate antiferromagnetic ordered phase at high magnetic field of 7.95 T and temperatures below 1 K in the layered metamagnet Sr$_3$Ru$_2$O$_7$ that was discovered using neutron diffraction [81]. Between $B = 7$ T (70000 G) and 9 T, with a center near 8 T, the Ru
spins undergo a continuous crossover in magnetization state, observed in resistivity \[82\] and magnetization \[83\], in a cooperative effect termed metamagnetism. We proposed to study the effects of uniaxial pressure on this material because it is known that the RuO octahedra are rotated by 6.1 degrees with respect to the lattice \[84\] while the in-plane symmetry is also spontaneously broken in the presence of an off-axis magnetic field \[85\]. By applying \( c \)-axis uniaxial pressure, we expected to further rotate the octahedra and stabilize magnetic order, resulting in a qualitative change in the inelastic fluctuation spectrum above the antiferromagnetic ordered phase.

Large Sr\(_3\)Ru\(_2\)O\(_7\) single crystals were grown and aligned using x-ray Laue diffraction by P. Li at Tulane University. Initial measurements of the \( H \) field dependence of the resistivity under uniaxial pressure were promising: at low temperatures and uniaxial pressure of 20 MPa, a splitting is clearly observed between the \( a \) and \( b \) axis directions that is maximized near \( H = 7.95 \) T (Fig. 3.17).
Figure 3.17: In-plane symmetry breaking due to $c$-axis uniaxial pressure in the resistivity of Sr$_3$Ru$_2$O$_7$ near 8 T.
Neutron scattering was carried out at HB-1A in the \( HK0 \) scattering plane with the Mag-E cryostat applying a \( c \)-axis field of \( B = 0 \) to 8 T. Our generation-2 compressed air-based uniaxial pressure instrument was used to apply controlled pressure along the \( c \)-axis, using a stick specially designed for the Mag-E sample space. Samples were coaligned using the neutron alignment station and glued into a stacked with small amounts of diluted superglue. Measurements were conducted at \( T = 1.7 \) K and 15 K, with HB-1A in an inelastic configuration with energy transfer of 1.2 meV, which was as close as possible to the elastic \( E = 0 \) condition given the energy resolution of the spectrometer. Constant-energy scans across the expected magnetic ordering position (Fig. 3.18) do not show a clear uniaxial pressure effect. Although there appears to be a qualitative change between applied pressures of 50 and 100 lbf in these scans (approximately 15 and 30 MPa in the samples, respectively), the final scan at 100 MPa with \( T = 15 \) K appears to be the same as the scan at low temperature, suggesting this is a background effect. Our experiments suggest that any magnetic processes contributing to the resistivity anisotropy under pressure near \( B = 8 \) T have an upper bound of 1.2 meV. However, since the experiment produced no reliable results, we conclude that further experiments are necessary to understand the inelastic fluctuation spectrum of the antiferromagnetic state in \( \text{Sr}_3\text{Ru}_2\text{O}_7 \).

### 3.10 Transport studies on \( \text{BaFe}_2(\text{As}_{0.70}\text{P}_{0.30})_2 \) with \( \text{P} \parallel (001) \)

I also show results of transport experiments on optimally-doped \( \text{BaFe}_2(\text{As}_{0.70}\text{P}_{0.30})_2 \) conducted by D. Hu using the generation-2 uniaxial instrument, shown in Fig. 3.19. This result is important because it demonstrates a novel way that uniaxial pressure interacts with the iron pnictide materials, which is that compression along the \( c \) axis does not change the \( c \) lattice constant, as one would first expect. Instead, it
promotes the in-plane orthorhombicity through bringing the Ba ions closer together and expanding the unit cell dimensions in the basal plane. This has the counterintuitive effect of decreasing the effective bond angle between Fe and As ions, thus moving the system to the left on the phase diagram as described in Ref. [86].

3.11 Transport studies on BaFe$_2$As$_2$ with P\|$\,(110)_O$

Transport experiments on BaFe$_2$As$_2$ and SrFe$_2$As$_2$ with pressure along the orthorhombic axes are discuss in Chapter 4 in the context of the nematic phase. Uniaxial pressure was also applied to BaFe$_2$As$_2$ along the direction diagonal to the detwinning direction, the (1,1,0) direction in orthorhombic units, or (1,0,0) in tetragonal (high-temperature) notation. The results are shown in Fig. 3.20. We find only very small changes in $T_N$ of at most 1 K under 40 MPa, which is what was expected because the in-plane symmetry should not be affected by pressure in this direction. We also observe that the resistivity anisotropy for temperatures immediately above and below $T_N$ does
not vary monotonically with the pressure. However, we note a remarkable effect at temperatures below $T_c \approx 20$ K, which is a large symmetry breaking between the $(1,1,0)$ and $(1,-1,0)$ directions. This effect could indicate a coupling between superconductivity and the $d_{xy}$ orbitals of $\text{BaFe}_2\text{As}_2$. More details about the mechanism of orbital selectivity are described in Chapter 5.

### 3.12 Future directions for uniaxial pressure

I conclude this chapter with a discussion on future uniaxial pressure experiments and methods. Our compressed air-based instrument is based on a design goal of 100 lbf, which achieves $\sim 50$ MPa on large single crystals appropriate for neutron scattering and $\mu$SR. In addition, it operates by applying controlled uniaxial stress, not strain. (In the experiments reported in this work, all stress has been compressive, although our instrument is also capable of applying tensile stress.) Of course, it is often worthwhile to investigate uniaxial pressure effects in different parameter regimes, such as the
Figure 3.20: Resistance of BaFe$_2$As$_2$ with uniaxial pressure along the (110) orthorhombic axes.

transport properties, where very small crystals are ideal, and under conditions of large and controlled strain, where an instrument such as the piezo-based yoke from Razorbill is wholly appropriate. Additionally, as pointed out in [87], the order parameter of a true electron nematic phase is divergent only in the case of constant strain, not constant stress.

Perhaps the most relevant observation for new directions in uniaxial pressure instruments is that varying the applied stress can result in very different values
or strain depending on the material properties under test, as discussed above for experiments with pressure applied and released in situ at low temperatures (Fig. 3.9). Therefore, building on our compressed air instrument, and with neutron scattering and \( \mu \)SR in mind, we are now in the process of developing a similar instrument capable of applying fixed strain. This new instrument, which we call generation-3, operates with a commercial thruster that is based on a coupled stepper motor and thus utilizes all electric power, without the need for compressed air. The design features are summarized in Fig. 3.21. M. Klemm and I are presently working to finish developing the software for this instrument.

Still, there are some samples, and experimental probes, that cannot be satisfied with a design like our uniaxial pressure instruments. One example is the case where one desires large crystals for neutron scattering, but the sample is extremely soft and would be crushed in our instrument. T. Chen, in our group, performed uniaxial pressure experiments in a neutron beam by gluing FeSe with hydrogen-free glue on a substrate consisting of pieces of BaFe\(_2\)As\(_2\) which were themselves detwinned with a clamp and spring [88]. The experiments show that FeSe achieves rotational anisotropy through partial detwinning induced by the detwinning of the BaFe\(_2\)As\(_2\) substrate, a situation that could not be achieved with the direct application of uniaxial pressure to FeSe because that material is extremely soft. This method, though very successful, relies on the specific properties of these two materials, since the anisotropy of spin fluctuations in FeSe can only be reliably measured from the energy of its spin wave gap, near 4 meV, up to the spin wave gap of detwinned BaFe\(_2\)As\(_2\), near 15 meV, which fortunately is the region of interest for studying the effect of spin fluctuations on superconductivity in FeSe.

Also to this example of soft materials, we conducted experiments using our generation-
Figure 3.21: Overall design and photo of generation-3 uniaxial pressure instrument
2 instrument on the alloy SSe developed by S. Susarla in the group of P. M. Ajayan at Rice. The interest in this material stems from its unique combination of high dielectric constant and high flexibility: under uniaxial pressure of 1 MPa, this material deforms into a flat wafer in a matter of minutes. Nevertheless, we were able to perform Raman scattering experiments at several pressures, during the short window of time while the sample was collapsing, finding an increase in the Raman mode frequency with pressure that was attributed to a bond angle between S and Se that also contributes to a shape memory effect in this material [89].

SSe is barely rigid enough to withstand values of uniaxial pressure of the order of 1 MPa, a pressure considered very small in the paradigm of iron-based superconductors; still other materials cannot withstand even these conditions. We attempted to measure the uniaxial pressure effect in the spin liquid candidate RuCl₃, but this material was found to be extremely soft, like butter; direct application of uniaxial pressure squishes it, as does touching the sample with a pair of tweezers. To apply uniaxial pressure to these materials, we have imagined a scenario where the sample could be constrained in a finite sample volume, such as at the bottom of a tube, which keeps the sample from squeezing out the sides while pressure is applied along the axial direction. But this is not uniaxial pressure at all: by confining the material, uniaxial pressure is converted in hydrostatic pressure. Nevertheless, there may be intermediate situations where a material might retain enough of a ragged edge along directions transverse to the pressure that the pressure is neither uniaxial nor hydrostatic, but a combination of these, so that the uniaxial component could be extracted by comparison with totally hydrostatic experiments.

At the other extreme, cuprate superconductors require a large uniaxial pressure at temperatures above room temperature. To detwin YBCO, we developed a device
that could work inside a tube furnace. The design, shown in Fig. 3.22 consists of a long stainless steel clamp where the spring is situated at the cold end of a tube furnace so that ordinary music wire springs or other materials could be used. In this device, the clamp may be used with many different springs depending on the desired uniaxial pressure. To test this device in preparation for uniaxial pressure experiments, our collaborator R. Hunt at ORNL annealed a single crystal specimen of YBCO in this device in an oxygen atmosphere and temperature sufficient to optimally dope the oxygen to approximately 6.5 holes per formula unit, which is near 675°C [90]. Resistivity data collected from this sample under controlled uniaxial stress is shown in Fig. 3.23, and although not of the best quality, indicates that a uniaxial pressure effect probably exists in this material. We look forward to conducting neutron scattering measurements on the inelastic fluctuation spectrum of YBCO.

Finally, in our group we have begun to develop clamps for applying uniaxial pressure under the conditions for large samples in a magnetic moment experiment capable of operating the VSM (vibrating sample magnetometer) insert for the PPMS. As its name suggests, the VSM vibrates the sample and measures the oscillations in a pickup coil, from which one can measure the magnetic susceptibility. Uniaxial pressure clamps or substrates for this instrument must be lightweight and capable of fitting inside a tiny straw with an inner diameter near 3 mm. One method that is being investigated involves gluing samples onto a fiberglass-impregnated substrate where the fibers are oriented uniaxially, giving rise to anisotropic strain when the material is cooled, which has so far been used effectively by X. Lu. Another method, based on an argument which to my knowledge was first presented in [91], is to use any plastic substrate but only glue the sample in two points, so that the overall two-dimensional contraction of the substrate only contracts the sample along one
direction. In the case of teflon, which is hydrogen-free, this method could easily work for neutron scattering experiments. A conceptually simpler but actually quite difficult method is to build a small clamp, with an even smaller spring, which would fit inside the VSM straw. I did manage to build such a clamp, but it did not apply enough uniaxial pressure to fully detwin BaFe$_2$As$_2$, according to measurements of $T_N$ through the sample magnetization. X. Teng in our group is now working on improving this design.
Figure 3.22: Detwinning device designed for YBCO
Figure 3.23: Uniaxial pressure effect in the resistivity of YBCO_{6.5}
Chapter 4

Unaixial pressure experiments in the high-temperature phase of iron superconductors

In this chapter, I present experiments on the iron superconductor systems Fe\(_{1+y}\)Te, BaFe\(_2\)As\(_2\), and SrFe\(_2\)As\(_2\), studying the effect of uniaxial pressure in the high-temperature phase above \(T_s/T_N\), using clamp-like devices as well as the generation-2 instrument discussed in the previous chapter. As described in Chapters 2 and 3, uniaxial stress breaks the lattice symmetry at high temperature, which leads to detwinning in the low-temperature ground state. At temperatures above the magnetostructural transition, uniaxial stress leads to a monotonic response in the uniaxial strain anisotropy, which is maximized at \(T_s\) and decreases again after entering the low-temperature orthorhombic phase [36]. Thus, the uniaxial pressure effect is largest at \(T_s\). In experiments first reported by I. Fisher’s group, it was deduced that since the rotational symmetry breaking of the resistivity along \(a\) and \(b\) orthorhombic axes diverges as \(T\) decreases toward \(T_s\) under fixed strain, but not under fixed stress, this implies that resistivity anisotropy is directly caused by an electronic mechanism rather than a structural one [87]. A similar divergence was soon found in many different iron superconductors, including pnictides and chalcogenides [92]. This result also naturally explains the observation that while the resistivity anisotropy is of order 1, the strain-induced anisotropy of the lattice is only of order \(10^{-4}\). The electronic symmetry breaking phase has been described as “nematic” in the sense that it breaks rotational symmetry without breaking translational symmetry.
It was shown in Chapter 3 that uniaxial strain along an in-plane orthorhombic direction increases the magnetic ordering temperature of iron pnicitides such as BaFe$_2$As$_2$, an effect which does not saturate as the strain is increased. Thus, the effect of increasing the orthorhombicity with uniaxial pressure is to promote the magnetically ordered phase through symmetry breaking. While small uniaxial pressure can reveal the existence of the underlying electronic anisotropy due to the detwinning effect, the lattice anisotropy of a single domain that is already in the preferred twin orientation will deform continuously, leading to a corresponding continuous increase in the magnitude of the electronic anisotropy. In a macroscopic picture, one may define a “nematic susceptibility”, which is the conjugate parameter to the strain field within the Ginzburg-Laudau free energy. We write [87, 93]:

$$F = \frac{a}{2} \Psi^2 + \frac{b}{4} \Psi^4 + \frac{c}{2} \epsilon^2 + \frac{d}{4} \epsilon^4 - \lambda \Psi \epsilon - h \epsilon,$$  \hfill (4.1)

where $a$, $b$, $c$, and $d$ represent the coefficients of the power series expansion of nematic ($\Psi$) and strain ($\epsilon$) order parameters, with $\lambda$ representing the coupling between strain and nematicity. Then upon minimizing $F$, the nematic susceptibility becomes $d\Psi/d\epsilon = \lambda/a$, which diverges in case $a = a_0(T - T_{\text{crit}})$ approaches the phase transition at $T_{\text{crit}}$ stemming from an electronic degree of freedom. The susceptibility under fixed stress, $d\Psi/dh$, does not necessarily diverge at the phase transition. Thus, the temperature dependence of the rotational anisotropy under fixed strain is the quantity of interest for experiments which aim to measure the magnitude of such anisotropy as a function of temperature, such as have been reported by I. Fisher’s group and others. Our experiments, however, could be accomplished under conditions of fixed stress. We investigated (a) the effects of uniaxial distortion on the temperature range over which rotational anisotropy could be observed, and (b) the linearity of the electronic/magnetic anisotropy to applied pressure, which are both quantities
that should be the same for constant stress or constant strain as long as one assumes that the stress/strain relation is in the linear regime. For these experiments, the absolute magnitude of the anisotropy, which is the nematic order parameter $\Psi$, is not extremely important. From the experimental perspective, therefore, it could be argued that fixed stress is the ideal probe since it can be precisely tuned in the case of large crystals, whereas controlling strain in these situations is challenging.

We investigated the nematic phase of iron superconductors under controlled uniaxial pressure. Resistivity was measured using the Montgomery method, with the edges of a square-shaped sample along the $a$ and $b$ directions and leads at the corners. In Fe$_{1+y}$Te, we observe an increase of the both resistivity anisotropy and low-energy spin fluctuation anisotropy under in-plane pressure. Above the critical pressure for complete detwinning, the anisotropy of low-energy spin fluctuations persisted to approximately 100 K in several samples with different interstitial iron content $y$. Since magnetic order in Fe$_{1+y}$Te is not connected to Fermi surface nesting of itinerant electrons, the existence of spin fluctuation anisotropy in the high-temperature phase of Fe$_{1+y}$Te may be due to interactions with polarized local moments. This perspective is reinforced by our polarized neutron scattering experiment on Fe$_{1+y}$Te under unaixial pressure, which suggests that quasi-elastic spin fluctuations in the high-temperature phase of Fe$_{1+y}$Te are slightly polarized along the $c$ axis, similar to inelastic fluctuations in the magnetically ordered phase, and do not change under in-plane uniaxial pressure of 15 MPa. This result points to a key difference between Fe$_{1+y}$Te and nematic spin fluctuations in BaFe$_2$As$_2$, which has an unusual $c$-axis susceptibility to in-plane strain [8]. Comparing pressure-induced resistivity anisotropy in BaFe$_2$As$_2$ and SrFe$_2$As$_2$ as a function of uniaxial pressure to spin fluctuation anisotropy measured by neutron scattering, we find that the nematic susceptibility is directly correlated with the
order of the magnetic phase transition [31]. Specifically, in SrFe$_2$As$_2$, where the magnetic and structural phase transitions are concomitant and strongly first order, both resistivity and spin fluctuation anisotropy disappear by about $T = 1.1T_N$ under 40 MPa in-plane pressure, whereas in weakly first order BaFe$_2$As$_2$ the anisotropy persists above $T = 1.5T_N$. Together, these results imply that resistivity anisotropy is directly caused by spin excitation anisotropy in the nematic phase of iron superconductors, which may not be the case for Fe$_{1+y}$Te.

4.1 Transport experiments on Fe$_{1+y}$Te with P||$(100)$

The high-temperature phase of Fe$_{1+y}$Te was investigated under uniaxial stress using the generation-2 uniaxial pressure instrument. Earlier experiments by Jiang and coworkers showed the existence of resistivity anisotropy in a detwinned sample using a clamp-based device, and a small region was found at $T_N < T < T_N + 2$ K in which anisotropy persisted into the high-temperature paramagnetic phase [94]. The interpretation put forward in that work connected the resistivity anisotropy to anisotropic hopping within a local-moment picture of the antiferromagnetic ordered phase.

Fig. 4.1(a) shows resistivity measured along directions parallel and perpendicular to the pressure in a square-shaped sample, using the Montgomery method, with uniaxial pressure between 1 and 20 MPa applied edgewise along the (100) direction in the notation of the high-temperature tetragonal chemical unit cell. The legend is in experimental order, yet successive measurements at pressures of 1, 3, and 20 MPa exactly overlap, which confirms that the pressure is highly controlled and repeatable. Kinks appear in the resistivity under low stress at $T = 53 – 54$ K and $T = 59 – 60$ K, indicating a split phase transition that consistent with the phase diagram reported
in [63] for an interstitial iron content near $y = 0.11$, as described in Chapter 2. A larger piece of this sample was also studied with neutron scattering, described in the next section, where a commensurate bicollinear ground state was seen below the lower transition, very similar to the sample studied in Fig. 6 of Ref. [64], which was reported by their methods to have $y = 0.09(1)$.

Similar to the experiments of Jiang et al. [94], we observe only a small effect of uniaxial strain on the magnetic ordering temperature of at most 3 K under 20 MPa for the higher temperature $T_N \approx 59$ K, consistent with a strongly first-order phase transition. Resistivity anisotropy at even higher temperatures is small, but persists to more than 65 K. For the lower transition at $T_N \approx 54$ K, an increase of at most 1 K was observed under 20 MPa. The following conclusions can be drawn from three temperature regimes: (1) in the low-temperature bicollinear phase ($T < 52$ K), curves at 15 and 20 MPa are very similar, suggesting that the critical pressure for complete detwinning in this material is about 15 MPa; (2) in the intermediate phase ($54 < T < 58$ K), the sample exhibits similar pressure dependence of the anisotropy as in the low-temperature phase, which suggests either that the physics stabilizing this intermediate phase has the same rotational symmetry as the true bicollinear ground state, and/or that some regions of the sample are already in the bicollinear ground state, similar to the perspective presented in [68]; (3) in the high-temperature paramagnetic phase ($T > 59$ K), the anisotropy smoothly varies as a function of pressure while the magnetic ordering temperature slightly increases.

In Fig. 4.1(b-c), the pressure range is extended to 55 MPa, for which the data quality especially in the direction perpendicular to pressure (Ch. 1) has some artifacts that may be the result of small pieces of sample fracturing or breaking off as the pressure increases, and thus the results are not normalized to the high-temperature
Figure 4.1: Resistance of Fe\textsubscript{1.11}Te under uniaxial pressure with $P\parallel(100)$. The data are taken on a square sample with leads connected at the corners in the Montgomery method. The data collected in Ch. 1 are measurements perpendicular to the pressure direction (antiferromagnetic stripe direction), while in Ch. 2 the resistance is parallel to pressure (ferromagnetic stripe direction).
values. Nevertheless, it is apparent that the higher temperature anomaly increases to as much as 70 K, a difference of 10 K, while the lower temperature one increases to approximately 55 K, an increase of only 1 K. Also in Fig. 4.1(b-c), the differences at temperatures below about 20 K show a pronounced decrease in resistivity in the direction perpendicular to the pressure (along the antiferromagnetic direction of the bicollinear stripes) at all pressures, with no feature in the parallel direction.

To study the uniaxial pressure dependence of the mixed phase (54 < T < 58 K), Fig. 4.2 shows the resistance of the sample along directions parallel and perpendicular to the pressure at T = 54 K. These values are simply averages of a few measurements taken from the data in Fig. 4.1. As pressure is increased from 1 to 15 MPa, the anisotropy between the two directions grows larger, but between 15 and 20 the values both begin to decrease. We interpret this result to indicate that the sample becomes detwinned at 15 MPa, the same pressure corresponding to complete detwinning in the low-temperature phase, and therefore suggests that the underlying mechanisms stabilizing these two phases are substantially the same. For pressures of 20 MPa and above, the resistivity decreases along both directions.

4.2 Inelastic neutron scattering on Fe$_{1+y}$Te with P∥(100)

In Chapter 2, time of flight neutron scattering experiments on Fe$_{1+y}$Te revealed that low-energy spin fluctuations stemming from the bicollinear ordered positions also extended above $T_N$ into the paramagnetic tetragonal phase. By directly subtracting low-energy data at 100 K from data at 5 K (Fig. 4.3), we observe that the fluctuations at high temperature are centered at incommensurate positions with respect to the lattice, consistent with previous publications [66, 75].

To better understand the temperature and unaixial pressure dependence of these
Figure 4.2 : Uniaxial pressure dependence of the resistivity of Fe$_{1.11}$Te at $T = 54$ K.

Figure 4.3 : Temperature-subtracted spin fluctuations in Fe$_{1+y}$Te at MERLIN with $E = 7 \pm 1$ meV, from [30]. Units are reciprocal lattice units with the bicollinear Bragg peaks in the low-temperature magnetically ordered phase visible as dark red spots.
fluctuations, we carried out neutron scattering experiments in the high-temperature phase of Fe$_{1+y}$Te at HB-1 using an aluminum clamp. To determine the efficacy of detwinning and measure the anisotropy of spin fluctuations simultaneously at both the “strong” $Q = (1/2, 0, 1/2)$ majority-domain and “weak” $Q = (0, 1/2, 1/2)$ minority-domain positions, we mounted the crystals in the $(1,0,1) \times (0,1,1)$ scattering plane, which intersects both peaks. Experiments were carried out on two samples, one approximately Fe$_{1.05}$Te which was studied under large uniaxial pressure, and the other, approximately Fe$_{1.11}$Te, under small and large pressure. We found that the detwinning was highly effective in both samples in the large pressure case, from the observation that elastic scattering at the “weak” magnetic Bragg peak position $Q = (0, 1/2, 1/2)$ was extremely small, as shown in Fig. 4.4(a) for the Fe$_{1.11}$Te sample. We also found that increasing the pressure roughly doubles the elastic intensity at the strong $Q = (1/2, 0, 1/2)$ position, consistent with the detwinning mechanism. Elastic temperature scans on the Fe$_{1.11}$Te sample show a $T_N$ increase under pressure at $Q = (1/2, 0, 1/2)$ of at most 1 MPa, from about 59 to 60 K. Temperature scans shown in red and brown were taken by letting the sample temperature stabilize at every point for good temperature accuracy, whereas in orange we used the method of sweeping the temperature, which has a much higher precision due to the large number of points, but exhibits a systematic error in the accuracy of the reported temperature due to the delay time between heat reaching the temperature sensor and being absorbed and equilibrated within the sample. To adjust the accuracy of the points collected with the sweep method to obtain both precision and accuracy, the data in orange has been shifted by a constant value (about 4 K) so that it overlaps the scan taken with stabilized temperature points, with excellent agreement. By comparing with the transport measurements in the previous section, which were taken on small pieces of
the same \( y = 0.11 \) sample, we infer that the values of pressure are about 1 and 20 MPa. An elastic temperature scan taken at the incommensurate position \( Q = (0.42, 0, 0.42) \) in the Fe\(_{1.11}\)Te sample shows a dome-like shape beginning near 45 K, reaching maximum intensity near 60 K, and decreasing to zero by about 65 K, roughly the same temperature scale corresponding to the loss of resistivity anisotropy under 20 MPa. In addition, we found that several nuclear Bragg peak intensities also decrease in both samples at 100 MPa upon entering the low-temperature orthorhombic phase (Fig. 4.5), consistent with the loss of multiple scattering processes in a detwinned sample through the extinction release mechanism [43].

Transverse elastic \( Q \) scans were also collected across the “strong” and “weak” magnetic Bragg peak positions as a function of temperature. Fig. 4.6 combines the scans taken on the Fe\(_{1.11}\)Te sample at 20 MPa in a two-dimensional area plot, with the intensity plotted on a log scale. The scale of the statistical error is about the size of the intensity variation over different points in the same region of the plot. These scans confirm that the single-point temperature scans in Fig. 4.4 accurately capture the \( Q \) and temperature dependence of the magnetic phases in Fe\(_{1.11}\)Te. We note that the features are much broader in \( Q \) compared to what was reported in [64], which is probably due to the large sample mosaic in our Fe\(_{1.11}\)Te sample, of about 5 degrees FWHM.

To study the energy and temperature dependence of low-energy spin fluctuations in Fe\(_{1.05}\)Te and Fe\(_{1.11}\)Te, temperature scans with \( E = 2 \) and 6 meV were conducted and the results are shown in Fig. 4.7. Under 20 MPa, both samples exhibit anisotropy at quasi-elastic energy scales around 2 meV, which although small in magnitude, persists well above \( T_N \) and possibly higher than 100 K (Fig. 4.7a and c). By comparing with equivalent data at 1 MPa (b) which is too small to create appreciable uniaxial
Figure 4.4: Elastic magnetic scattering from the strong and weak Bragg peaks in Fe$_{1.11}$Te and small and large uniaxial pressure. In (a), a commensurate and a longitudinally incommensurate position were studied for both the majority and minority domain directions. In (b), stabilized and sweep method temperature scans were used to study the $T_N$ shift of Fe$_{1+y}$Te under pressure as described in the text. Since the pressure calibration was not known at the time of the experiment, the legend in (b) reports values of 5 and 100 MPa although a better estimate using the transport data is 1 and 20 MPa, as described in the text.
Figure 4.5: Temperature dependence of nuclear elastic scattering in (a) Fe$_{1.05}$Te and (b) Fe$_{1.11}$Te.
Figure 4.6: Elastic longitudinal $Q$ scans with $P=20$ MPa across the (a) strong and (b) weak magnetic Bragg peak positions in Fe$_{1.05}$Te, and (c-d) Fe$_{1.11}$Te, demonstrating a transition from commensurate to incommensurate positions with increasing temperature that is much more pronounced in the sample with high excess iron. The data is plotted with a logarithmic intensity scale.
distortion of the lattice in the high-temperature regime, it is clear that the anisotropy under 20 MPa is a real effect. At $E = 6$ meV, totally anisotropic spin fluctuations were observed in both samples (d and e), confirming the efficacy of the uniaxial pressure detwinning and showing that spin fluctuations at this energy are associated with the formation of long-range magnetic order.

To further clarify the $Q$ and energy dependence of spin fluctuations in paramagnetic phase of uniaxial-strained Fe$_{1+y}$Te, we carried out inelastic $Q$ scans (Fig. 4.8) and energy scans (Fig. 4.9). The $Q$ scans at $E = 2$ meV clarify that the quasi-elastic fluctuations above $T_N = 60$ K are incommensurate to the lattice and are present only in the high-temperature phase. The anisotropy between the strong and weak positions persists above 80 K, as shown in Fig. 4.7. Energy scans appear to show that for the case of Fe$_{1.11}$Te (c-d), the energy scale associated with spin fluctuations undergoes a smooth crossover from 6 to 2 meV when the temperature is raised through the phase transition, while for Fe$_{1.05}$Te there is a discontinuity in the spectrum clearly differentiating these energy scales. This result suggests that the energy of spin fluctuations associated with the the long-ranged incommensurate phase follows the continuous $Q$ dependence observed in the elastic channel for Fe$_{1.11}$Te (Fig. 4.6[c]).

4.3 Polarized inelastic neutron scattering on Fe$_{1+y}$Te with $P \parallel (100)$

In a spin-driven electron nematic phase, electronic correlations are the driving force which cause broken rotational symmetry of the lattice and perhaps, through spin-orbit coupling, the orbital occupancies at the iron sites [95, 96]. In 2017, Kissikov and coworkers reported a uniaxial pressure experiment on BaFe$_2$As$_2$ in which it was shown
Figure 4.7: Inelastic neutron scattering intensity as a function of temperature, with $E = 2$ meV for (a) Fe$_{1.05}$Te at 20 MPa, (b) Fe$_{1.11}$Te at 1 MPa, (c) Fe$_{1.11}$Te at 20 MPa, and with $E = 6$ meV for (d) Fe$_{1.05}$Te at 20 MPa and (e) Fe$_{1.11}$Te at 20 MPa.
Figure 4.8: Inelastic $Q$ scans along the $[H, 0, H]$ (left column) and $[0, K, K]$ directions (right column) in Fe$_{1.05}$Te under 20 MPa at $E = 2$ meV (a-b) and $E = 6$ meV (c-d). The intensity is plotted on a logarithmic scale.
Figure 4.9: Energy scans in Fe$_{1.05}$Te under 20 MPa at $Q = (1/2, 0, 1/2)$ (a) and $Q = (0, 1/2, 1/2)$ (b), and the same scans in Fe$_{1.11}$Te (c-d). The intensity is plotted on a logarithmic scale.
that in-plane pressure drives an increase in the $c$-axis spin susceptibility [8]. This result shows that nematic fluctuations have an internal degree of freedom that does not simply follow the lattice symmetry, an observation that is additionally supported by very recent neutron scattering experiments on uniaxially strained BaFe$_2$As$_2$ [Dai et al., in preparation]. Since it was previously suggested that the resistivity anisotropy of Fe$_{1+y}$Te could be interpreted simply as the result of coupling to local moments with broken rotational symmetry [94], rather than driven by a spin-nematic phase, we conducted polarized inelastic neutron scattering experiments at HB-1 in the $H0L$ scattering plane, using the generation-2 instrument with unaixial pressure along the (100) direction, to search for uniaxial-pressure induced changes in the spin polarization of dynamical fluctuations.

No changes were observed between 1 and 15 lbf (about 1 and 15 MPa), more consistent with the interpretation that high temperature paramagnetic spin fluctuations are critical scattering processes associated with the magnetic phase transition, rather than nematic fluctuations of the same origin as those observed in BaFe$_2$As$_2$. In Fig. 4.10, we observe that low-energy spin excitations near the bicollinear position at $Q = (0.42, 0, 1/2)$ have approximately twice the signal in the $S_{xx}$ scattering channel, with neutrons polarized perpendicular to $Q$, compared to the $S_{yy}$ and $S_{zz}$ channels. Magnetic spin-flip scattering may only occur in the case where the spin polarization of the fluctuations is both perpendicular to $Q$ and perpendicular to the neutron spin polarization; thus, for spin-isotropic scattering, the $S_{xx}$ channel should contain twice the signal as the other two, since for $S_{yy}$ and $S_{zz}$ the neutron spin and $Q$ are orthorhgonal. Thus, Fig. 4.10 shows that spin fluctuations are nearly spin-isotropic, with a slightly higher intensity in the $S_{zz}$ channel that is consistent with fluctuations slightly polarized along the $c$ axis direction, similar to the fluctuation spectrum within
the bicollinear ordered ground state near $E = 10$ meV that was reported in Chapter 2.

Figure 4.10: Energy dependence of inelastic neutron scattering in the spin-flip channel in the paramagnetic phase of Fe$_{1+y}$Te at $T = 75$ K, with the horizontal axis in meV, measured at HB-1. Points at $E = 2$ meV and below contain elastic contamination due to the energy resolution of the spectrometer.

Measurements along the $H$ and $L$ directions with constant energy $E = 1.5$ meV (Fig. 4.11) demonstrate that spin fluctuations in the high temperature phase peak near $H = 0.4$ ($L = \frac{1}{2}$) and near $L = 0.4$ ($H = 0.42$), with no observable changes in the balance between spin polarization channels as a function of uniaxial pressure. For scans along $L$ we find $S_{zz} > S_{yy}$, consistent with spin polarization along the $c$ axis, while scans along $H$ appear nearly spin-isotropic. This apparent inconsistency could be due to a more complicated shape of the background scattering than the diagonal line presented in (a), which should be characterized in future investigations.
Figure 4.11: Spin-polarized $H$ and $L$ scans in Fe$_{1+y}$Te at $E = 1.5$ meV for $P=1$ and $15$ lbf, approximately equivalent to $1$ and $15$ MPa.
4.4 Resistivity measurements on BaFe$_2$As$_2$ and SrFe$_2$As$_2$ with P∥(100)$_O$ and their comparison with neutron scattering

Both SrFe$_2$As$_2$ and BaFe$_2$As$_2$ exhibit a tetragonal-to-orthorhombic phase transition and stripe antiferromagnetic order, as well as low-energy spin fluctuations at the magnetic ordering positions above $T_N$. Spin fluctuations in the high-temperature phase of BaFe$_2$As$_2$ system have been studied in detail [24, 33, 35, 87, 97] and anisotropy has been observed up to a temperature well above $T_s$, while $T_s$ and $T_N$ are split by light doping, indicative of a weakly first order phase transition [98]. On the other hand, SrFe$_2$As$_2$ has a strongly first order-like magnetostructural phase transition [99, 100], similar to Fe$_{1+y}$Te. Resistivity anisotropy across the phase diagram of detwinned Sr(Fe,Co)$_2$As$_2$ was previously argued as strong evidence for an orbitally selective Mott transition within a range of dopings near the purported nematic quantum critical point. Such a Mott transition would gap out the orbital states contributing to transport along the direction parallel to pressure, raising the resistivity in that direction by eliminating the scattering channel involving those orbital states [101]. If rotational anisotropy in the high-temperature paramagnetic phase of Sr(Fe,Co)$_2$As$_2$ is generated by electron nematic fluctuations, it is important to compare the temperature scale associated with its rotational symmetry breaking to another system like BaFe$_2$As$_2$ to determine the effect of the strongly first order phase transition on the nematic susceptibility. For instance, if SrFe$_2$As$_2$ is near an orbitally selective Mott transition, it may also exhibit some critical scattering processes where anisotropy is generated by interactions with localized magnetic moments, similar to the arguments considered above in the context of Fe$_{1+y}$Te.

To measure the temperature scales associated with electron nematicity in SrFe$_2$As$_2$
and BaFe$_2$As$_2$, we carried out measurements of the resistivity and resistivity anisotropy as a function of controlled uniaxial pressure along the orthorhombic [010] direction using the generation-2 instrument. Fig. 4.12 demonstrates that the onset of resistance anisotropy is associated with different temperature scales in these two materials. In SrFe$_2$As$_2$, the anisotropy vanishes near $T/T_N = 1.1$, while in BaFe$_2$As$_2$ it persists above $T/T_N = 1.5$. Within the low-temperature magnetically ordered phase of each material ($T/T_N < 1$), we find an increase in the resistance along the $b$ axis direction parallel to the pressure (the ferromagnetic direction along the stripes), and decrease along the perpendicular direction. The resistance values, as well as the qualitative shape of the $R(T)$ curves, appear to saturate in both materials at pressures above 15 MPa, which we identify as the pressure associated with complete detwinning.

To further clarify the uniaxial pressure dependence of the resistivity at different temperatures, data points are sampled from Fig. 4.12(a-b) at various temperatures and plotted as a function of pressure in Fig. 4.13(b) for SrFe$_2$As$_2$ and Fig. 4.13(a) for BaFe$_2$As$_2$. The data are plotted in experimental order, showing good repeatability at low pressure. For both materials, in the antiferromagnetic ordered phase below $T_N$ we find a qualitative change between low pressures $0 < P < 20$ MPa where the sample is still partially twinned, compared with a monotonic change for $P > 20$ MPa. The upward shift of $T_N$ with pressure in both materials, shown in panel (b) in both figures, is found to be about 0.25 K/MPa in BaFe$_2$As$_2$, consistent with the measurements in Chapter 2, and 0.15 K/MPa in SrFe$_2$As$_2$. Scaling these numbers by the absolute values of $T_N$, we arrive at the very different numbers for the proportional increase in $T_N^{(p)}/T_N^{(0)}$ at 10 MPa of $2.5/140=1.8\%$ for BaFe$_2$As$_2$ and $1.5/200=0.8\%$ for SrFe$_2$As$_2$.

Comparing these results with neutron scattering experiments, we find that above the critical pressure corresponding to detwinning (right and second from right in Fig.
Figure 4.12: Resistance and resistance anisotropy of SrFe$_2$As$_2$ and BaFe$_2$As$_2$ under controlled uniaxial pressure, from [31]. (a-b) Normalized resistance $\tilde{R} = (R[T,P] - R[T_{\text{max}}, P]) / R[T_{\text{max}}, P]$, i.e. normalized to the value at $T = 300$ K (SrFe$_2$As$_2$) or 200 K (BaFe$_2$As$_2$) measured at each pressure. (c,d) Uniaxial pressure effect on the normalized resistance, $\Delta_P \tilde{R} = \tilde{R}[T,P] - \tilde{R}[T,P = 1]$. (e,f) Anisotropy $\delta_{ab}[T,P] = |\Delta_P \tilde{R}_a - \Delta_P \tilde{R}_b| / (\Delta_P \tilde{R}_a + \Delta_P \tilde{R}_b)$ of the pressure-induced resistivity changes between $a$ and $b$ orthorhombic axes.
Figure 4.13: Uniaxial pressure dependence of (a) the resistivity and (b) \( T_N \approx 200 \) K in \( \text{SrFe}_2\text{As}_2 \).
Figure 4.14 : Uniaxial pressure dependence of (a) the resistivity and (b) $T_N \approx 140$ K in BaFe$_2$As$_2$. 
the resistivity anisotropy of SrFe$_2$As$_2$ and BaFe$_2$As$_2$ nearly exactly matches the anisotropy of low-energy spin fluctuations. The precise agreement in both systems suggests that spin fluctuations are directly correlated with resistivity anisotropy in iron pnictides with a nematic phase, a situation that was not observed in Fe$_{1+y}$Te. Since rotational symmetry breaking persists to higher temperature in the more weakly first order BaFe$_2$As$_2$ system compared to SrFe$_2$As$_2$, our results suggest that nematic fluctuations are related to critical spin fluctuations. Since superconductivity may arise in a system with nematic critical fluctuations [102–105], understanding the origin of low-energy fluctuations is a step toward a unified picture of the origins of unconventional superconductivity.

Figure 4.15 : From [31], $T/T_N$ dependence of the resistivity anisotropy $\delta_{ab}$ at in-plane uniaxial pressures of (a) $P = 5$ MPa, (b) $P = 15$ MPa, (c) $P = 30$ MPa, and (d) $P = 40$ MPa for detwinned BaFe$_2$As$_2$ and SrFe$_2$As$_2$, compared to spin excitation anisotropy $(I_{10} - I_{01})/(I_{10} + I_{01})$ for detwinned BaFe$_2$As$_2$ and SrFe$_2$As$_2$, measured at $E = 10.6 \pm 2.8$ meV with incident neutron energy $E_i = 80$ meV. Below $P \approx 15$ MPa, the finite twinning of the samples obscures the connection to spin excitation anisotropy, but for 30 and 40 MPa the connection is robust. The data for SrFe$_2$As$_2$ show sharp changes across $T_N$, indicative of the first order nature of the transition, and similar but broader features in BaFe$_2$As$_2$. 
Chapter 5

Orbital selectivity of spin excitations in iron superconductors

The nematic phase of iron superconductors is characterized by spontaneously broken rotational symmetry of the lattice by low-energy electronic fluctuations. In Chapter 4, I argued that the nematic fluctuations are driven by the spin degree of freedom in these materials, based on evidence that the anisotropy of resistivity anisotropy in SrFe$_2$As$_2$ and BaFe$_2$As$_2$ exactly matches the anisotropy of low-energy spin fluctuations in these materials in a detwinned sample. Since iron superconductors exhibit spin-orbit coupling, fluctuations in spin space must also have an effect on the real-space charge fluctuations.

Previous work on the orbital selectivity of spin fluctuations has demonstrated the importance of intra-orbital scattering channels for magnetic and superconducting processes [38]. In LiFeAs [106], two high-energy branches of spin fluctuations were observed, and DMFT calculations identified the band with finite spectral bandwidth as associated with localized $d_{xy}$ electrons, while the band with incommensurate branches extending to high energies was associated with itinerant $d_{xz}/d_{yz}$ intra-orbital fluctuations that were also closely linked to superconductivity, in part due to the RPA calculations presented in this chapter. In Co-doped NaFeAs below the superconducting $T_c$, two spin fluctuation resonances were observed above the superconducting gap and both were highly anisotropic, which was understood in an orbitally differentiated model with both resonances stemming from $d_{yz}-d_{yz}$ processes [107]. Several theoretical
studies have proposed that the origin of magnetism is connected to fluctuations in orbitally differentiated models [108–110]. Orbital selectivity was leveraged by early RPA calculations which considered a two-orbital model consisting of only $d_{xz}$ and $d_{yz}$ orbitals [111] which produced a spin susceptibility very similar to those produced using more sophisticated models such as the 5-, 10-, and 16-orbital models described in Chapter 6.

Signatures of orbital selectivity are particularly evident in FeSe, where strong, localized electronic coupling has been predicted on account of the small Fermi surface [112]. ARPES observed a splitting between the $d_{yz}$ and $d_{xy}$ bands in FeSe that exhibited momentum dependence and could therefore not be attributed to a simple on-site occupation difference, but would lead to symmetry breaking of dynamical fluctuations [113–116]. With increasing temperature, it was also found that the $d_{xy}$-dominated bands of FeSe become increasingly localized, entering an orbitally-selective Mott phase [113, 117] and thus completely disappearing from the ARPES measurements above 150 K while the $d_{yz}$ band remains itinerant [113]. The onset of nematicity in FeSe was also associated with a shrinking of the $d_{xz}/d_{yz}$ Fermi surface, a situation that could be explained within a combined ARPES and theoretical study considering the effects of anisotropic spin fluctuations on the orbital channel [118]. However, some magnetic scattering processes in FeSe do not seem to select a single orbital: recent NMR experiments in FeSe observed signatures of the nematic phase at the Se nuclei, which are located exactly between four Fe ions and should be completely insensitive to fluctuations of the $d_{xz}$ and $d_{yz}$ orbitals, thus necessarily involving $d_{xy}$ [119]. In other words, there must exist an energy scale where hybridization between the $d_{xz}/d_{yz}$ and $d_{xy}$ orbitals allows the $d_{xy}$ orbital to participate in fluctuations with broken rotational symmetry.
NaFeAs seems to share the properties of both of strong and weak electronic coupling regimes, as it has a relatively large active Fermi surface but also characteristics of strong coupling. Systematic DMFT calculations showed that NaFeAs should exhibit relatively strong electronic correlations [65], possibly due to the height of the As anions above the Fe-Fe basal plane [120]. Additionally, ARPES experiments have revealed that the electronic bands along the (1,0) direction are dominated by $d_{yz}$ and $d_{xy}$ orbital weight, with strong band renormalization ($R=7.0$) in the $d_{xy}$-dominated band in NaFeAs compared to the same band in BaFe$_2$As$_2$ ($R=3.5$) [38, 121, 122]. As such, NaFeAs occupies a parameter space between iron pnictides and iron chalcogenides and at the boundary of local versus itinerant physics. Thus, similar to the effect of anisotropic spin fluctuations on the ground state of FeSe, it is interesting to consider the situation in reverse and ask whether the spin fluctuation spectrum in NaFeAs exhibits signatures of orbital selectivity.

To better understand the connection between the spin and charge fluctuation channels in iron superconductors, I carried out RPA calculations of the spin fluctuation spectrum in parent compound and electron-doped LiFeAs, which are compared to neutron scattering experiments to argue that spin fluctuations arising in the $d_{xz}/d_{yz}$ intra-orbital channel are a necessary condition for superconductivity to occur [106]. I also conducted inelastic neutron scattering experiments on detwinned NaFeAs, a major experimental challenge, and we compare these to DMFT calculations to show that fluctuations within the $d_{yz}$-$d_{yz}$ channel are marked by excellent agreement with the experimentally observed spin fluctuations up to an energy scale of about 110 meV, whereas spin fluctuations at higher energies are associated with the $d_{xy}$-$d_{xy}$ channel. We conclude that low energy spin fluctuations are orbitally selective in the $d_{yz}$-$d_{yz}$ channel, while $d_{xy}$-$d_{xy}$ intra-orbital scattering processes control the bandwidth.
of spin fluctuations in the iron pnictides via local moment superexchange through the As \textit{p}-orbitals. Since our experiments also show that the symmetry of high-energy spin fluctuations also remains partially anisotropic, these measurements suggest the existence of a high energy scale at which there exists coupling between the $d_{yz}-d_{yz}$ and $d_{xy}-d_{xy}$ intra-orbital scattering channels in the low-temperature phase of NaFeAs. However, I also show that there is no evidence for magnetic frustration or competition with a quasi-degenerate ground state, as there is in the case of Fe$_{1+y}$Te presented in Chapter 2, and in the case of FeSe, which exhibits competition between stripe order and checkboard Neél-type order [123]. Finally, I present the temperature dependence of the magnetic fluctuation spectrum of NaFeAs, which shows that spin excitations above $\sim 20$ meV remain anisotropic at temperatures above 90 K, far above $T_N \approx 45$ K.

5.1 LiFeAs

Neutron scattering experiments were conducted by Y. Li on LiFeAs and LiFe$_{0.88}$Co$_{0.12}$As [106]. Unlike other iron pnictides, within this system it is the parent compound that is superconducting, while the 12\% substituted member is not, which has led to the suggestion that LiFeAs is “naturally” electron doped. DMFT calculations conducted by Z. P. Yin agree well with the spin fluctuation spectrum, where two branches were observed at high energies above 150 meV that agree well with the DMFT fluctuation spectrum in the $d_{xz}-d_{xz}/d_{yz}-d_{yz}$ and $d_{xy}-d_{xy}$ intra-orbital pairing channels, respectively.

To better understand the role of intra-orbital scattering processes in low-energy spin fluctuations that could be involved in the superconducting mechanism, I conducted RPA calculations of dynamical fluctuations in the LiFeAs system. Fig. 5.1 shows the
three-dimensional Fermi surfaces of (a) LiFeAs and (b) LiFe$_{0.88}$Co$_{0.12}$As, which is at the edge of the superconducting phase. The Fermi surface exhibits a sheet centered at (0,0) in the basal plane, and $k_z$ at the Brillouin zone boundary, that appears in the superconducting parent compound but not in the 12% electron doped system. Fig. 5.1 shows transverse cuts of the imaginary part of the bare (noninteracting) and RPA spin susceptibility, which is associated with dynamical fluctuations, for the two compounds. The RPA spin susceptibility is calculated by tracing over the bare (noninteracting) susceptibility before applying interactions, so it is not possible to directly project this result back into the basis of orbitals. However, the components of the bare susceptibility give a clear indication which sections arise from which parts of the Fermi surface. In LiFeAs, the transversely incommensurate peaks at $Q = (\pm 0.3, 1, 1)$ in the one-Fe Brillouin zone arise from Fermi surface nesting of the $d_{xz}$-$d_{xz}/d_{yz}$-$d_{yz}$ intra-orbital fluctuation channel (with the choice of $Q = (1, \pm 0.3, 1)$ rather than $(\pm 0.3, 1, 1)$, the channel is $d_{yz}$-$d_{yz}$). In LiFe$_{0.88}$Co$_{0.12}$As, this peak disappears at the expense of a significant enhancement of the commensurate peak at $Q = (1, 0, 1)$ which is dominated by $d_{xy}$-$d_{xy}$ fluctuations.

Figures 5.2 and following show the areas of the Fermi surface responsible for scattering processes at the values of $Q$ relevant to spin fluctuations in LiFeAs and LiFe$_{0.88}$Co$_{0.12}$As. These maps overlay the Fermi surface of the material at $k_z = 1$ in red (using the notation $k_z = \pi$ in the figures), with the Fermi surface at $k + Q$ in pink, which is shifted by $Q = (q_x, q_y, q_z = 1)$ and therefore has $k_z = 0$. Behind the Fermi surfaces, the intensity of the bare susceptibility is shown on a log scale with maximum values at $\log_{10}(I) = 1.2$. These contour maps show the regions that are connected at these different $Q$, and are plotted across four Brillouin zones ($-1 < k_x < 3, -1 < k_y < 3$). Among the selected $Q$, the largest peaks at each doping
Figure 5.1: Fermi surfaces and dynamical spin susceptibility along transverse cuts in LiFeAs and LiFe$_{0.88}$Co$_{0.12}$As
\( Q = (0.12, 1, 1) \) for LiFeAs, Fig. 5.4; and \( Q = (0, 1, 1) \) for LiFe\(_{0.88}\)Co\(_{0.12}\)As, Fig. 5.6) are especially strong due to multiple Fermi surface nesting conditions. On the other hand, the peak at \( Q = (0.3, 1, 1) \) in LiFeAs (Fig. 5.3) is generated by Fermi surface nesting with the inner hole sheet surrounding \((0,0,L)\). This is a unique feature of the parent compound and suggests that the existence of this pocket is important for superconductivity. Explicit calculations of the superconducting pairing states in LiFeAs are described in Chapter 6, where it is found that this central hole pocket stabilizes \( s \) wave superconductivity, which is also the case for electron-doped BaFe\(_2\)As\(_2\) [41]. Thus, the spin fluctuations directly associated with superconductivity in LiFeAs arise within the \( d_{xz}-d_{xz}/d_{yz}-d_{yz} \) orbital selective channel.

![Intra-orbital \( \chi_0(k) \) at \( q=(0.5, 1.5, 1) \), \( k_z=\pi \)](image)

Figure 5.2: \( k \)-resolved map of \( \chi''_0[\text{Im}] \) at \( Q = (0.5, 1, 1) \) in the one-Fe Brillouin zone of LiFeAs, corresponding to a small peak resulting from chiefly \( d_{xy}-d_{xy} \) orbital fluctuations.
Figure 5.3: $k$-resolved map of $\chi_0'' [\text{Im}]$ at $Q = (0.3, 1, 1)$ in the one-Fe Brillouin zone of LiFeAs, corresponding to a peak resulting from chiefly $d_{xz}$-$d_{xz}$ orbital fluctuations, unique among the peaks studied in this material and possibly important for the superconducting pairing mechanism.
Figure 5.4: $k$-resolved map of $\chi''_0$ [Im] at $Q = (0.12, 1, 1)$ in the one-Fe Brillouin zone of LiFeAs, corresponding to the largest peak for this doping resulting from chiefly $d_{xy}-d_{xy}$ orbital fluctuations.
Figure 5.5: $k$-resolved map of $\chi''_0$ [Im] at $Q = (0.5, 1, 1)$ in the one-Fe Brillouin zone of LiFe$_{0.88}$Co$_{0.12}$As, corresponding to a small peak with chiefly $d_{xy}-d_{xy}$ orbital fluctuations.
Figure 5.6: $k$-resolved map of $\chi''_0 [\text{Im}]$ at $Q = (0, 1, 1)$ in the one-Fe Brillouin zone of LiFe$_{0.88}$Co$_{0.12}$As, corresponding to the large commensurate peak with chiefly $d_{xy}-d_{xy}$ orbital fluctuations.
5.2 NaFeAs

A described above, we searched for orbital selective processes in detwinned NaFeAs because of its large electronic correlation strength. After neutron scattering studies on FeSe were published revealing a temperature-dependent competition between stripe and checkerboard antiferromagnetic order in this material [123], we became interested in whether NaFeAs might be similar, since NaFeAs has the strongest degree of band renormalization among iron pnictides, pushing it toward the limit of the chalcogenides. Adding to the evidence for this situation, in our group’s experiments on twinned NaFeAs, a small feature had been noticed at the checkerboard position $Q_{\text{Neel}} = (1, 1, L)$ at about 60-70 meV, similar to the case of FeSe. However, after experiments were carried out, we find no evidence of this checkerboard instability or magnetic frustration at any energy scale, suggesting that electronic fluctuations in NaFeAs are not on the verge of an orbitally-selective Mott transition, nor dominated by competition with other magnetic ground states as in the case of FeSe [123] and $\text{Fe}_{1+y}\text{Te}$ [30, 70]. Instead, we reveal orbitally selective physics within the spin fluctuation spectrum of NaFeAs.

A growth process producing large NaFeAs single crystals suitable for neutron scattering was developed in our group chiefly by C. Zhang, and neutron scattering experiments were carried out by several group members, notably by S. Carr, who measured the momentum and energy dependence of the entire spin fluctuation spectrum for five values of Co-doping across the magnetic and superconducting regions [60, 120]. In these experiments, it was found that, taking twinning into account, spin waves could be successfully modeled within a local-moment Heisenberg model using linear spin wave theory. The unusual property of this model was that the exchange couplings among nearest-neighbor Fe ions were found to be antiferromagnetic along
both the ferromagnetic and antiferromagnetic directions of the static spin stripes, which suggested that stripe magnetic order was not intrinsically stable off the elastic line and therefore could be somewhat unstable to perturbations such as doping. Nevertheless, S. Carr found that the spin wave spectrum was essentially unchanged with Co-doping across the superconducting dome, except in the low-energy region below $E \approx 50$ meV where small changes might indeed be expected due to band folding and restructuring of the Fermi surface upon entering the antiferromagnetically ordered state.

To search for direct evidence of magnetic frustration in NaFeAs, I carried out neutron scattering experiments at 4SEASONS using the same samples studied by C. Zhang. The experiment revealed precisely no temperature dependence, and at first it was assumed this was due to poor statistics or degraded samples. However, during this time I also conducted simulations of the scattering pattern using linear spin wave theory, shown in Fig. 5.7, which demonstrate that a peak may in fact appear at $Q = (1, 1, L)$ purely due to the twinning effect, which would then simply follow the temperature dependence of the spin wave features at the other positions, as I had observed at 4SEASONS. In other words, to resolve whether NaFeAs exhibits a separate checkerboard instability as in the case of FeSe, it became apparent that an experiment on detwinned NaFeAs would be required in order to see if the peak at $(1,1)$ would appear in the absence of twinning.

Detwinning single crystals of NaFeAs is an experimentally challenging task for several reasons. Firstly, NaFeAs single crystals are very soft compared to BaFe$_2$As$_2$ and SrFe$_2$As$_2$, thus the pressure required for detwinning may damage them. More importantly, NaFeAs is extremely air sensitive, reacting with atmosphere (probably water vapor) in a matter of seconds and degrading the samples into dust in minutes.
Figure 5.7: Predictions of linear spin wave theory for constant-energy slices at $E = 95$ meV for (a) 50% detwinned and (b) 100% detwinned NaFeAs. These calculations show how an artificial peak at $Q = (1, 1, L)$ may be generated by the twinning effect. The patterns are generated for the values of $L$ that would be observed in a neutron scattering experiment with $c \parallel k_i$ and $E_i = 150$ meV, as it was at 4SEASONS.
This implies that the samples could not be handled in the usual way of cutting with a high precision wire saw and mounting in an aluminum manifold. The standard handling procedures developed in our group for NaFeAs involves wrapping air-sensitive samples in aluminum foil with a small amount of hydrogen-free Cytop M glue as a potting material between the foil and the sample. Often, the samples are wrapped twice, in an origami-like process perfected by W. Wang.

To conduct inelastic neutron scattering experiments on detwinned NaFeAs, Y. Xie, W. Yu, and I first grew an entirely new batch of single crystals, a process involving 25 separate crucibles each containing 20 or 30 g of starting materials and a detailed and time-consuming growth procedure. Raw materials, including small hand-cut pieces of soft Na metal, are sealed in alumina crucibles inside welded Ta or Nb tubes, then sealed inside quartz tubes containing partial pressure of argon, reacted twice in box and tube furnaces with very specific thermal gradients, and finally extracted in three steps of varying degrees of violence, beginning with smashing the quartz, then careful removal of the metal tube using a specially-designed drill chuck apparatus, and finally hand-hammering of the crucible and remaining flux. Y. Xie and I developed a tool to cut these samples inside the glove box, shown in Fig. 5.8. The tetragonal (100) direction of each sample was determined by eye and two parallel cuts were made oriented at 45 degrees along the orthorhombic (100). The samples were potted in Cytop and foil and individually transferred out of the glove box into a Laue xray diffractometer, were the sample orientation was checked directly through the foil wrapper. Finally, the samples were individually mounted in clamps with aluminum springs shown in Fig. 5.9 that were specially designed with interchangeable parts to accommodate the wide range of NaFeAs sample sizes that were grown.

Inelastic neutron scattering experiments were carried out at SEQUOIA at 10, 38,
Figure 5.8: Adjustable slicer for cutting NaFeAs single crystals of any thickness inside the glovebox. The razor blade at the center of the device presses the sample into a rubber pad as one or both of the screws on the sides are tightened into the threaded holes below, slicing the samples with brute force. The device applies a very large force and easily cuts through NaFeAs crystals up to several millimeters thick.
Figure 5.9: Detwinning clamps for NaFeAs (a-b) and corresponding machine drawings (c-d) showing how interchanging some components can accommodate a large range of crystal sizes. Dimensions are inches. Inside each clamp is a rectangular piece of aluminum acting as a spring. Two crystals were found to be misaligned by about 10 degrees and these were rotated in the final sample array.
52, 70, and 90 K, and at MERLIN at 5, 52, and 62 K. This range covers the low-temperature antiferromagnetic orthorhombic phase \((T < 45 \text{ K})\), the paramagnetic orthorhombic phase \((T_N = 45 \text{ K} < T < T_s = 60 \text{ K})\), and the high-temperature paramagnetic phase that is tetragonal in the absence of uniaxial distortion \((T > 60 \text{ K})\) [124]. Using the method presented in Chapter 2 for determining the detwinning ratio from inelastic positions using the same \(L\) values as the magnetic Bragg peaks, I find that the detwinning ratio is 3:1, or 50%, which is nevertheless acceptable considering the softness of the material and the possible inefficacy of unaixial pressure in the first place.

The assignment of different parts of the spin fluctuation spectrum to different intra-orbital scattering channels comes from detailed comparisons with DMFT calculations that were performed by Z. P. Yin. The agreement between the neutron scattering measurements and DMFT calculations is revealed clearly in Fig. 5.10(a), which shows that the energy dependence of spin fluctuation anisotropy in the low-temperature phase is entirely captured within the \(d_{yz}-d_{yz}\) channel, and in Fig. 5.11, which shows the dispersion of spin fluctuations along high-symmetry directions also agrees precisely with the \(d_{yz}-d_{yz}\) calculations. Considering the temperature dependence shown in Fig. 5.10(b), NaFeAs shows a relatively constant anisotropy as a function of energy, with a sharp change in the anistropy at all energies across \(T_s \approx 60\) K. While this analysis does not capture all the details of the energy dependence, which is clarified in later figures, the overall picture is reminiscent of a classical antiferromagnet. It is strikingly different from BaFe\(_2\)As\(_2\) [34], where the energy dependence of the anisotropy changes with temperature, such that the anisotropy vanishes at progressively lower energy as the temperature is raised above \(T_s\), as illustrated with black lines in the figure.

To better demonstrate the energy and temperature dependence of spin fluctuations
Figure 5.10: Inelastic neutron scattering anisotropy and DMFT results for detwinned NaFeAs. (a) Top: magnetic susceptibility as a function of energy, from inelastic neutron scattering at SEQUOIA that is integrated in the diamond-shaped zones in Fig. 2.1(b), for the strong (solid symbols) and weak positions (open symbols). Predictions of orbitally selective DMFT in the $d_{yz}-d_{y\bar{z}}$ channel (green) best explains the anisotropy. Bottom: anisotropy of the integrated intensity, demonstrating anisotropy as high as 150 meV. The purple line from the linear spin wave model agrees well, as does the $d_{yz}-d_{y\bar{z}}$ orbital scattering channel. (b) Energy dependence of the spin fluctuation spectrum shown at temperatures in all three phases of NaFeAs.
Figure 5.11: Dispersion of the $d_{yz}-d_{yz}$ scattering channel in the DMFT model, with peak positions exactly matching the neutron scattering data. Above $\sim 110$ meV, the excitations are observed at (1,1) and are more consistent with the $d_{xy}-d_{xy}$ scattering channel.

In NaFeAs, Fig. 5.12 shows constant-energy slices, in orthorhombic units, as a function of energy (a) and temperature (b). A paraboloidal background has been subtracted from the raw data using the procedure described in Chapter 2, and the intensity has been normalized in absolute units using a vanadium standard. As a function of energy, it is evident that spin waves stemming from the (1,0) and (-1,0) magnetically ordered positions disperse transversely toward the (1,1) positions, where they spread out into broad areas of scattering. As a function of temperature, it is visible that anisotropy decreases in these low-energy slices, with a significantly greater difference between left-right and top-bottom positions in the panels at 70 and 90 K compared to those below $T_s \approx 60$ K.

By comparing the neutron scattering data in the low-temperature magnetically ordered phase (Fig. 5.12(a)) with the patterns generated using DMFT (Fig. 5.13(a)) and linear spin wave theory (Fig. 5.13(b)), it is clear that excitations near $\sim 100$ meV
Figure 5.12: Inelastic neutron scattering measurements of the energy and temperature dependence of spin fluctuations in NaFeAs, from SEQUOIA. (a) Top row: constant-energy slices in the HK plane at $T = 10$ K after background subtraction, for energy $E = 6.5 \pm 2.5$, $17.5 \pm 2.5$, $50 \pm 5$, $65 \pm 10$, $85 \pm 5$, and $120 \pm 10$ meV, with color scale shown above. (b) Temperature dependence of background-subtracted constant energy slices with $E = 6.5 \pm 2.5$ meV, at $T=10$, 38, 52, 70, and 90 K, with the color scale used for all panels shown at right.
are in an intermediate crossover regime between \(d_{yz}-d_{yz}\) and \(d_{xy}-d_{xy}\) fluctuations. The original model proposed in [120] with antiferromagnetic exchange couplings found for the two nearest neighbors continues to agree very well with the detwinned data, unlike the story of BaFe\(_2As_2\) [34]. With only a small modification to the exact values of energy used for the slices in the figure, this model captures the scattering patterns in the data in good detail. This similarity reinforces the general notion that NaFeAs is more strongly correlated than other iron pnictides. On the other hand, since the linear spin wave model is just a parametrization fit, the significance of the sign of the exchange couplings is unclear.

While it is clear from the scattering patterns shown in Fig. 5.13 that high-energy spin waves are generally consistent with DMFT calculations in the \(d_{xy}-d_{xy}\) scattering channel, we do not observe a complete relaxation to fourfold rotational symmetry in the experimental data, as demonstrated by the nonvanishing anisotropy summarized in Fig. 5.10. To prove that some symmetry breaking extends to high energies, unlike the case of BaFe\(_2As_2\) presented in [34], I show raw data in Fig. 5.14 projected directly into the \(HK\) plane along with one-dimensional cuts along transverse directions through the antiferromagnetic ordering positions. The one-dimensional cuts shown in blue are across the “weak” \((0,1)\) peaks show a very obvious dip in intensity near \(H = 0\), while the cuts shown in red along the strong side are entirely flat. From neutron scattering data, it is unclear whether these fluctuations are separate intra-orbital processes which happen to overlap in reciprocal space, or fundamental excitations with a multi-orbital character. We conclude that high energy excitations stem predominantly from fluctuations involving the \(d_{xy}\) orbital, but it remains unclear whether the high-energy data contain contributions from the \(d_{yz}-d_{yz}\) channel or if the \(d_{xy}\) orbital has an intrinsic broken symmetry.
Figure 5.13: Comparison of intra-orbital spin fluctuations from DMFT to a linear spin wave model proposed for NaFeAs [120].
Figure 5.14: Constant-energy slices with $E = 150$ and 170 meV in NaFeAs (left column), and transverse cuts through (1,0), (-1,0), (0,1), and (0,-1) (right column), demonstrating the existence of twofold rotational symmetry breaking in this regime. The red diamonds are a guide to the eye representing the “strong” peak area.
The temperature dependence of the peak intensity and transverse widths of low energy spin fluctuations are shown in Fig. 5.15, while the longitudinal peak widths are shown in Fig. 5.16. At low temperatures and low energies ($E = 10 - 20$ meV), we find a complete relaxation in the peak height anisotropy above $T_s \approx 60$ K, with good agreement between datasets at different $E_i$, suggesting that spin fluctuations are highly two-dimensional since the coupling between $E_i$ and $L$ renders different $L$ values in these cases. The transverse peak width in the inelastic channel, which is much wider than the elastic sample mosaic, shows an increase in intensity above $T_N \approx 45$ K, with the same values for the strong and weak directions at all temperatures. Puzzlingly, at a higher energy of 45 meV, the peak height anisotropy persists to temperatures above 90 K, again with good agreement between the different $E_i$, which suggests that the uniaxial pressure effect remains significant at this energy scale. This could imply that other degrees of freedom play a role in the high-temperature paramagnetic tetragonal phase of NaFeAs besides electron nematic fluctuations. This may indeed be the case, since in an electron nematic phase one expects strong anisotropy in the spin-spin correlation length in a detwinned sample, which is measured by the longitudinal peak width [125]. At the lowest energies available, our measurements show identical values for the longitudinal peak width along the strong and weak-domain directions (Fig. 5.16). Therefore, the relaxation of twofold anisotropy at low energies up to about 20 meV in the high temperature paramagnetic phase is not fully understood at this time.

At an energy scale of 80 meV, we also observe that rotational anisotropy relaxes across $T_s$, but not across $T_N$. Fig. 5.17 shows constant-energy slices with $E = 80$ meV at three temperatures in the MERLIN experiment. Even at this high energy scale, we find no obvious relaxation in the rotational anisotropy between $T = 5$ and
Figure 5.15: Temperature dependence of the peak height (top row) and transverse width (bottom row) of low-energy spin fluctuations in NaFeAs, from SEQUOIA, for [with units in meV] (a) $E_i = 80, 10 < E < 15$, (a) $E_i = 150, 15 < E < 20$, (a) $E_i = 80, 40 < E < 50$, and (a) $E_i = 150, 40 < E < 50$. 
Figure 5.16: Temperature dependence of the longitudinal peak width of low-energy spin fluctuations in NaFeAs

52 K, whereas above $T_s$ at 62 K, intensity appears on the weak-domain side between the (0,1) and (1,1) positions.

Finally, I return to the issue of the temperature dependence of high energy excitations at the (1,1) position, which was found in FeSe to increase in intensity above $T_s$ and interpreted as evidence for competition between magnetic ground states [123]. If spin fluctuations at (1,1) are representative of a competing ground state, then subtracting neutron scattering data at different temperatures should show the existence of a feature at this position. In Fig. 5.18, which shows temperature-subtracted $Q-E$ slices along transverse cuts through (1,1), this is clearly not the case. Although a feature is observed when crossing through the peak along the weak domain side, as in (b), in this case it is expected because spin fluctuations from the strong domain are approach the (1,1) position near $E = 100$ meV. However, crossing through along the strong domain side, shown in (a), it is apparent that
Figure 5.17: Temperature dependence of spin fluctuations in NaFeAs at $E = 80 \pm 10$ meV, from MERLIN. The raw data (top row) has been treated with background subtraction (middle row) and twofold symmetrization along the up-down and left-right directions (bottom row).
no feature exists. Thus, the peak at (1,1) observed in twinned experiments is an artifact of twinning, as illustrated in Fig. 5.7, which reiterates the utility of unaixial pressure as an experimental tool in general in the study of the ground state of iron superconductors.

Figure 5.18: Temperature subtraction of NaFeAs data from SEQUOIA along the transverse cut directions (a) [1,K] and (b) [H,1]. In (a), statistics have been maximized by combining the datasets in the paramagnetic phase at $T = 70$ and 90 K, which was subtracted from the combined datasets in the low-temperature antiferromagnetic phase at $T = 10$ and 38 meV. The data has been folded and white areas represent regions with no unique data. In (b), which shows $T = 90 - T = 10$, a feature is expected at $H = 1$ that corresponds to crossing over the spin wave that stems from the strong (1,0) peak and disperses in the transverse direction. Similar cuts using the MERLIN data yielded the same conclusions.
Chapter 6

Spin fluctuations and superconducting pairing in iron-based superconductors and UPt$_3$

Unconventional superconductivity describes systems that do not rely on phonons for the pairing interaction, as it is with BCS superconductors such as metals, but instead rely on momentum-dependent electronic fluctuations [12, 126, 127]. Examples of such materials include iron-based superconductors and heavy fermion actinide systems. Spin fluctuations are a natural source of bosonic fluctuations in these materials because they have magnetic constituents and exhibit dynamical spin fluctuations.

A neutron spin resonance in unconventional superconductors has been hailed as evidence that the superconducting gap changes sign between disconnected parts of the Fermi surface. This interpretation arises from the viewpoint that low-energy spin fluctuations are particle-hole excitations, a so-called spin exciton: when a superconducting gap with energy $\Delta_0$ is opened, single-particle states are pushed outside the gap, where they are separated by $2\Delta_0$, while a sign change maximizes the coherence factor for excitations involving these states [53, 54, 128, 129]. The energy associated with the spin resonance has been observed to scale with the superconducting transition temperature, $E \sim 6k_BT_c$, across a wide variety of unconventional superconductors [130]. Detailed comparisons between RPA calculations and neutron scattering experiments showed that the resonance feature generated in a spin-excitonic picture could predict the functional form of the superconducting gap [131] as well as interpret the observation of two resonances in Co-doped NaFeAs through the lens of orbital selectivity [107].
To better understand the conditions favorable to superconducting pairing in iron superconductors, I carried out calculations of the superconducting pairing states using the RPA spin and charge susceptibilities in the linearized gap formalism described in Chapter 1. In the LiFeAs system, I find a leading $s$ wave superconducting gap for the parent compound which is replaced by a leading $d$-wave at 12% electron doping, which is precisely the location in the phase diagram where superconductivity disappears in the real material, which I described in Chapter 5. In the BaFe$_2$As$_2$ system, I find that models with 5 and 10 orbitals are insufficient to stabilize $s$-wave superconductivity in the electron-doped regime. However, when the usually-neglected $p$ orbitals of the As ions are included, these sufficiently hybridize with the Fermi surface states so as to remove $d_{xy}$ orbital weight on the electron pockets. The result is that the $s$ wave becomes the leading solution until a doping of 0.475 electrons per unit cell, which again is the precise location in the phase diagram of electron-overdoped Ba(Fe,Ni)$_2$As$_2$ where superconductivity vanishes. These results show that the gap structure of iron-based superconductors can be well described by a purely weak-coupling spin-excitonic picture and that the precise orbital content of the single-particle states is an important ingredient in these models.

The heavy fermion superconductor UPt$_3$ also contains magnetic constituents and exhibits dynamic spin fluctuations. The proponderance of experimental evidence now favors the $E_{2u}$ symmetry group for the superconducting pairing state of UPt$_3$, which is an odd-parity $f$-wave with chiral degeneracy in the order parameter. As such, UPt$_3$ is one of the best candidates for topological superconductivity. Degeneracy of time reversal-symmetric $f$-wave pairing states in the low-temperature B phase is lifted in the high temperature A phase, where it has been argued that the symmetry breaking could be attributed to magnetic degrees of freedom. Static magnetic order with a
single $Q$ structure was indeed observed in the 1980s, however, some unusual features suggested that magnetic order could be localized at defects and not intrinsic to the material. These features include its extremely low ordered moment $(0.02 \pm 0.01 \mu_B)$, total insensitivity to small doping by Pd or Th, a large magnetic Gruneisen parameter suggesting sensitivity of electronic states to structural defects, the actual observation of stacking faults and the increase of $T_c$ upon their removal, and the direct observation of random internal symmetry-breaking magnetic fields below $T_c$ by $\mu$SR that also vanished when the sample quality was improved. If the antiferromagnetic order is accidental and only occurs in small areas of the sample, then static order cannot fully explain the lifting of the degeneracy between chiral superconducting state, and the question becomes directed at how dynamical fluctuations enter the picture in UPt$_3$.

The origin of magnetic order in UPt$_3$ was partially resolved by recent neutron scattering experiments on samples grown in the group of W. Halperin, which I present below. Measurements at ILL conducted by W. Gannon on a highly pure sample showed no sign of a neutron resonance feature. Moreover, measurements at MACS conducted by S. Carr in our group on an ultra-pure sample showed no magnetic order or neutron resonance. Instead, the intensity of fluctuations at the magnetic ordering position was shown to slightly decrease below the expected resonance energy $E \sim 6k_BT_c$. Thus, magnetic fluctuations are local and quasi-static, and probably tied to structural defects.

To better understand the relationship between spin fluctuations and superconductivity in UPt$_3$, we conducted inelastic neutron scattering experiments on an ultrapure sample without long-range magnetic order to generate a complete three-dimensional map of spin fluctuations. Measurements of the shape and intensity of the fluctuation spectrum confirm that magnetic fluctuations obey the hexagonal symmetry of the
lattice, which is different from the in-plane fourfold rotational symmetry of the $f$-wave pairing states. Spin fluctuations at positions such as $Q = (0, 0, \frac{1}{2})$, $Q = (1, 0, \frac{1}{2})$ and $Q = (\frac{1}{2}, \frac{1}{2}, 1)$ exhibit similar energy dependence, consisting in a peak below $E = 3$ meV. Fluctuations at the magnetic ordering position $Q = (\frac{1}{2}, 0, 1)$, on the other hand, rapidly disperse away from that position in a unidirectional fashion toward $Q = (\frac{1}{2}, \frac{1}{2}, 1)$ with intensity peaking at 2 meV and rapidly decreasing for higher energy. This observation offers further evidence that spin fluctuations at $Q = (\frac{1}{2}, 0, 1)$ are unlike the other fluctuations in this material and therefore more likely to be extrinsic. We also observe that ferromagnetic fluctuations at the $(0,0,1)$ position appear to be partially gapped at an energy scale of roughly 3-4 meV, while they merge with spin fluctuations stemming from the antiferromagnetic $Q = (0, 0, \frac{1}{2})$ position near 8-10 meV, near the energy at which an optical phonon appears to cross both spin branches. Strikingly, the intensity of magnetic fluctuations only increases slightly at very low energies, with the bulk of the magnetic fluctuation spectrum the same between 2 K and 50 K, a situation strongly reminiscent of iron superconductors and other strongly correlated electronic materials.

### 6.1 5-, 10-, and 16-orbital models for BaFe$_2$As$_2$

The real part of the RPA spin and charge susceptibilities is involved in the calculation of the possible superconducting pairing states, as described in Chapter 1. Early efforts to calculate the pairing symmetry by Mazin and coworkers predicted an $s$-wave like state with signs reversed between the hole sheets at $(0,0)$ and electron sheets at $(1,0)$, the $s^\pm$ state [128]. The existence of an $s$-wave state in doped BaFe$_2$As$_2$ is broadly supported by experiments including ARPES, muon spin relaxation, optical reflectivity, heat capacity, neutron scattering, and other techniques [37, 132–134].
RPA calculations also predicted an s-wave [135] but also suggested that a $d_{x^2-y^2}$ state, with nodes around the hole sheets at (0,0) and alternating signs at the electron pockets at (1,0) and (0,1), could be promoted by electron doping [51, 52]. The stabilization of the $d$ wave was attributed to the existence of a ridge-like structure around the (1,1) position dominated by inter-band scattering from the electron sheets [136]. However, there is no experimental evidence for a ridge around (1,1) at low energies, nor for a change to $d$-wave gap symmetry at small doping levels.

In Fig. 6.1 I show the real RPA spin susceptibility for electron-doped BaFe$_2$As$_2$ within a 5-orbital model. The ridge around (1,1) is greatly enhanced by interactions, as are the peaks incommensurate to (1,0) which are associated with peaks in the fluctuation spectrum measured by neutron scattering.

Figure 6.1: Bare and RPA spin susceptibility for electron-doped BaFe$_2$As$_2$ within a 5-orbital model, in the region $0 < q_x < 1$ and $0 < q_y < 1$ with units of Å$^{-1}/2\pi$ along the axes.
To address the role of the ridge of scattering around (1,1), we studied the effect of orbital hybridization in the BaFe$_2$As$_2$ system. Unlike many other iron pnictides, BaFe$_2$As$_2$ crystallizes in the $I4/mmm$ symmetry class which has an inversion center; as a result, the unit cell has two inequivalent iron sites. Thus, it was believed that projection of the electronic structure of BaFe$_2$As$_2$ into a 5-orbital model, which only considers one Fe ion, might be oversimplified. On an even finer level, since neutron scattering shows that Fe-As layers contain appreciable exchange coupling between next-nearest neighbor Fe ions, which must take place across an As ion, the hybridization between Fe $d$ orbitals and As $p$-orbitals, although small, could also have an effect on calculations of the spin susceptibility. With the goal of studying the effects of these assumptions on the RPA spin susceptibility and superconducting pairing states, we conducted calculations using 10 and 16 orbital models for BaFe$_2$As$_2$, which were created from density functional theory (DFT) calculations performed by T. Berlijn.

Fig. 6.2 shows a comparison of orbital weights between the 10- and 16-orbital models on the Fermi surface sheets, with solid and dashed lines, respectively, for equivalent doping of 0.4 electrons per formula unit in each model which is near the electron-overdoped edge of the phase diagram. The orbital weights are calculated as simply the squared orbital matrix elements participating in the expression for the bare electronic susceptibility, Eq. 1.6. In each panel in the figure, the horizontal axis is the angular coordinate along the semicircular direction plotted in red in the cartoon to the right of the plot, with dashed lines again indicating the 16-orbital model. Part (a) shows results for the hole pocket, which is open only at the Brillouin zone boundary at $k_z = 1$, while for each of the two fully cylindrical electron sheets the results are shown for $k_z = 0$ (b) and $k_z = 1$ (c). Since fluctuations along the
electron sheets clearly contain a large contribution from $d_{xy}$ orbital weight, which leads to significant contributions to the spin susceptibility at the $Q = (1, 1, L)$ position directly connecting different electron sheets. As we report in [41], by summing the contribution of orbital weights along each Fermi surface sheet, we find a greater reduction in $d_{xy}$ orbital weight on the electron sheets for the 16-orbital model. Thus, the 16-orbital model has a reduced susceptibility in the $d_{xy}$-$d_{xy}$ intra-orbital channel.

The effect of reduced $d_{xy}$ susceptibility is to suppress the ridge of scattering around (1,1) for a range of electron dopings, as detailed in Fig. 6.3. The ridge is located midway between (1,0) and (1,1) and is dramatically suppressed at all dopings, whereas the susceptibility at (1,0) is enhanced in the 16 orbital model up to a doping of 24.475, or 0.475 electrons per formula unit in the 16-orbital model, corresponding to approximately BaFe$_{1.76}$Ni$_{0.24}$As$_2$. Looking at the inelastic channel at the incommensurate position near (1,0) where spin fluctuations are maximized, we find that in the 16-orbital model, fluctuations are pushed to higher energy (Fig. 6.3(d)), consistent with the larger energy splitting required for scattering processes between hole and electron sheets at well-nested $Q$. Fig. 6.4 shows the RPA spin susceptibility across the full region of $Q$ space used for calculations of the superconducting pairing gaps for electron-doped BaFe$_2$As$_2$, which shows more clearly how the susceptibility changes qualitatively as a function of doping between the two models.

Calculations of the superconducting pairing states proceeded from the results of the RPA spin and charge susceptibilities as described in Chapter 1, and in Fig. 6.5 I show the eigenvalues for various pairing solutions as a function of doping, where a larger eigenvalue corresponds to a more stable state. In both models, the eigenvalues and solutions for the parent compound (doping 0) is somewhat unreliable since we have ignored the effects of magnetic order. The functional forms of the pairing states
Figure 6.2: Orbital weights around the Fermi surface pockets in the 10- and 16-orbital models for BaFe$_2$As$_2$ near the electron-overdoped edge. The different parts in each plot are described in the text.
Figure 6.3: RPA spin susceptibility of electron-doped BaFe$_2$As$_2$ in the 10- and 16-orbital models. In (a), cuts of the real part of the spin susceptibility are shown along directions from (0,0) to (1,0) to (1,1). Reproduced from [41]. In (b-c), the band structure of the 16-orbital model at dopings of 0.4 and 0.6 electrons per unit cell, is shown along with the purple bar representing the width of the Fermi function at 20 K, along with the range of energies spanned by a 300 meV about the Fermi level. The corresponding imaginary spin susceptibility in (d) at (1,0.2) in orthorhombic notation, shows that as a function of doping, spin fluctuations are pushed to higher energies.
Figure 6.4: RPA spin susceptibility for electron-doped BaFe$_2$As$_2$ in the 10- (left column) and 16-orbital models (right column), for dopings of 0 (parent compound), 0.2 (near optimal doping), and 0.4 electrons per formula unit. The RPA parameters were $U' = U/2$, $J' = J = U/4$, with a different choice of $U$ between models, and between the parent compound and other doping levels, as shown in the figure labels.
at 0.2 electrons per formula unit, corresponding to near optimal doping, are shown in Fig. 6.6 for the leading solutions, with Fig. 6.7 covering a few other $d$-wave solutions found with lower eigenvalues.

Figure 6.5: Superconducting pairing state eigenvalues in electron-doped BaFe$_2$As$_2$ within the 10- and 16-orbital models. The $d_{x^2-y^2}$ solution considered as the subleading state in the real materials is shown in orange, and the $s$ wave in green, while the other $d$ wave solutions described in Fig. 6.7 are shown in orange and purple.

Finally, for the specific case of vanishing superconductivity at the electron-overdoped edge of the phase diagram, we investigated the differences in the RPA spin susceptibility between doping levels of 0.4 and 0.475 electrons per formula unit, a filling where superconductivity is experimentally observed to disappear and also precisely where our $s$ wave solution becomes sub-leading to the $d$ wave. In electron-overdoped BaFe$_{1.7}$Ni$_{0.3}$As$_2$, neutron scattering experiments reported in Ref. [137] and reproduced in Fig. 6.8(a) show the existence of an energy gap of nearly 60 meV for transversely incommensurate spin waves near the stripe antiferromagnetic $(1,0)$ position. I conducted RPA calculations of the inelastic spin fluctuations at this position (imaginary part of $\chi_{\text{RPA}}$) which show that the peak near $Q = (1, \pm 0.2, L)$ is visible at 60 meV in
Figure 6.6: Leading and subleading pairing solutions in optimally electron-doped BaFe$_2$As$_2$, with eigenvalues shown in green and orange in Fig. 6.5, at a filling near optimal doping with 0.2 electrons per unit cell. (a) shows the sign-switched $s\pm$ wave while (b) show the $d_{x^2+y^2}$-wave solution. The strength of the gap is encoded as the size of the point plotted around each Fermi surface pocket, with opposite signs of the gap shown in red/blue. At right is shown a plot of the gap strength around each pocket in the angular direction, where electron pockets are labeled $\beta_{1a}$, $\beta_{1b}$, etc., and the hole pockets at the zone center are labeled $\alpha_1$, $\alpha_2$. The corresponding pairing strength eigenvalues $\lambda$ are shown above each plot.
Figure 6.7: Other $d$-wave pairing solutions in optimally electron-doped BaFe$_2$As$_2$, with eigenvalues shown in purple and red in Fig. 6.5, at a filling near optimal doping with 0.2 electrons per unit cell. (a) shows a $d$-wave solution with a line node at $k_z = 0$, thus the plot here contains no useful data, but appears similar to the state in (c); (b) shows another $d$-wave solution with nodes on the electron pockets along diagonal directions in tetragonal notation; and (c) exhibits four nodes around each pocket along the tetragonal (1,0) and (0,1) directions. The corresponding pairing strength eigenvalues $\lambda$ are shown above each plot.
the case of 0.4 electrons (b-d), while it is suppressed at 0.475 (f-h). In (e) and (i) I show the Fermi surface for these two dopings, where it is clear that at 0.475 the system has undergone a Lifshitz transition near the zone center which breaks the hole pocket at \((0, 0, L)\) along the \(L\) direction. Together, these results suggest that the existence of a complete cylindrical pocket at the zone center is a necessary and sufficient condition for the stabilization of \(s\) wave superconductivity in a weak-coupling picture of \(\text{BaFe}_2\text{As}_2\).
Figure 6.8: Incommensurate peak in electron-overdoped BaFe$_2$As$_2$ and its connection to the RPA spin susceptibility and Lifshitz transition as described in the text. The data in (a) are taken from Ref. [137].
6.2 10-orbital models for LiFeAs

To test whether the hypothesis that a central hole pocket is necessary for $s$-wave superconductivity in other iron superconductors, I carried out RPA spin fluctuation pairing calculations within a 10-orbital model for LiFeAs derived from ARPES [57] that was used to study the orbital selectivity of spin fluctuations in Chapter 5. Previous ARPES observations in LiFeAs had reached conflicting viewpoints about the anisotropy of the superconducting gap [138, 139], while pairing calculations conducted using our model were carried out for parent and hole-doping, where an $s^\pm$-wave solution was considered the most plausible candidate [57].

The RPA spin susceptibility for LiFeAs and LiFe$_{0.88}$Co$_{0.12}$As is shown in Fig. 6.9, which shows incommensurate peaks near (1,0) in the case of the superconducting compound (in this case parent compound LiFeAs) and strong commensurate peaks at (1,0) in the case where superconductivity is suppressed (LiFe$_{0.88}$Co$_{0.12}$As). The Fermi surfaces for these two materials are shown back in Fig. 5.1 where it is clear that a large hole sheet exists around (0,0) in both compounds, while an inner pocket also appears in the parent compound which is partially sunk below the Fermi level near the Γ point (0,0,0).

The pairing eigenfunctions found for LiFeAs are shown in Fig. 6.10, while the results for LiFe$_{0.94}$Co$_{0.06}$As and LiFe$_{0.88}$Co$_{0.12}$As are shown in Fig. 6.11 and 6.12, respectively. As with the case of electron-doped BaFe$_2$As$_2$, we find a leading $s$ wave solution in the case of the parent compound, in this case of the conventional $s$ type, with a sub-leading $d$ wave. It is interesting to note the differences between these calculations and previous results using our model, which considered the case of slight hole doping, which produced a leading $s^\pm$ state [57]. In the case of LiFe$_{0.94}$Co$_{0.06}$As and LiFe$_{0.88}$Co$_{0.12}$As, the $d$ wave is the leading solution, with a margin widening from
Figure 6.9: RPA spin susceptibility for (a) LiFeAs and (b) LiFe$_{0.88}$Co$_{0.12}$As displayed in coordinates of the tetragonal unit cell which is rotated 45 degrees to the one-Fe unit cell, so that the (1,0) position discussed in the text is located at (1,1) in the figures.

28% to 44% as the doping is increased. These calculations are consistent with the results for BaFe$_2$As$_2$ that show a loss of $d_{yz}$-$d_{yz}$ fluctuations at the expense of $d_{xy}$-$d_{xy}$ is unfavorable for superconductivity. By comparing the LiFeAs and BaFe$_2$As$_2$ systems, I conclude that the superconducting pairing symmetry of LiFeAs is a conventional $s$-wave that vanishes at the expense of strong stripe antiferromagnetic fluctuations in its electron-doped members.
Figure 6.10: (a) Leading conventional s-wave and (b) subleading d-wave pairing solutions in LiFeAs, with $k_z = 0$. The plot formatting follows the description in 6.6.
Figure 6.11: (a-b) Leading $d$-wave solutions and (c) $s$-wave pairing solution in 6% electron-doped LiFeAs (LiFe$_{0.94}$Co$_{0.06}$As), with $k_z = 0$. The plot formatting follows the description in 6.6.
Figure 6.12: (a-b) Leading $d$-wave solutions and (c) $s$-wave pairing solution in 12% electron-doped LiFeAs ($\text{LiFe}_{0.88}\text{Co}_{0.12}\text{As}$), with $k_z = 0$. The plot formatting follows the description in 6.6.
6.3 Superconducting pairing in UPt3

Superconducting pairing states in UPt$_3$ are thought to belong to the $E_{2u}$ representation [140, 141]. Within this theory, two superconducting phases belonging to the same symmetry class are chirally degenerate in the low-temperature B phase [140, 142–144]. It has been suggested that weak antiferromagnetic order at $Q_{AF} = (1/2, 0, 1)$ provides a symmetry breaking field (SBF) that can explain the double superconducting phase boundary in zero field [145], and more generally creates a tetracritical point in the $H - T$ phase diagram separating the B phase from the topologically trivial A (high-temperature) and C (high-field) phases. In the A phase, a single $E_{2u}$ component has line nodes around the $k_x - k_y$ direction, while in the low-temperature B phase the real and imaginary components of the vector order parameter are both stabilized, leading to a vanishing of the line nodes [144, 146]. Since the tetracritical point cannot be removed by applying an external magnetic field [147], the existence of three phases is considered an intrinsic property of UPt$_3$, independent of the strength of the SBF [142]. Since topological materials such as UPt$_3$ could be used for computing or other applications due to the existence of surface states [143], it is crucial to determine the origin of the SBF and its effect on time reversal symmetry breaking of the superconducting order parameter.

Weak antiferromagnetic order at $Q_{AF} = (1/2, 0, 1)$ has been observed in a number of experiments. The ordered magnetic moment has been reported to be $0.01 \pm 0.02 \mu_B$ with the integrated intensity of the Bragg peak ceasing to increase below $T_c$ [148, 149]. Since magnetism was observed to vanish above the critical pressure of 3-4 kbar, the same pressure at which the splitting of the superconducting transition also vanishes, antiferromagnetism was considered the natural candidate for the SBF [145, 150]. However, it has also been noted that even for samples with extremely high chemical
purity, structural defects may also locally stabilize magnetic order, especially in light of the large Gruneisen parameter that could significantly change the local electronic structure around such defects [142]. In particular, stacking faults were observed to exist in up to 3% of the sample volume even for high quality samples [151]. Using a zone refining technique, it was observed that removing defects through annealing systematically improves $T_c$ [152], suggesting that defects also play a role in promoting magnetism and destabilizing superconductivity. The possibility that local defects could be responsible for “accidentally” generating regions of local magnetic order could explain several additional features of the magnetic ordered state, such as the fact that the antiferromagnetic $T_N \approx 5.5$ K does not change with Pd doping [153], and that no signature has been observed in specific heat near 5 K [154]. These observations suggest that antiferromagnetism is not an intrinsic property of UPt₃.

In the iron superconductors, a neutron resonance mode has been interpreted as evidence of a sign-changing order parameter. A neutron resonance mode has also been observed in a variety of heavy fermion superconductors, such as UPd₂Al₃ [155], CeCoIn₅ [156], and CeCu₂Si₂ [157], which have also been interpreted within a spin excitonic scenario [158, 159], although recent experiments on CeCoIn₅ now demonstrate that the dispersion of the resonance mode in that compound is more likely a damped magnon-like mode [160]. Since UPt₃ is another heavy fermion superconductor, it is important to show whether UPt₃ has an associated neutron resonance especially in light of its exotic odd-parity superconducting state which could have unknown consequences in a spin exciton scenario. However, it has also been argued theoretically that a three-dimensional superconductor such as an $f$ wave should have a suppressed resonance mode compared to lower dimensional systems [161]. It is also consistent with work showing that only $p$-wave chiral superconductors
should exhibit a resonance mode, and not $f$-wave, at least in the absence of significant defects scattering such as surface roughness [162, 163].

To investigate the magnetic fluctuations and the possible existence of a neutron resonance, experiments were carried out on large single crystals of UPt$_3$ purified through the technique of zone refinement. By plotting the residual resistivity ratio (RRR) against $T_c$, it was shown that this technique improves the superconducting properties, reaching a theoretical maximum of 0.563 K in a perfect bulk crystal [152, 164]. Two samples were studied, the first (labeled ZR8) was found to have RRR=450 and $T_c = 0.54$ K suggesting a high degree of purity, and the second (ZR11) with an even better RRR=990 and $T_c = 0.56$ K. In neutron diffraction experiments on ZR8 carried out at ILL by W. Gannon, the competition between superconductivity and magnetic order was observed, similar to measurements in [148], but leading to a decrease in peak intensity below $T_c$ rather than a plateau, as well as a broadening of the peak width consistent with a lowering of the spin-spin correlation length (Fig. 6.13). Similar experiments conducted at MACS on ZR11 by S. Carr exhibited no signs of magnetic order.

Inelastic neutron scattering was carried out on ZR8 and ZR11 to search for a spin resonance at the antiferromagnetic ordering position $Q = (\frac{1}{2}, 0, 1)$. No resonance was found (Fig. 6.14[top row]), but both samples exhibited a decrease in intensity below the energy associated with $T_c$, $E = 6k_B T_c$ [130]. Moreover, the temperature dependence of the quasi-elastic spin fluctuation spectrum was found to follow the shape of the magnetic order parameter (Fig. 6.14[bottom row]), showing that quasi-elastic spectral weight follows the shape of the magnetic order parameter. For long-range magnetic order, one expects quasi-elastic spectral weight to disappear in the magnetically ordered phase, thus these measurements are more consistent with short-
Figure 6.13: (a) Magnetic order parameter of UPt$_3$ from ILL experiments, and (b) its competition with superconductivity manifest as a decrease in peak height and concomitant increase in peak width below $T_c \approx 0.5$ K.
range magnetic order.

### 6.4 Magnetic fluctuation spectrum in UPt3 and its connection to superconductivity

Having addressed the issue of the neutron resonance in UPt3, I turn to the larger issue of the overall spin fluctuation spectrum. If superconductivity in UPt3 is generated through magnetic interactions, it is crucial to characterize the momentum and energy dependence of low-energy spin fluctuations. Beginning around 1987, Aeppli and coworkers studied two types of fluctuations with different energy and temperature scales. Next-nearest neighbor interactions between U ions, located at relative positions of \((0, 0, a)\) or \((0, 0, c)\) in reciprocal lattice units, were observed to fluctuate with a characteristic energy of about 10 meV and persist to temperatures above 150 K [71, 165]. Antiferromagnetic correlations between next-nearest neighbor U ions, located in adjacent crystallographic planes with a separation of \((1/3, 1/3, 1/2)\) in reciprocal lattice units, were observed to peak near 0.2 meV, with the intensity of fluctuations increasing by about 20% at 0.5 K compared to 5 K [148]. The persistence of magnetic fluctuations to temperatures above the magnetic ordering temperature \(T_N \approx 5\) K recalls another unconventional system, the iron superconductors, where the spin fluctuations found in the low-temperature antiferromagnetic phase were found to persist well into the paramagnetic state of BaFe\(_2\)As\(_2\) [166]. In addition to these magnetic fluctuations, long-wavelength spin fluctuations with \(\lambda = 0.1 - 0.3\) Å were also shown to exist which account for about 20% of the static spin susceptibility [142, 167].

Measurements of spin fluctuations in UPt\(_3\) conducted by S. Carr at MACS were carried out in the \(H0L\) scattering plane. Near the antiferromagnetic ordering position
Figure 6.14: Inelastic neutron scattering measurements demonstrating no resonance feature in UPt$_3$. Top row: temperature subtraction across $T_c$ of energy scans in the magnetically ordered RRR=450 sample (left) and RRR=990 sample (right), demonstrating a decrease in the observed intensity below $6k_B T_c$ rather than the expected resonance feature. Bottom row: temperature scans at quasi-elastic energies in the magnetically ordered (RRR=450) sample (f) Temperature dependence of the quasi-elastic spin fluctuation channel in the magnetically ordered RRR=450 sample (left) and RRR=990 sample (right).
$Q = (\frac{1}{2}, 0, 1)$ it was observed that fluctuations rapidly disperse away from this position along the $(H, 0, 0)$ direction, peaking near 0.2 meV and disappearing entirely near $q_x \approx 0.8$ r.l.u. and 4 meV. However, as the $H0L$ scattering plane cannot access positions such as $(\frac{1}{2}, \frac{1}{2}, 1)$, it was not understood whether spin fluctuations might be dispersing out of the $HL$ plane. A similar problem exists in case one wants to determine the relationship between the nearest and next-nearest neighbor correlations as a function of energy, since the fluctuations at $(0, 0, \frac{1}{2})$ and $(0, 0, 1)$ may broaden along directions out of the scattering plane.

To investigate the full three dimensional momentum and energy dependence of spin fluctuations in UPt$_3$, I studied the ultra-pure RRR=990 sample (ZR11) at SEQUOIA. Experiments were carried out at $T = 2$ K with neutron incident energies $E_i = 40$ and 21 meV using the high-flux mode of the spectrometer, and at $E_i = 12$ meV in the high-resolution mode. Additional measurements were carried out with $E_i = 21$ at $T = 50$ K. Fig. 6.15(a) shows constant-intensity contours of spin fluctuations in three dimensions, revealing that the spin waves adopt the hexagonal symmetry of the lattice. From this contour plot, it can be observed, for instance, that fluctuations at $(0, 0, 1)$ have a smaller intensity compared with those at $(0, 0, \frac{1}{2})$. Fluctuations can also be observed centered around the forbidden structural $(1, 0, 1)$ peak, including a region of strong intensity near $(1, 0, \frac{1}{2})$. The temperature dependence of peaks in the $H0L$ scattering plane is revealed in (b) by subtracting the data at $T = 50$ from that at $T = 2$ K (after subtracting the background from each dataset using method described in Chapter 2, and correcting the $T = 50$ K data for the bose factor). A clear low-temperature enhancement is visible at $(0, 0, \frac{1}{2})$ and $(1, 0, \frac{1}{2})$, which are connected to antiferromagnetic fluctuations, and at $(0, 0, 1)$.

To study the crossover between ferromagnetic and antiferromagnetic fluctuations
Figure 6.15: (a) Equal-intensity contours showing the three-dimensional profile of spin fluctuations in UPt$_3$ out of the $H0L$ scattering plane at $4 < E < 6$ meV. (b) Temperature enhancement of the spin fluctuation spectrum of UPt$_3$ for $3 < E < 5$ meV in the $H0L$ scattering plane ($T = 2 - T = 50$ K, after background subtraction).
that occurs below $T \approx 20$ K [71], ultimately providing for the stability of short-range magnetic order below $T_N \approx 5$ K in structurally disordered samples, it is important to determine whether fluctuations at these positions coexist at the same energy scale. To answer this question, we examine the two peaks at $(0, 0, \frac{1}{2})$ and $(0,0,1)$. In Fig. 6.16, which is a constant-energy cut with $8 < E < 12$ meV using neutrons with $E_i = 40$ meV, the peaks stemming from these two positions appear to merge into a single bar-like structure. Interestingly, a similar bar-like structure also appears that connects $(1, 0, \frac{1}{2})$ and $(1, 0, -\frac{1}{2})$ across the $(1, 0, 0)$ position. We conclude that this energy scale links the ferro- and antiferromagnetic fluctuations, and it is interesting to note that this is also the energy scale of an optical phonon of UPt$_3$ [168], suggesting the possibility that phonons may play a role in breaking the symmetry between the two types of magnetic fluctuations.

Figure 6.16 : Constant energy slice in UPt$_3$ in the $H0L$ scattering plane at $E = 10$ meV, taken with $E_i = 40$ meV neutrons.
To better understand the dispersion of magnetic fluctuations, data with $E_i = 21$ meV at both temperatures are projected into the $HK$ planes at constant energy $4 < E < 8$ meV in Fig. 6.17, with (a) $L = \frac{1}{2}$ and (b) $L = 1$. As a function of $L$, there is a clear change in the position of spin fluctuations from $(1, 0, \frac{1}{2})$ to $(\frac{1}{2}, \frac{1}{2}, 1)$, with some intensity also visible between $(1, 0, \frac{1}{2})$ and $(0, 1, \frac{1}{2})$, at $(\frac{1}{2}, \frac{1}{2}, 1)$. The $L = 1$ data in (b) also show no sign of a peak at the antiferromagnetic ordering position $Q = (\frac{1}{2}, 0, 1)$. Measurements collected at MACS in the $H0L$ scattering plane in this energy range showed fluctuations at $Q = (\frac{1}{2}, 0, 1)$ apparently dispersing toward $(1,0,1)$, but in the SEQUOIA data we find that the dispersion probably also moves in a transverse direction, merging with the structure near $(\frac{1}{2}, \frac{1}{2}, 1)$. Since excitations at $(\frac{1}{2}, \frac{1}{2}, 1)$ are also observed at low energy as shown in the other figures in this section, our data shows that the magnetic ordering position $(\frac{1}{2}, 0, 1)$ does not stem from a strong feature in the spin fluctuation spectrum of UPt$_3$, which offers further evidence that static magnetic structure with this spin arrangement probably occurs only accidentally at structural faults.

To better understand the energy dependence of spin fluctuations in UPt$_3$, $Q - E$ cuts are shown in Fig. 6.18, along directions parallel to $[H00]$ (a) and parallel to $[00L]$. Note that in these plots, positions are given in terms of the crystallographic coordinates, so that $\langle H, 1, 1 \rangle$ describes a direction parallel to $[H00]$ passing through the position $(0, 1, 1)$. Therefore, in this cut the position with the coordinate 0.5 on the horizontal axis is the crystallographic position $(0, 1, 1)$. Intensity at most magnetic positions disappears by about 5 meV, with the notable exceptions of $(0, 0, \frac{1}{2})$ and $(0,0,1)$. The strongly dispersive bands observed in this data are not magnetic features: intense scattering stemming from $(2,0,0)$ or $(0,0,2)$ are a combination of UPt$_3$ phonons and phonons from the aluminum sample holder, while the nearly horizontal bands
Figure 6.17: Temperature dependence of spin fluctuations in UPt$_3$ in the $HK$ directions at (a) $L = \frac{1}{2}$ and (b) $L = 1$. 
near 10 and 18 meV are identified as UPt$_3$ phonons. No dispersive features stemming from magnetic positions are observed with this energy resolution, only broad $Q$-independent columns of scattering. Comparing the energy dependence of $(0,0,1/2)$ and $(0,0,1)$, in the center and rightmost panel in the top row of (a), the former are clearly gapless while $(0,0,1)$ appears to reach a minimum in intensity near 6 meV.

To better clarify the existence of a possible gap-like feature in the energy dependence of $(0,0,1)$, in Fig. 6.19 I show cuts along the $(0,0,L)$ direction at base temperature $T = 2$ K using data with lower neutron $E_i$ than the previous figure and thus better energy resolution. With the lowest resolution (approximately 1.8 meV using $E_i = 12$), no intensity is observed in (a) at $(0,0,1)$ below 3-4 meV. By subtracting data with $T = 50$ K from the data at $T = 2$ K, shown in (c), it is at least clear that no intensity is gained in this energy range, whereas an intensity gain is very obvious at the $(0,0,1/2)$ and $(0,0,3/2)$ positions. This result shows that antiferromagnetic fluctuations are gapless in UPt$_3$, while the ferromagnetic fluctuations associated with next-nearest neighbor correlations are strong only above 6 meV, an energy scale that was within the energy resolution of early experiments [71]. However, since the data collected at MACS shows a very small amount of intensity at $(0,0,1)$ in this energy range, it is probably not accurate to call the intensity minimum at $(0,0,1)$ a true energy gap.

Finally, Fig. 6.20(a) summarizes the energy dependence of fluctuations at $T = 2$ K integrated in a narrow region around different positions in reciprocal space. Clearly visible are peaks near $E = 18$ meV which correspond to a combination of optical phonons and aluminum phonons from the sample holder. At $(0,0,1)$, there is a dip at 6 meV relative to the overall decreasing trend at this position, consistent with the $Q-E$ cuts shown in Fig. 6.18. In (b) with $E_i = 21$ meV, the background measured at positions around the central peak have been averaged and subtracted, and the $T = 50$
Figure 6.18: $Q - E$ cuts in UPt$_3$ with $E_i = 40$ meV. Directions in (a) are parallel to the $[H00]$ direction and in (b) parallel to $[00L]$. Positions of interest are marked below the axis in crystallographic coordinates.
Figure 6.19: Spin fluctuations in UPt$_3$ along the (0, 0, $L$) direction at low energies with $T = 2$ K, using $E_i = 12$ meV (a) and $E_i = 21$ meV (b-c). In (c), $T = 50$ data has been subtracted. K data corrected for the bose factor, before performing temperature subtraction. The result shows an intensity gain developing as low temperature below $E = 10$ meV with the same energy dependence observed at the $Q = (0, 0, \frac{1}{2})$, (0,0,1), and ($\frac{1}{2}, \frac{1}{2}, 1$) positions, while no gain is observed at the magnetic ordering position ($\frac{1}{2}, 0, 1$). The fact that this position does not follow the profile of the others is consistent with the idea that magnetic order is not an intrinsic property of UPt$_3$. 
Figure 6.20: (a) Energy cuts of the spin fluctuation spectrum in UPt$_3$ at positions where low-energy intensity is observed. (b) Temperature-subtracted energy cuts showing a similar gain in intensity at ferromagnetic and antiferromagnetic positions, but no intensity gain at the “accidental” magnetic ordering position $Q = (1/2, 0, 1)$. 
Chapter 7

Other experiments in magnetism and superconductivity

Other experiments and calculations were conducted on systems that remain unexplored with uniaxial pressure, but retain promise for future experiments. For BaFe$_2$As$_2$ just below optimal doping, in the region exhibiting incommensurate antiferromagnetic order, I conduct RPA calculations showing a smooth evolution of incommensurability whereas neutron scattering experiments show a sharp transition and glassy spin structure that is incompatible with a weak-coupling picture. In Ce$_2$Zr$_2$O$_7$, a spin liquid candidate where inelastic neutron scattering shows evidence of fractionalized spin excitations, $\mu$SR experiments demonstrate the absence of magnetic order down to 19 mK with a qualitative change across $T \approx 150$ mK observed in zero field, longitudinal field, and transverse field measurements. $\mu$SR also demonstrates that spin fluctuations are dynamical at base temperature, consistent with the spin liquid hypothesis, as well as a diamagnetic muon Knight shift as the temperature is decreased from 5 to 1.5 K. I discuss several plausible microscopic scenarios to explain the qualitative change of the muon decay asymmetry above and below $T = 150$ mK. I show data suggesting the possibility that external magnetic flux becomes trapped in the material after the field is removed, like a superconductor. Finally, I show the results of $\mu$SR experiments on single crystals of tetragonal FeS, a iron-based superconductor with $T_c \approx 5$ K analogous to FeSe but with the addition of disordered magnetism below 15 K which may be percolated locally by impurities consisting of
small clusters of iron. Our experiments confirm that magnetism and superconductivity compete in this material despite the lack of magnetic order. We also find that the internal magnetic field in FeS, though small in magnitude, is anisotropic between the in-plane and $c$ axis directions.

7.1 Spin glass in electron-doped BaFe$_2$As$_2$: RPA

Neutron scattering experiments using polarized triple axis and neutron spin echo spectrometers were carried out by X. Lu on Ba(Fe,Ni)$_2$As$_2$ with Ni-doping in the range 0.065-0.096 per formula unit. These samples were found to exhibit a transition from commensurate to incommensurate order beginning with the BaFe$_{1.915}$Ni$_{0.085}$As$_2$ sample and observed at all higher dopings [169]. Crucially, this BaFe$_{1.915}$Ni$_{0.085}$As$_2$ sample is different from the samples also reported to be BaFe$_{1.915}$Ni$_{0.085}$As$_2$ that were studied in Chapter 3, where commensurate magnetic order was found [15, 79]. In X. Lu’s experiment, both spectrometers were used to measure $T_N$, with conflicting results attributed to the difference in energy resolution, which was interpreted as a signature that the magnetic moments comprise a disordered spin glass. However, no canting of the moments in the $b$ axis direction was observed in the spin glass phase, leading to the conclusion that moments remain oriented along $a$ in the stripe antiferromagnetic phase but with moment amplitude modulation that explains the incommensurability. It was suggested that the glassy dynamics could be an indication that superconductivity is competing with both spin and charge ordering.

RPA calculations of the imaginary part of the spin susceptibility in electron-doped BaFe$_2$As$_2$ reveals no sudden change in incommensurability near this doping regime [169], consistent with the interpretation that strongly-coupled local moments are responsible for glassy dynamics in BaFe$_{1.915}$Ni$_{0.085}$As$_2$ and optimally superconducting
BaFe$_{1.9}$Ni$_{0.1}$As$_2$, since these are beyond the scope of the weakly-coupled RPA picture. Using a 5-orbital model, these calculations reveal a large incommensurate peak with a transverse splitting of $2\delta$ with $\delta \approx 0.17 - 0.18$ in orthorhombic reciprocal lattice units. As shown in Fig. 7.1, the calculated incommensurability $\delta_{\text{cal}}$ is not very sensitive to the doping, evolving by at most 0.01 r.l.u. between dopings corresponding to 0.082 to 0.096 Ni per formula unit. A smaller peak at $\delta \approx 0.07$ was also observed, which more closely matches the experimentally observed values of $\delta_{\text{exp}} \approx 0.03$ r.l.u.

The Fermi surface nesting conditions and their relationship to the RPA spin susceptibility were studied in the same manner presented in Chapters 5 and 6, by overlaying the Fermi surfaces connected at $k$ and $k + Q$. The results are shown in
Fig. 7.2 for the two values of $Q$ corresponding with peaks in the RPA susceptibility, $Q = (0.07, 1, 1)$ and $Q = (0.18, 1, 1)$. The strongest nesting condition is established at $Q = (0.18, 1, 1)$ where two pairs of hole and electron pockets form near-perfect nesting conditions as evidenced by the hot spots in the bare (noninteracting) spin susceptibility shown in Fig. 7.2(b) and (d).

Since spin fluctuations are only weakly three dimensional, with little variation along the $c$ axis, I also evaluate the two-dimensional Fermi surface nesting conditions at $Q = (0.07, 1, 0)$ and $Q = (0.18, 1, 0)$, shown in Fig. 7.3. The results show similar values of incommensurability in the dynamical spin susceptibility and suggest that nesting may occur for a range of $q_z$. However, the near-perfect nesting conditions observed at $Q = (0.18, 1, 1)$ are not observed in the two-dimensional case. Thus, low-energy spin fluctuations in a weak-coupling RPA picture of electron-doped BaFe$_2$As$_2$ remain three-dimensional, a situation not supported by the experimental evidence suggesting moment modulation along an in-plane direction. We conclude that spin fluctuations in Ni-doped BaFe$_2$As$_2$ in the spin glass phase near optimal superconductivity arise through a strong coupling mechanism that is not captured within the RPA formalism.
Figure 7.2: Fermi surface nesting and spin susceptibility for $Q = (0.07, 1, 1)$ and $Q = (0.18, 1, 1)$ within the 5-orbital model for BaFe$_2$As$_2$ with electron filling near optimal superconductivity. (a) Nesting at $Q = (0.07, 1, 1)$ with $k = (k_x, k_y, k_z = 0 \rightarrow 1)$ and (b) $k = (k_x, k_y, k_z = 0 \rightarrow 1)$. (c) Nesting at $Q = (0.18, 1, 1)$ with $k = (k_x, k_y, k_z = 0 \rightarrow 1)$ and (d) $k = (k_x, k_y, k_z = 0 \rightarrow 1)$. 
Figure 7.3: Fermi surface nesting and spin susceptibility for $Q = (0.07, 1, 0)$ and $Q = (0.18, 1, 0)$ within the 5-orbital model for BaFe$_2$As$_2$ with electron filling near optimal superconductivity. (a) Nesting at $Q = (0.07, 1, 0)$ with $k = (k_x, k_y, k_z = 0)$ and (b) $k = (k_x, k_y, k_z = 1)$. (c) Nesting at $Q = (0.18, 1, 0)$ with $k = (k_x, k_y, k_z = 0)$ and (d) $k = (k_x, k_y, k_z = 1)$. 
7.2 Spin liquid in Ce$_2$Zr$_2$O$_7$: muSR

In unconventional superconductors such as cuprates, the superconducting state emerges upon doping a Mott insulating antiferromagnetic ground state. In the resonating valence bond picture, the ground state of such materials exhibits long-range entanglement with an extremely large degeneracy, and this configurational disorder may be a key precursor to superconducting pairing. Fundamental spin excitations of such a system would correspond to energy carried by a single spin, leading to a fractionalized spinon fluctuation spectrum rather than the conventional bosonic magnons. Spin liquids are also expected to exhibit long range entanglement and, as the name suggests, a lack of magnetic order down to the lowest temperatures. Spin liquid candidate materials have been proposed previously, such as Ce$_2$Sn$_2$O$_7$ [170], but conclusive proof was lacking because single crystals could not be grown to measure the spinon fluctuation spectrum.

In 2018, single crystals of Ce$_2$Zr$_2$O$_7$ were synthesized in our group by B. Gao using a floating zone furnace, and neutron scattering experiments were conducted on these crystals by B Gao and T. Chen which provided evidence for fractionalized excitations that agree with a model proposed by G. Chen and strongly suggest that the system is a spin liquid [171]. Various other observed properties of Ce$_2$Zr$_2$O$_7$ also show the system is consistent with a spin liquid, including magnetic susceptibility, specific heat, and diffuse neutron scattering, while neutron diffraction proves that the samples have very small site disorder.

Since $\mu$SR is ideally suited to testing for existence of magnetic order even in small regions within bulk samples, I carried out measurements at the LTF and GPS spectrometers at PSI to study the magnetic properties of Ce$_2$Zr$_2$O$_7$. At LTF, we ground the crystals into a coarse powder and used a dilute solution of GE varnish to
paste it on a high-purity silver plate with well-characterized \( \mu \)SR relaxation. At GPS, a piece of single crystal, unaltered since the floating zone growth, was mounted on the sample stick between layers of aluminized mylar tape. The GPS sample had some oxidation on the surface due to brief exposure to air during the sample preparation, a property that has led to Ce\(_2\)Zr\(_2\)O\(_7\) being proposed as a catalytic material for industrial applications [172].

Zero field (ZF) measurements shown in Fig. 7.4 show no oscillations and long relaxation times of 0.05-0.3 \( \mu s^{-1} \). The asymmetry may be equally well modeled using a stretched exponential form \( A_0 e^{-(t/T_1)^\beta} \) first proposed to model spin glasses [48, 170], with the fitted relaxation time and decay exponent shown in Fig. 7.4(b), or within a phase-separated model shown in (c) consisting of the dynamical relaxation function \( A_0 e^{-t/T_1} \) within the entire sample volume as well as a volume fraction containing random static fields and exhibiting a Gaussian relaxation functional form \( A_0 e^{-t^2/\sigma^2} \). In the second case, the random static fields were observed to be nonzero only below 150 mK. Overall, by combining this data with ZF measurements taken at GPS at higher temperatures, shown in (d), the results are consistent with a qualitative change in the shape of the asymmetry below \( T = 150 \) mK.

Measurements on Ce\(_2\)Zr\(_2\)O\(_7\) in longitudinal field (Fig. 7.5) were conducted to estimate the strength of the internal magnetic field at the muon stopping site. The observed field required to decouple the muon spin from the internal fields was very large, about 0.3 T, which suggests that magnetic moments do not form static arrangements, but remain dynamical at all temperatures [48]. In these measurements, another aspect of the qualitative change below 150 mK was noted, which is a slower relaxation of the asymmetry at \( B = 1.4 \) T, 19 mK compared to 0 and 1.4 T at both 450 mK and 750 mK.
Figure 7.4: Zero field $\mu$SR experiments on Ce$_2$Zr$_2$O$_7$ at LTF and GPS.
Figure 7.5: Longitudinal field $\mu$SR experiments on Ce$_2$Zr$_2$O$_7$ at LTF.
At the suggestion of J. Verezhak, measurements were conducted at GPS in transverse fields with $B = 7800$ G (0.78 T), which cause rapid oscillations of the asymmetry. These experiments were analyzed by Fourier analysis within the MUSRFIT software. In Fig. 7.6(a) the Fourier transform of the transverse field spectra were fitted with three peaks, where one peak is assumed to have the exact frequency imposed by the applied field, $\omega = \gamma_\mu B$, corresponding to muons landing in the nonmagnetic surface oxide (the numbers in the figure are reported in units of field strength). Two other muon stopping sites are observed to shift diamagnetically (to lower frequency) with lowering temperature (Fig. 7.6(b)), reaching a 1-2% decrease at 1.5 K. To obtain good fitting, we modeled each peak with a pseudo-Voigt lineshape consisting of a sum of a Gaussian and Lorentzian function, with the balance between the two components as an adjustable parameter. The increasing value of the Gaussian component with decreasing temperature as shown in Fig. 7.6(c) suggests that magnetic fluctuations in Ce$_2$Zr$_2$O$_7$ are smoothly evolving between different relaxation mechanisms in this temperature range. Similar results demonstrating a 0.6% diamagnetic frequency shift at 1.5 K were also obtained with weak transverse field measurements in 50 G at GPS.

In low applied fields at LTF, we obtained results that, while inconclusive, suggest very interesting possibilities for the ground state of Ce$_2$Zr$_2$O$_7$. In longitudinal field with values in the range 10-50 G, there appears to be another phase with much faster relaxation rates, as shown in Fig. 7.7(a). These exact field values seem to have been narrowly missed by the earlier measurements shown in Fig. 7.5. The origin of this phase is unknown, and it is unlikely to be involved with the formation of long-range magnetic order, since no oscillations were observed. However, using a stretched exponential form, the fitted parameters are a significant departure from the range of values observed in zero field and for fields above 100 G, as shown in Fig. 7.7(b) (see
Figure 7.6: Transverse field $\mu$SR experiments ($B=7800$ G) on $\text{Ce}_2\text{Zr}_2\text{O}_7$ at GPS.
the caption for information on the fields corresponding to each curve).

These measurements were collected directly after carrying out the longitudinal field measurements at fields as high as 1.4 T. Thus, I initially assumed the sample environment was simply magnetized on the order of 10-100 G. However, this hypothesis was proved incorrect upon rotating the incoming muon spin and measuring transverse oscillations using the detectors in the direction perpendicular to the longitudinal field coils: the measured remnant field at the sample was only 4 G. Could the ground state of Ce$_2$Zr$_2$O$_7$ be externally magnetized such that flux is trapped at low fields, but not at high fields? Another possibility pointed out by A. Hallas is that the muons themselves are perturbing the spin liquid system, which is a possibility, but it is unclear why this should only affect a narrow range of applied fields and not appear in the zero field or weak transverse field measurements.

To further investigate the effects of low magnetic field trapping in Ce$_2$Zr$_2$O$_7$, I measured differences in the oscillation frequency in weak transverse field of 30 G after field-cooling the sample from 500 mK in 30 and 40 G. The black curve in Fig. 7.7(c) is taken in 30 G transverse field at 19 mK, after cooling from 500 mK in 30 G, whereas the red curve is taken in 30 G at 19 mK after cooling in 40 G. The Helmholtz coils responsible for generating these values of weak transverse field are repeatable to much better than 1 G, yet the two curves shown in Fig. 7.7(c) are visibly different and are fitted to sinusoidal curves representing internal fields of 30.52 and 32.06 G, respectively. Therefore, in the case of field cooling in 40 G, the sample has apparently retained about 1.5 G within the sample when cooled through 150 mK. Further experiments are necessary to study this effect, but if it is a real property of the sample, this is among the first evidence that a correlated spin liquid material can trap and retain magnetic flux at very low applied fields.
Figure 7.7: Possible novel effects at low fields 10-50 G in Ce$_2$Zr$_2$O$_7$, from measurements at LTF in longitudinal field (a-b) and weak transverse field (c). In (b), the “true” zero field data are shown with bright green hollow triangles, while the remnant effect of application of 1.4 T at $T = 19$ mK, which registers a magnetization of 4 G, is shown with hollow blue diamonds.
To further test the hypothesis that field cooling has an effect on the ground state magnetization of Ce$_2$Zr$_2$O$_7$, weak transverse field measurements were carried out at LTF within the temperature range of 19 to 750 mK in 30 G, after field cooling in 30 and 40 G, and at 100 G. The results also exhibit qualitative change near 150 mK, but the choice of physical model gives different results. I show three possibilities in Fig. 7.8(b-d), which are all plausible in the limit of certain physical assumptions. All data analysis was carried out with MUSRFIT, while globally constraining some parameters such as the relaxation in the paramagnetic silver sample holder. In Fig. 7.8(b), I consider a model wherein the sinusoidal oscillation is modulated by Gaussian relaxation, such as would result in the case of random static internal fields across the entire sample. Under this method, the fitted oscillation frequencies at 30 G and 100 G display opposite trends in the frequency shift with temperature. In panels (c) and (d), I consider phase-separated models consisting of regions with dynamical depolarization as well as depolarization resulting from static fields. In (c), the two regimes are fully phase separated, with the fraction of muons experiencing static depolarization shown in the panel at right and exhibiting nearly volume fractions between the two phases. In (d), the static fields are presumed to coexist with the dynamical fields generated in the remaining sample volume, where the result is that the volume fraction changes with applied field. Since each of these scenarios present plausible temperature trends in the other fitted parameters, with a feature near 150 mK and smooth evolution at higher temperatures, further experiments are necessary to establish which of these models may be closest to a correct description of the low-temperature dynamical spin liquid state of Ce$_2$Zr$_2$O$_7$. 
Figure 7.8: Weak transverse field $\mu$SR experiments on $\text{Ce}_2\text{Zr}_2\text{O}_7$ at LTF.
7.3 Glassy islands in FeS: muSR

Tetragonal FeS is an iron-based superconductor \((T_c = 5\text{ K})\) with neutron scattering experiments observing no signatures of either long-range magnetic order or nematic fluctuations \([173]\). However, signatures of quasi-static magnetism were observed in this compound by \(\mu\)SR on powder samples \([174, 175]\), which established the existence of “islands” of glassy magnetic order surrounding small iron impurities that were left over from the hydrothermal synthesis process. Since FeS has a small Fermi surface and exhibits glassy spin dynamics, this material should exhibit signs of strong coupling, similar to the case of the spin glass phase in \(\text{Ba(Fe,}\text{Ni})_2\text{As}_2\) described above. Thus, we carried out \(\mu\)SR experiments at M20 on FeS single crystals to investigate the dynamics of short-range spin correlations and establish the existence of symmetry breaking between the \(a/b\) and \(c\) axis directions.

Tetragonal FeS single crystals were synthesized with the hydrothermal method in our group by H. Man, who also used inelastic neutron scattering to show the existence of weak stripe-antiferromagnetic spin fluctuations that do not change across \(T_c\), and the total lack of rotational symmetry breaking under uniaxial pressure, precluding the existence of a nematic phase. An array of many small samples were coaligned in a small sachet made of aluminized mylar tape, with the \(c\) axis along the direction of the muon beam, and the \(a/b\) axes in the plane perpendicular to the beam.

Due to the possible presence of a very fast relaxation component and the weak strength of expected internal magnetic fields, very precise calibration of the M20 spectrometer was performed to meet these challenging conditions. Since the samples consisted of very thin flakes, the array of samples was determined to be thin enough that many muons passed directly through the foil sachet without being stopped. To increase the number of muons stopping in the sample, we decreased the incoming
muon momentum by 10% using the Wien filter on the M20 beamline, which we found produced the optimal ratio of useful events to rejected events. As pointed out by D. Arseneau, with low muon momentum one expects muons to stop in the sample space even before reaching the sample, such as in the veto scintillator, therefore decreasing the momentum further is not advantageous. We also carried out a calibration of the pulse shapes produced by the pulse rectifier, and their effect on the early-time part of the time spectra below 0.02 µs, using hematite powder (Fe₂O₃), which has a strongly depolarizing effect on muons due to large internal fields. This test showed glitching in the pulse shapes, which we were able to mitigate with the use of D. Arseneau’s “deglitch” program, a work of magic. After correcting for the glitches, we found no evidence for a fast relaxing component from iron cluster impurities in FeS, which suggests either that it does not exist in our samples, or that it is so strong so as to completely depolarize the muon spins within the first 20 ns. No experiments could be performed at M20 to resolve this question.

Proceeding with zero field experiments, we found very good fitting using a relaxation function derived from the stretched exponential form used in Ref. [174] for powder FeS samples. Due to the low incoming muon momentum, we added a background term corresponding to muon implantation in the aluminized tape. We note that a different functional form was used in Ref. [175], which did not agree with our data, possibly due to the background. The differences in zero field relaxation functions are shown in Eq. 7.1:
\[ A_{ZF}(t) = A_{maj}\left(\frac{2}{3}e^{-\sqrt{\lambda}ZFt} + \frac{1}{3}\right) + (1 - A_{maj})\left(\frac{2}{3}e^{-\lambda t} + \frac{1}{3}\right) \quad \text{(Holenstein, ref. [174])} \]
\[ A_{ZF}(t) = A_1e^{-\lambda_1t} + A_2e^{-\lambda_2t} \quad \text{(Kirschner, ref. [175])} \]
\[ A_{ZF}(t) = A_{tape}e^{-\lambda_{tape}t} + A_{sample}(1 - A_{Fe})e^{-\sqrt{\lambda_{glass}t}} + A_{sample}A_{Fe}e^{-\lambda_{Fe}t} \quad \text{(this work)} \] (7.1)

Zero field experiments in spin-rotated configuration (muon spins along \(a/b\)) shown in Fig. 7.9, show an increase in the fast relaxation rate below 20 K, which we attribute to short-range, glassy magnetic order. The fitted relaxation rates begin to decrease below 5 K, clearly indicating competition between magnetism and superconductivity, while the magnetic volume fraction also appears to decrease, consistent with real-space phase separation between magnetic and superconducting ground states. Comparing weak transverse field measurements in spin-rotated mode, shown at left, to those in the non-spin-rotated configuration (muon spins along \(c\)), shown in Fig. 7.10, we find that the onset of superconductivity, clearly indicated in the diamagnetic muon Knight shift (top row at right), is accompanied by a decrease in the dynamical depolarization rate in the magnetic regions, labeled Ordered rate, and a concomitant increase in the depolarization rate due to random static fields, labeled Gaussian rate. In the non-spin-rotated data, in which muon spins are initially polarized along the sample \(c\) axis and therefore probe transverse fluctuations in the \(a/b\) basal plane, the ordered rate appears to approach zero as \(T\) decreases, while for muon spins probing out-of-plane fluctuations in spin rotated mode, the decrease is much less pronounced. In addition to these measurements, we also observed somewhat different muon depolarization rates along the \(c\) axis and in the \(a/b\) plane in longitudinal field (LF) measurements. Such LF experiments are made possible possible in FeS because the low internal field strength makes it possible to use the Helmholtz coils at M20 for longitudinal fields, whereas
with larger internal fields one requires a high-field magnet. Thus, single crystals of tetragonal FeS exhibit signs of anisotropy in the magnitude of dynamical fluctuations in- and out-of-plane. Thus, our experiment confirms the presence of small-moment disordered magnetism, which Z. Guguchia points out makes it quite similar to FeSe under 9 GPa hydrostatic pressure. In the future, if uniaxial pressure experiments can be carried out on FeS, strain-induced anisotropy may prove to compete with the natural anisotropy in this system.
Figure 7.9: Weak transverse field $\mu$SR experiments on tetragonal FeS with initial muon spins polarized along $a/b$ (spin-rotated mode).
Figure 7.10: Weak transverse field $\mu$SR experiments on tetragonal FeS with initial muon spins polarized along $c$ (non-spin-rotated mode).
Appendix

On the following pages is included the manual for the generation-2 uniaxial pressure instrument described in Chapter 3. The version included here was given to operators of the $\mu$SR experiments conducted on doped BaFe$_2$As$_2$ and SrFe$_2$As$_2$ samples at M20.
PNEUMATIC UNIAXIAL APPARATUS, M1600, AUGUST 2016

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AUGUST 5, 2016

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1. Description.

![Complete apparatus, fitted for PPMS (Dynacool) cryostat.](image)

The device was originally built at Rice in the summer/fall of 2015 and redesigned in summer 2016. It employs a mixture of commercial devices and custom components, as listed in the following table. In addition, it requires compressed air up to a maximum of 155 psi (15 psi above the linear slide maximum of 140 psi; the electronic regulator’s inlet maximum is 165 psi).

The linear slide, load cell, and load cell preamplifier are new components not used for the previous M1600 experimental run. The preamp operates off the same 24 VDC power supply that was used before. The electronic regulator is the same one used before. The other parts of the device have been redesigned for the low-background insert so, for instance, the tubes are smaller diameter. The operating principle and pressure range is essentially the same as what was done before.

<table>
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<th>Part</th>
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<tr>
<td>Electronic air regulator</td>
<td>Proportion Air MPG-PR93BQ250SGAMXL</td>
<td>regulate pneumatic pressure</td>
<td>505</td>
</tr>
<tr>
<td>Linear slide</td>
<td>PHD OCG111/2X5</td>
<td>convert air pressure to force</td>
<td>75</td>
</tr>
<tr>
<td>Load cell preamplifier</td>
<td>Futek FSH03863 (IAA100)</td>
<td>convert strain gauge signal to +/- 10 VDC</td>
<td>425</td>
</tr>
<tr>
<td>Load cell</td>
<td>Futek FSH00098 (LSB200)</td>
<td>measure force in vacuum space</td>
<td>500</td>
</tr>
<tr>
<td>NIST-traceable calibration for load cell and preamp</td>
<td>Futek (recommend yearly recalibration)</td>
<td>375</td>
<td></td>
</tr>
<tr>
<td>USB data acquisition module</td>
<td>National Instruments USB-4411</td>
<td>real-time pressure control and monitor</td>
<td>189</td>
</tr>
<tr>
<td>Spring</td>
<td>e.g. McMaster 96485K138 (234 lbf/in, max 304 lb)</td>
<td>translate sample stick</td>
<td>15</td>
</tr>
<tr>
<td>Inner and outer stainless steel tubes</td>
<td>McMaster 8457K56 &amp; 89495K405</td>
<td>transfer force to sample</td>
<td>32</td>
</tr>
<tr>
<td>Sample holder body</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KF flanges and components</td>
<td>Kurt Lesker</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>24 VDC power supply</td>
<td>ORNL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Assorted machined pieces</td>
<td>in-house</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (not including air tank &amp; regulator)</td>
<td></td>
<td></td>
<td>2,700</td>
</tr>
</tbody>
</table>

The top part of the assembly contains a pneumatic linear slide with a stroke length of 3 inches and a maximum force of 272 lbf at 140 psi. If all of the load is held by the spring, the potential energy is 18 J. The pressure in the slide is set by a feedback-controlled regulator that was used before for M1600. The slide is coupled to an aluminum piston tube that moves in and out of the KF-50 tee through a compression o-ring seal, where it connects to one side of an S-beam load cell. The other end of the load cell is coupled to a stainless steel tube (5/16 in. OD) that runs inside another stainless steel tube (7/16 in. OD) down to the sample area, where it applies mechanical force to the sample.
2. Head assembly.

As the pressure in the linear slide is increased, the inner stick pushes against a spring. After the far end comes in contact with the sample, the stick no longer moves, and further increasing the pressure in the slide applies uniaxial compression to the sample. If the sample is attached (epoxied or clamped) to its mounting plates, by letting pneumatic pressure out of the system, the spring force generates uniaxial tension in the sample.

Just below the spring, the inner stick enters the vacuum space through an o-ring seal attached to a KF-50 tee. Inside this space an S-beam load cell measures the force in the inner stick, and its signal is passed through a hermetic amphenol connector at the side port of the KF tee. In this way, the load cell can be used to maintain constant force during heating and cooling, and makes the system insensitive to the friction in the o-ring seal when the pressure is changed.

For safety, the inner stick can be immobilized at any time. This is accomplished by tightening a screw in the plate that pushes against the spring, fastening it to the aluminum support plate.

On the other side of the KF tee, a cryostat-specific coupler attaches the apparatus to the cryostat. The photos in this document show the KF-40 coupler used for our PPMS; see below for the LAMPF design.

All shaft couplers have vented screw holes, and the inner stainless steel tube is also vented. The stick successfully holds full vacuum in the PPMS and we anticipate no issues with holding vacuum at TRIUMF.
Figure 3. Components in the head.
3. Sample stick and holder.

The sample stick consists of two concentric stainless steel tubes. The samples can be pre-mounted (epoxied) or clamped between aluminum plates, enabling experiments under uniaxial tension. For this experiment, we plan to study the samples under compression, so they will be held between free-floating aluminum plates with a small groove.

The outer stainless steel tube is brazed (cadmium-free) into a brass KF-50 flange on the head side, and on the sample side to a custom brass piece that attaches to the sample holder. The inner stainless steel tube has two brass plugs brazed into the ends that are tapped 1/4-20. The brass plugs slide freely but somewhat snugly in the outer stainless steel tube.

On the sample holder side, the inner stick is attached with a titanium screw to a 3/8 in. diameter aluminum piston. The piston is half-round and has a #8-32 tapped hole in the direction transverse to the uniaxial stress.

The “lower plate” touching the sample (side farthest from the load cell) is fixed into the sample holder frame by screwing in two #4-40 aluminum or titanium screws with conical tips that mate into conical dimples in the plate. By gripping the plate in two non-collinear places, the plate cannot rotate when pressure is applied, and thus keeps the force applied on the sample at a fixed angle. A small brass shim is also wedged between the plate and the frame to ensure a tight fit. The sample height is adjustable in increments of 1/8 in., the distance between pairs of screw holes in the sample holder.

The “upper plate” touching the sample (side nearest the load cell) has a #8 hole that is used to attach it to the aluminum half-round piston.

Once the sample and plates are mounted in the sample holder, the pneumatic pressure in the linear slide is increased, compressing the spring, until the half-round piston fits over the upper sample plate. Then, the upper plate is fastened...
to the piston. This sets the “zero point” for pneumatic pressure, at which everything is rigidly connected but there is no force on the sample. From this point, applying more or less pneumatic pressure applies uniaxial compression or tension to the sample under study.

At TRIUMF, the top of the sample holder and both upper and lower sample plates will be covered with 0.25 mm silver foil, glued with small beads of epoxy; muons will enter from the opposite side.
4. **Software control.**

The apparatus is controlled entirely via the USB-6001 data acquisition module and can be manipulated manually through Measurement & Automation Explorer or in Labview. We have written simple programs and we will decide how to use them at the time of the experiment.

The most important feature of the control program is a negative feedback loop that is used to maintain constant force in the inner stick during the experiment, including during thermal cycling. This feature is also useful during vacuum purging, and during fast cooling and warming, both of which may induce additional stresses in the inner stick and can fracture the more delicate samples.

The electronic regulator output is wired on channel AO0, and the regulator setpoint monitor is channel AI3 (differential mode). Both regulator signals are 0-10 VDC. The load cell signal is channel AI1 (also differential mode) and reads +/-10 VDC, with negative values for compression and positive values for tension.

We do not plan to integrate the control system with CAMP, but we will provide a laptop to be set up in the experimental area (or just outside) through which we will adjust the pressure. If the laptop can be connected to the internet, we can use screen-sharing software to control the pressure from the M20 cabin.

The load cell has a maximum capacity of 100 lbf, in tension or compression, and it is important not to exceed this limit. Overloading could occur by exceeding 100 lbf applied to the sample (not including the initial pressure that moves the piston up to the sample), or, in experiments under tension, by applying greater than 100 lbf to the spring/sample (including the initial pressure that moves the piston) and letting the system relax to low pressure. Our Labview programs attempt to prevent this behavior, but all operators must be aware of this limitation. For example, in a tension experiment, the software would not prevent catastrophic relaxation if the compressed air tank runs out.
5. **Sample stick for LAMPF.**

The sample stick is to be inserted in the low-temperature insert in the LAMPF cryostat. Four brass baffles are brazed onto the stick.

In order to accommodate the extra length of PMTs outside the low-background insert, we have added two aluminum bracing supports extending 10 in. from the port to the beginning of the KF tee containing the load cell. The interior of both the outer and inner stainless steel tubes, as well as the KF tee, are connected to the vacuum space. However, we do not expect the entire weight of the head components to be supported entirely by the port plug, and we would like to support the weight with an additional method (an extra table with a scissor stand?).

We will borrow TRIUMF’s Cernox temperature sensor as we did for the previous M1600 experimental run. The sensor wires will run from the sample holder, along the outside of the outer tube, then between the inner and outer tubes in the region between the PMTs, then into the KF tee and through the hermetic amphenol connector.

**Figure 5.** Sample stick designed for LAMPF low-background insert.
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