ABSTRACT

Title of dissertation:	SUPERCONDUCTING ENHANCEMENT AND ELECTRONIC NEMATICITY IN SUBSTITUTED $BaNi_2As_2$	
	Christopher Eckberg Doctor of Philosophy, 2019	
Dissertation directed by:	Professor Johnpierre Paglione Department of Physics	

Inspired by the frequent presence of nematicity in the high T_c superconducting systems, this thesis is focused on the interplay of nematic and superconducting order in a system that does not possess long range magnetism. Here I describe my measurements of the physical properties of Ba(Ni_{1-x}Co_x)₂As₂ and Ba_{1-x}Sr_xNi₂As₂ intermetallic compounds, characterizing both superconductivity and nematicity in these series.

Thermodynamic, transport, and magnetic properties of single crystals synthesized using a flux growth technique are reported. Using the results of these physical property measurements, I construct the electronic phase diagrams of the $Ba(Ni_{1-x}Co_x)_2As_2$ and $Ba_{1-x}Sr_xNi_2As_2$ series. In both substitution series, increasing x smoothly suppresses a tetragonal-triclinic structural phase transition. At the low temperature structural phase boundary, a large enhancement in superconducting T_c is observed in both systems.

The $Ba_{1-x}Sr_xNi_2As_2$ series was further characterized through measurements of

symmetry isolated components of the fourth-rank elastoresistivity tensor. I observe a divergence in elastoresistivity over a wide range of temperatures and x values in Ba_{1-x}Sr_xNi₂As₂ crystals, indicative of electronically driven rotational symmetry breaking in this series. The low temperature elastoresistivity is peaked in the vicinity of optimal T_c , suggesting the enhanced superconducting pairing observed in this region is born from strong nematic fluctuations in the system.

SUPERCONDUCTING ENHANCEMENT AND ELECTRONIC NEMATICITY IN SUBSTITUTED $BaNi_2As_2$

by

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Foreword

I have contributed to the following works, either published or currently under review. The results presented in this thesis are largely published in Refs. [1–3], which are marked with asterisks in the list below

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Table of Contents

Acknowledgements	ii
Foreword	v
List of Tables	xi
List of Figures	xii
List of Abbreviations	xiv
 Introduction Superconductivity BCS Theory of Superconductivity High Temperature Superconductivity Superconducting Pairing Mechanism Superconducting Gap Structure Superconducting Gap Structure Superconducting Value Superconductors BaNi₂As₂ This Work 	$1 \\ 1 \\ 3 \\ 7 \\ 10 \\ 11 \\ 14 \\ 19 \\ 24$
 2 Methods 2.1 Flux Crystal Growth	27 27 32 34 37 37 38 39 41 42 43
2.5 Bulk Characterization Techniques	46

	2.5.1 Heat Capacity		47
	2.5.2 Dc Magnetic Susceptibility		51
	2.5.3 Ac Magnetic Susceptibility		53
3	Nematic Susceptibility		60
	3.1 Point Groups		60
	3.2 The D_{4h} Point Group		64
	3.3 Nematic Susceptibility		67
	3.3.1 Theory		68
	3.3.2 Experiment		71
	$3.3.2.1 B_{1g}$ Susceptibility		73
	$3.3.2.2 B_{2g}$ Susceptibility		74
	3.4 Experimental Details		76
4	BaNi ₂ As ₂ : Structural Transition, CDW, and Ne	maticity	85
	4.1 Introduction \ldots		85
	4.2 Methods \ldots \ldots \ldots \ldots \ldots		88
	4.3 CDW Order		88
	4.4 Elastoresistivity		91
	4.5 Phenomenology of a Tetragonal-Triclinic P	hase Transition	95
	4.6 Conclusion \ldots		102
5	$B_{2}(N_{1}, C_{0}) A_{2}$ Evolution of Structure and	Superconductivity	103
0	5.1 Introduction	Superconductivity	103
	5.2 Methods		104
	5.3 Physical Properties		108
	5.4 CDW Order		112
	5.5 Discussion		116
	5.6 Conclusion		120
6	$Ba_{1-x}Sr_xNi_2As_2$: Tuned Nematicity and Superco	onductivity	121
	6.1 Introduction	•••••••••••••	121
	6.2 Methods	•••••••••••••	122
	6.3 CDW Order		124
	6.4 Resistivity, Magnetization, and Specific He	at	128
	6.5 Elastoresistivity	· · · · · · · · · · · · · · · ·	136
	6.6 Analysis	· · · · · · · · · · · · · · · ·	142
	6.7 Conclusion		149
7	Conclusions		150
	7.1 Summary of Main Results		150
	7.2 Future Work		152
A	. Ginzburg-Landau Model of $Ba_{1-x}Sr_xNi_2As_2$ Ser	ies	154
Li	ist of Growths		158

Bibliography

List of Tables

3.1	Multiplication table for C_{2v} point group	62
3.2	C_{2v} character table	64
3.3	D_{4h} character table	65
3.4	Structural transitions in $BaNi_2As_2$ and $BaFe_2As_2$ crystals	67
5.1	$Ba(Ni_{1-x}Co_x)_2As_2$ crystallographic data	07

List of Figures

1.1	Generic phase diagram for iron and cuprate superconductors	9
1.2	Illustration of s, s_{+-}, s_{++} , and d wave superconducting order param-	
	eters	11
1.3	Schematics illustrating the structure of iron-based superconductors.	12
1.4	Illustration of nematic order	14
1.5	Fermi surface of $BaNi_2As_2$	21
1.6	Signatures of the structural transition in $BaNi_2As_2$	22
1.7	Schematic of the $BaNi_2As_2$ triclinic structure	23
2.1	Photograph of a sealed quartz ampule containing a growth	30
2.2	Images of growth lab facility	31
2.3	Details of Pb and NiAs flux growth methods for $BaNi_2As_2$	35
2.4	Images of decomposition of $Ba_{1-x}Sr_xNi_2As_2$ crystals in air	36
2.5	Photographs of two Quantum Design ⁴ He cryogenic refrigeration sys-	
	tems	40
2.6	Image of four-terminal resistance measurement configuration	45
2.7	Example of heat capacity data taken using an extended heat pulse.	52
2.8	Illustration of basic principle of <i>ac</i> susceptibility technique	55
2.9	Photograph of <i>ac</i> susceptibility coil set	58
2.10	Example of rotated ac susceptibility measurement	59
3.1	Symmetries of the irreducible representations of the D_{4h} point group.	66
3.2	Predictions for free energy and thermodynamic susceptibility approach-	
	ing a continuous phase transition.	71
3.3	Schematic of B_{1g} symmetric nematic susceptibility measurement	75
3.4	Schematic of B_{2g} symmetric nematic susceptibility measurement	77
3.5	Schematic of the experimental electronics configuration for nematic	
	susceptibility measurements.	79
3.6	Photographs of elastoresistivity probe.	81
3.7	Laue pattern from $BaNi_2As_2$ single crystal	82
4.1	K-space x-ray scattering intensity mapping in $BaNi_2As_2$	90
4.2	Electronic nematic susceptibility measurement in $BaNi_2As_2$	93

4.3	Comparison of BaNi ₂ As ₂ $\chi^{B_{1g}}_{nem}$ and $\chi^{B_{2g}}_{nem}$ nematic susceptibilities 94
4.4	B_{1g} and B_{2g} symmetric distortions of the transition metal sublattice. 96
4.5	Relationship between elastoresistivity and CDW evolution
5.1	Structural and chemical characterization of $Ba(Ni_{1-x}Co_x)_2As_2$ single
	crystals grown from Pb-flux
5.2	Transport measurements in $Ba(Ni_{1-x}Co_x)_2As_2$ single crystals grown
~ 0	from Pb flux. \dots 109
5.3	Heat capacity of Ba $(N_{1-x}Co_x)_2As_2$ single crystals
5.4	Physical properties of nearly optimally substituted $Ba(Ni_{1-x}Co_x)_2As_2$ sin-
	gle crystal
5.5	H_{c2} data collected on an optimally substituted Ba(Ni _{1-x} Co _x) ₂ As ₂ sam-
	ple of $x = 0.083$ grown from Pb flux
5.6	Phase diagram for $Ba(Ni_{1-x}Co_x)_2As_2$ system
5.7	Simulated evolution of electronic density of states in $Ba(Ni_{1-x}Co_x)_2As_2119$
6.1	Structural and chemical properties of $Ba_{1-x}Sr_xNi_2As_2$ single crystals. 126
6.2	I-CDW x-ray reflections in $Ba_{1-x}Sr_xNi_2As_2$ single crystals
6.3	CDW phase diagram in $Ba_{1-x}Sr_xNi_2As_2$
6.4	Physical properties of $Ba_{1-x}Sr_xNi_2As_2$ single crystals
6.5	Structural phase diagram of $Ba_{1-x}Sr_xNi_2As_2132$
6.6	Physical properties of a single $Ba_{1-x}Sr_xNi_2As_2$ crystal with Sr content
	$x = 0.68 \dots \dots \dots \dots \dots \dots \dots \dots \dots $
6.7	Superconducting phase diagram of $Ba_{1-x}Sr_xNi_2As_2$
6.8	Heat capacity measurements for $Ba_{1-x}Sr_xNi_2As_2$ series
6.9	B_{1g} symmetric elastoresistivity of $Ba_{1-x}Sr_xNi_2As_2$ single crystals 138
6.10	Nematic susceptibilities of $Ba_{1-x}Sr_xNi_2As_2$ single crystals 140
6.11	Elastoresistivity in $Ba_{1-x}Sr_xNi_2As_2$ crystlas with $x = 0.63$
6.12	Physical properties of optimally substituted $Ba_{1-x}Sr_xNi_2As_2$ 143
6.13	Evolution of structural, charge and nematic orders in $Ba_{1-x}Sr_xNi_2As_2$ 144
6.14	Heat capacity measurements in over-substituted $Ba_{1-x}Sr_xNi_2As_2$ sin-
	gle crystals
6.15	Electronic heat capacity measurements in slightly over-substituted Ba _{1-x} Sr _x Ni ₂ As ₂ single crystals
Δ 1	Simulated phase diagram for the coupled structural nomatic transition 156
A 2	Simulated nematic susceptibility in structurally-driven and electronically-
11.4	driven systems

List of Abbreviations

BCS	Bardeen, Cooper, Schrieffer (theory of superconductivity)
C-CDW	Commensurate charge density wave
CDW	Charge density wave
CNAM	Center for Nanophysics and Advanced Materials
DFT	Density functional theory
DOS	Density of states
EDS	Energy dispersive spectroscopy
I-CDW	Incommensurate charge density wave
Irrep	Irreducible representation
MPMS	Magnetic Property Measurement System
PPMS	Physical Property Measurement System
SQUID	Superconducting Quantum Interference Device
T_c	Superconducting critical temperature
T_{nem}	Nematic transition temperature
T_S	Structural transition temperature
UMD	University of Maryland
VSM	Vibrating sample magnetometry
WDS	Wavelength dispersive spectroscopy

Chapter 1: Introduction

1.1 Superconductivity

In 1911, cryogenics pioneer Heike Kamerlingh Onnes observed a transition from finite to apparently zero electrical resistance at a critical temperature T_c of 4.2 K in elemental mercury [4]. This measurement was the first evidence for a new electronic phase of matter that became known as superconductivity. In the years to follow it was demonstrated that, in addition to exhibiting true zero electrical resistance, superconductors expel external magnetic fields from their bulk [5] and display signatures of macroscopic quantum coherence. All three of these properties have significant technological promise. However, superconductivity in all presently known materials is a relatively low temperature phenomenon, limiting the degree to which they may be commercialized.

As a result, efforts to increase superconducting transition temperatures have been widespread and well documented over the past century. The success of these efforts is reflected in part in the 1913, 1972, 1973, 1987, and 2003 Nobel Prizes in Physics, all of which were awarded to researchers studying superconductivity. A particularly notable discovery among the many advancements in the field was the 1986 report of superconductivity in a class of copper-oxide ceramics by Johannes Bednorz and Karl Müller [6]. Some of these compounds were found to exhibit remarkably high critical temperatures, far beyond those of any previously known superconducting materials. Crucially, some cuprate superconductors superconduct at temperatures above the boiling temperature of liquid nitrogen (77 K), making superconductivity accessible in a way that was never before possible.

It did not take long after the first reports of high T_c superconductivity in the cuprates for it to become clear that the superconducting mechanism in these compounds was different from other known superconductors. As a result, the study of cuprate superconductors quickly became a field unto itself, with the hope that better understanding of these compounds could enable the development of materials with even higher critical temperatures. Despite these efforts, the copper-oxide superconductors stood alone as the only class of high T_c materials until 2008, when high temperature superconductivity was discovered in a new family of iron-pnictide intermetallic compounds [7]. While critical temperatures in the iron-based superconductors are lower than the cuprates, interest in these materials has been expansive, generating over 15,000 publications in the decade since their discovery [8].

As with the cuprate compounds, the iron-pnictide superconducting mechanism is unlike that of most low T_c superconductors, and the theory of high temperature superconductivity is incomplete compared to the existing theoretical understanding of most low temperature superconductors. The rest of this chapter briefly reviews the physics of conventional superconductivity, and how high temperature superconductors deviate from this behavior. I will then discuss BaNi₂As₂, a simplified platform within which some of the physics of the high T_c compounds may be studied.

1.2 BCS Theory of Superconductivity

In 1957, John Bardeen, Leon Cooper, and Robert Shrieffer developed a microscopic theory of superconductivity that captures the behavior of the vast majority of known superconducting materials [9]. For this theory, they were awarded the 1972 Nobel Prize in Physics. This theory is very well known, and many descriptions of it may be found in the literature. My outline of the Bardeen, Cooper, Schrieffer (BCS) theory of superconductivity provided below is adopted from Tinkham's description [10].

BCS theory was not conjured from the air, but rather was motivated by considerable preexisting experimental and theoretical understanding of superconductivity. For instance, before BCS theory was developed, experimental efforts had established a vanishing electronic density of states in the superconducting phase, indicating that a gap opens at the Fermi energy below T_c . The heat capacity increases exponentially approaching the transition temperature from below, implying the energy gap narrows and is eventually overcome by thermal excitations at T_c . Additionally, magnetic fields were known to decay exponentially in the bulk of a superconductor. This behavior was first predicted by brothers Fritz and Heinz London in the 1930's [11], and later observed experimentally. In the early 1950's Fritz London correctly argued that a quantum mechanical justification of this phenomenon required long range quantum coherence. BCS theory was then developed with the knowledge that any comprehensive microscopic description of superconductivity must include both an energy gap and exponential screening of external fields, and likely required long range quantum coherence.

A key step in the development of the BCS theory occurred in 1956 when Cooper showed that, in a simple model, electrons experiencing an attractive potential at the Fermi Surface are unstable to the formation of bound pairs [12]. In the real system, the condensation of many such pairs would open a gap at the Fermi energy, consistent with thermodynamic measurements in the superconducting state [12]. Cooper constructed his model by considering the addition of two electrons to the zero temperature Fermi sea of a normal metal, and assuming that these electrons experience an attractive interaction from the electron-electron scattering potential shown below:

$$\begin{cases} V_{k,k'} = -V & |\epsilon_k - E_f| \le \hbar \omega_c \\ V_{k,k'} = 0 & |\epsilon_k - E_f| > \hbar \omega_c \end{cases}$$
(1.1)

where ϵ_k is the electron energy, E_f is the Fermi energy, and ω_c is a characteristic frequency quantifying a finite energy range around the Fermi energy within which electrons will experience this attractive interaction. To minimize total energy, the two electron wavefunction will have zero net momenta (*i.e.* the two electrons have momenta \mathbf{k} and $-\mathbf{k}$). Given the attractive interaction, and anticipating the formation of bound electron pairs, Cooper further assumed that the electrons form a spin singlet due to the close spacial proximity admitted in the radial component of the singlet wavefunction.

Substituting the proposed singlet wave function and the potential of Eqn. 1.1 into an appropriately formulated Schrödinger equation, the energy of the two particle wave function can be shown in the small V limit to be [12]:

$$E \approx 2E_F - 2\hbar\omega_c e^{-2/N(0)V} \tag{1.2}$$

where N(0) is the electronic density of states at the Fermi level. Since the energy, E, is lower than $2E_F$, this bound state, known as a Cooper pair, is energetically favorable compared to that of two free electrons.

Following Cooper's insight, the next major step towards the BCS theory was the formulation of a many-bodied wavefunction to describe the system at equilibrium following the condensation of Cooper pairs out of the Fermi sea. At first glance, a microscopic system of electrons presents a prohibitively large space for the formulation of an exact wavefunction describing such a system. BCS argued, however, that a mean-field wavefunction as shown below would capture the relevant physics of the physical system.

$$|\psi_{BCS}\rangle = \prod_{\mathbf{k}_i} \left(u_{\mathbf{k}} + v_{\mathbf{k}} c^*_{\mathbf{k}\uparrow} c^*_{\mathbf{k}\downarrow} \right) |\psi_0\rangle \tag{1.3}$$

Here $c_{\mathbf{i}\sigma}^*$ are creation operators for electrons with momentum **i** and spin σ , $|\psi_0\rangle$ is the vacuum state, and the coefficients $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ satisfy the relation $|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$. Within this formulation $|v_{\mathbf{k}}|^2$ represents the probability that a singlet pair of given momenta are occupied, while $|u_{\mathbf{k}}|^2$ provides the probability it is unoccupied.

Solving Schrödinger's equation for the occupation coefficients $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ through a variational calculation produces the key physics of the superconducting state. Notably, Cooper's pairing potential (Eqn. 1.1) produces a \mathbf{k} independent energy gap Δ , such that:

$$\Delta = 2\hbar\omega_c e^{-1/N(0)V} \tag{1.4}$$

The gap Δ turns out to be an order parameter for the superconducting phase, and grows when the system is cooled below T_c . One can also show that Δ is related to the superconducting critical temperature by:

$$\frac{\Delta}{k_B T_c} = 1.764\tag{1.5}$$

in the weakly coupled limit.

While two electrons will experience a repulsive Coulomb interaction, in solids there are other interaction mechanisms that may offset the Coulomb contribution and produce a net negative potential. Although the general BCS theory does not assume a specific microscopic origin of this force, in the model of low- T_c superconductors it is due to the exchange of phonons.

Assuming a phonon mediated superconducting pairing in the weak coupling limit, Eqns. 1.4 and 1.5 may be combined to yield:

$$k_B T_c = 1.13\hbar\omega_D e^{-1/\lambda} \tag{1.6}$$

where ω_D is the Debye frequency of the material, and λ is related to the electronphonon coupling strength and the electronic density of states. The validity of Eqn. 1.6 has been well established in a number of materials, in part through experiments in isotopic substitution [13–15], which hinge on the fact that the Debye frequency scales with the atomic mass M as $M^{-1/2}$.

Based on the BCS theory and experimental results, conventional superconductivity, as it will be defined throughout this text, has the following hallmarks: i) a superconducting gap with constant phase around the Fermi surface (*i.e.* s-wave pairing), ii) spin singlet electron pairs, and iii) Cooper pairing mediated by the exchange of lattice excitations (phonons).

1.3 High Temperature Superconductivity

Many materials are known to exist that don't appear to satisfy the criteria I have outlined for conventional superconductivity. These include proposed p-wave superconductors such as Sr_2RuO_4 [16] and UTe_2 [17], heavy fermion superconductors $CeCoIn_5$ [18] and $CeCu_2Si_2$ [19], and topological superconductors such as substituted Bi_2Se_3 [20] to name a few. Notably, both the cuprate and iron-based high temperature superconductors also exhibit behaviors inconsistent with conventional superconductivity [21–25].

1.3.1 Superconducting Pairing Mechanism

Both iron-based and cuprate high temperature superconductors display superconducting phase diagrams that would be highly unusual for a phonon mediated superconductor (see Fig. 1.1). High T_c in both iron and cuprate materials generally occurs in systems that are formed by heavily doping or pressurizing a magnetic and non-superconducting parent compound. In these compounds, long range antiferromagnetism or spin density wave order is suppressed through the external tuning parameter (*i.e.* chemical doping, pressure, *etc.*) and superconductivity only emerges near the magnetic quantum critical point. The occurrence of superconductivity in a region near magnetic criticality, where magnetic fluctuations are peaked, is quite remarkable as long range magnetic order is generally at odds with superconducting pairing. Tuning far from the magnetic phase in these materials rapidly suppresses T_c , however, suggesting a cooperative rather than competitive relationship between superconductivity and magnetism in these compounds.

Although it is suggestive, a phase diagram alone cannot disqualify the existence of a conventional superconducting mechanism, nor provide direct evidence for a link between superconductivity and magnetism. However, electron-phonon coupling in these compounds is far too weak to produce such high transition temperatures $\begin{bmatrix} 30, 31 \end{bmatrix}$. Rather, given the existence of nearby magnetic phases, it has been suggested that Cooper pairing may be mediated by magnetic interactions. In such a model, magnetic excitations rather than phonons are exchanged by electrons at the Fermi energy, producing the attractive interaction necessary in the BCS Hamiltonian. This assumption is supported by a number of experimental probes. Arguably, the most direct evidence for magnetically mediated superconductivity is the observation of a linear correlation between T_c and magnetic resonance energies observed in inelastic neutron scattering studies of cuprate and iron-based superconductors [23, 32]. Whether magnetic fluctuations are responsible for pairing is not universally agreed upon, however, and there are other theories for the pairing interaction [33-35].

¹It must also be noted here, however, that an isotope effect is observed in both the iron and cuprate materials, indicating that phonon effects are not entirely absent in these compounds [28,29].





Figure 1.1: Generic phase diagram for iron (a) and cuprate (b) superconductors. These phase diagrams are complex contain magnetic, superconducting, pseudogap, charge density wave (CDW), and nematic orders. Nevertheless, they share the common feature that superconductivity occurs through the suppression of a magnetic order in a nonsuperconducting parent compound. The iron superconducting phase diagram was published originally by Fernandes, *et al.* [26] and the cuprate phase diagram was published by Kordyuk [27].

1.3.2 Superconducting Gap Structure

In addition to unconventional superconducting pairing mechanisms, both the cuprate and iron-based superconductors are believed to have superconducting gaps of greater complexity than low T_c s-wave superconductors.

In the cuprate superconductors, it is now well established that the superconducting order parameter Δ has the following **k** dependence:

$$\Delta_{\mathbf{k}} \approx \Delta_0(\cos(k_x) - \cos(k_y)) \tag{1.7}$$

This means the order parameter has a $d_{x^2-y^2}$ symmetry, experiencing maxima along certain crystallographic axes, and vanishing along others. That the cuprate order parameter has a *d*-wave symmetry has been shown using experimental techniques such as STM [36], scanning SQUID microscopy [37], ARPES [38], etc [39, 40].

Although experimental evidence has not ruled out all other possible symmetries, superconductivity in the iron-based superconductors is commonly believed to be of a so-called s_{+-} symmetry [41]. In this case, (π, π) nested Fermi surface pockets, common to many of the iron-based compounds, would be fully gapped, but the pockets would also have a π phase difference in their superconducting order parameter. In this theory, superconductivity is mediated by spin fluctuations that typically provide a repulsive coupling between electrons. A net attractive interaction is produced, however, if the excitation is exchanged between parts of the Fermi surface where the superconducting order parameter changes sign [41]. Alternatively, a sign conserving s_{++} order parameter, where the nested Fermi surfaces have gaps of the



Figure 1.2: Illustration of s (a), d (b), s_{++} (c), and s_{+-} (d) superconducting order parameters. Figure from Ref. [42].

same phase, is favored in the case of orbital fluctuation mediated pairing, and has been proposed as a possible alternative to s_{+-} superconductivity [33,35]. Figure 1.2 shows a visual representation of these different order parameter symmetries.

1.3.3 122 Fe-based Superconductors

In this section I will focus on the normal state properties of a family of iron superconductors that is particularly relevant to my thesis.

 $BaFe_2As_2$ is among the most widely studied of the iron based superconductors, due largely to availability of large, high quality single crystals. Belonging to the 122



Figure 1.3: Schematics illustrating the structure of iron-based superconductors. A number of different iron-based superconductor structure types is provided in (a). Common to all these structures is a two dimensional square lattice of iron atoms that form the center of Fe-Pn (Pn=P, As) tetrahedra shown in (b). Illustration of the antiferromagnetic order with wave vector (π, π) in these compounds is also provided in (b). Figure from Ref. [23]

class of compounds, so named for their ATm_2Pn_2 stoichiometry (A=Alkali or alkaline earth; Tm=Transition metal; Pn=Pnictogen), BaFe₂As₂ forms in the tetragonal ThCr₂Si₂ structure type at room temperature. Iron atoms in this structure reside in a two-dimensional square lattice, and form the center of iron-pnictogen tetrahedra (see Fig. 1.3). These tetrahedra are themselves spaced by the larger alkali or alkaline earth ions. The unit cell contains two unique iron sites, at in plane positions (1/2, 0) and $(0, 1/2)^2$ [Fig. 1.3 (b)].

BaFe₂As₂ is a metallic compound with circular Fermi surface sheets at the high symmetry points of the Brillouin zone that are nested by a (π, π) wave vector. BaFe₂As₂ is not itself a superconductor. Rather, upon cooling below $T_N = 135$ K a spin density wave appears along the (π, π) direction. In the magnetic phase, the iron moment is directed parallel to the direction of iron nearest neighbors, with spins oriented antiferromagnetically along the direction of the iron moment, and ferromagnetically in the orthogonal direction [Fig. 1.3 (b)]. This magnetism breaks the four-fold rotational symmetry of the square lattice, and magnetic order coincides with a structural distortion along the (1 1 0) crystallographic axis, reducing the symmetry of the tetragonal BaFe₂As₂ cell to a new, orthorhombic structure. Electron doping, for instance Co replacement for Fe, may split the structural and magnetic transitions, such that the structural transition will occur at temperatures above T_N [23].

Critically, this structural transition is proposed to be driven by spin fluctua-

 $^{^{2}}$ An alternative, one iron unit cell is often used in theoretical calculations. This one iron unit cell is rotated at a 45° angle from the unit cell used throughout this work.

tions rather than a softening lattice as is more traditional [26]. Any comprehensive theory of the electronic phase diagram of BaFe₂As₂ and its various substitution series must thus account for this rotational symmetry breaking electronic phase. This rotational symmetry breaking order, referred to as the "nematic" phase, has been a subject of increasing interest in recent years.

1.4 Electronic Nematicity

The term nematic or nematicity is generically applied to a phase or transition that reduces the rotational symmetry of a system. Crucially, a nematic transition breaks exclusively point group symmetries, *i.e.* it is a $\mathbf{q} = 0$ order.



Figure 1.4: Illustration of crystal, isotropic, smectic, and nematic phase of liquid crystals. Nematic order breaks the rotational symmetry of the isotropic phase without breaking any additional symmetries. This image is from Ref. [43].

The study of nematics in condensed matter physics originated in studies of the behavior of liquid crystals. In a nematic liquid crystal, the liquid is isotropic at high temperatures but orients when cooled below a critical temperature T_{nem} . Although constrained by the symmetries of the underlying crystal lattice, an *electronic* point group symmetry breaking phase, analogous to the nematic phase in liquid crystals, has been observed in a number of systems. For example, a purely electronic analog to a nematic liquid crystal has been demonstrated in a highly clean two-dimensional electron gas formed in GaAs/GaAlAs heterostructures [44]. In this system, a large in-plane resistivity anisotropy was observed to develop at the half filling of several $N \geq 2$ fractional Landau levels [44]. A similar in-plane electrical transport anisotropy under large magnetic fields was later observed in Sr₃Ru₂O₇ single crystals, providing evidence for a nematic Fermi liquid in a bulk crystalline material [45, 46].

While these results provide perhaps the most straightforward examples of electronic nematicity in condensed matter systems, extensive experimental evidence has been gathered for the widespread existence of electronic nematic phases in a number of high temperature superconductors. In BaFe₂As₂, for instance, the tetragonal to orthorhombic structural transition breaks the four-fold in plane rotational symmetry of the tetragonal cell. While such a symmetry breaking structural transitions is generally unremarkable, the ratio between the transport anisotropy and the lattice anisotropy in the low symmetry phase $\left(\frac{\rho_{aa}-\rho_{bb}}{\rho_{aa}+\rho_{bb}}/\frac{a-b}{a+b}\right)$ has been reported to be nearly 500 [47–49], indicating electronic anisotropy far outpacing structural anisotropy. Ba(Fe_{1-x}Co_x)₂As₂ crystals were also reported to transition from a low symmetry (nematic) crystal structure back to a higher symmetry phase when cooled below their superconducting T_c [50]. That the structural distortion is overcome through competition with strengthening superconductivity suggests it is electronically driven.

Electronic nematicity has also been demonstrated in the copper-oxide superconductors through observations of effects such as a highly anisotropic Nernst coefficient in the pseudogap phase of YBa₂Cu₃O_y [51]. Additional evidence for electronic nematicity in the cuprates can be found in resonant soft x-ray scattering experiments that probe the anisotropy of Cu-3d orbitals. These studies have produced evidence of intra-unit cell electronic nematicity in underdoped copper-oxide superconductors [52]. More comprehensive reviews of nematicity in both cuprate and iron-based high temperature superconductors may be found in Refs. [26, 53].

Although nematicity in the Fe-based compounds is generally believed to originate from coupling to the spin degrees of freedom [54–56], competing theories propose that it may be driven by orbital ordering [57]. In the cuprates it has been proposed that nematicity in the pseudogap phase is simply a remnant of a failed charge order [58]. In this theory, the systems natural predisposition is believed to be the formation of long range unidirectional and incommensurate charge density wave stripes. In addition to introducing a new periodicity to the system, unidirectional stripes would break the rotational point group symmetry of the tetragonal crystal. A nonzero amount of quenched disorder is expected to prevent the formation of such a long range stripe order, however [58]. The nematic phase, though, is of a different symmetry class than the CDW stripes, and will survive even in their absence. This remnant nematic phase has been referred to as a "vestigial" nematic order, as it exists only as a shadow of the failed CDW [58].

Kuo, *et al.* have argued that nematic quantum criticality coincides with optimal T_c in a number of iron-based superconductors, hinting at a potential relationship between nematicity and enhanced superconducting pairing [59]. However, the proximity to magnetic criticality makes it very challenging to definitively extract what role, if any, nematic fluctuations play in high temperature superconductivity.

In the absence of a simple model nematic system in which the interaction between superconductivity and nematicity may be isolated, several theoretical studies have investigated the implications of critical nematic fluctuations to superconductivity [60–64]. These studies agree that, in the presence of an existing superconducting interaction, nematic fluctuations are expected to contribute to the electron pairing interaction, *i.e.* the λ parameter in Eqn. 1.6 will be renormalized as:

$$\lambda \to \lambda + \delta \lambda \tag{1.8}$$

where $\delta\lambda$ is the nematic contribution to the electron-electron coupling and will scale as $\sqrt{\chi_{nem}}$ in two dimensions and as $\log(\chi_{nem})$ in three dimensions, where χ_{nem} is the materials thermodynamic nematic susceptibility. The $\delta\lambda$ term may contribute significantly to Cooper pairing in the vicinity of a nematic quantum critical point where nematic correlations diverge, and could, in principle, greatly enhance superconductivity.

Equation 1.8 is arrived at by assuming an existing pairing mechanism, and is expected to apply irrespective of the precise nature of this mechanism. Therefore, nematic fluctuations tuned to criticality may enhance superconductivity in unconventional materials, such as the iron-based superconductors, as well as phonon mediated compounds. Additionally, magnetic quantum critical fluctuations are typically peaked at nonzero \mathbf{q} , and will create a preference for a particular superconducting order parameter symmetry. In contrast, nematic quantum critical fluctuations do not favor particular symmetries, and may instead enhance superconductivity in many different symmetry channels.

While some theories have been focused on the impact of nematic fluctuations in the presence of an existing superconducting pairing, additional quantum Monte Carlo simulations studying the potential of nematic fluctuations to themselves facilitate superconductivity have also been performed [61]. In one such study, Lederer, *et al.* reported that nematic mediated superconductivity may persist to temperatures as high as $0.03T_F$, where T_F is the Fermi temperature. This result was only achieved, however, using a rather large value for the electron-nematic coupling constant and within the same study smaller values of this parameter produced no superconducting pairing in the temperature range explored.

These theoretical results suggest promise in the application of tuned nematic criticality to superconducting order, though they also depend on the strength of the electric-nematic coupling, a physical parameter that has not yet been well characterized in materials of interest. These results suggest the importance of continued investigation and characterization of known nematic systems as well as targeted research on simpler nematic systems.

$1.5 \text{ BaNi}_2\text{As}_2$

The coexistence of magnetism, unconventional superconductivity, and electronically driven nematicity in the iron-based superconductor compounds makes it challenging to understand the impact of each phenomena on the others. These difficulties have contributed to outstanding controversies in the iron-based superconductors, including the role of electronic nematicity in superconducting pairing. My thesis research was motivated in large part through a belief that the intermetallic BaNi₂As₂ may prove to be a simpler analog to the 122 iron-based superconductors, in which some of the same physics may be studied. In particular, I hoped to investigate how nematic and superconducting orders may interact in a system void of magnetism.

BaNi₂As₂ forms in the same ThCr₂Si₂ crystal structure as the 122 superconductors [65, 66]. BaNi₂As₂, unlike its iron-based analog BaFe₂As₂, is a superconductor with a T_c of 0.7 K. Thermal conductivity measurements in BaNi₂As₂ show a vanishing thermal conductance in the superconducting state in the zero field, zero temperature limit, suggesting it is a fully gapped superconductor [67]. It is argued, however, that BaNi₂As₂ cannot host a sign changing s_{+-} order parameter due to the complexity of its Fermi surface. While BaFe₂As₂ has a relatively simple Fermi surface, with pockets centered around the high symmetry points of the Brillouin zone, the Fermi surface in BaNi₂As₂ is much more complicated (Fig. 1.5). Thus, any nodal planes in the BaNi₂As₂ superconducting order parameter would necessarily intersect the Fermi surface, producing nodes that are not observed in the
thermodynamic experiments [68, 69]. Additionally, the calculated electron phonon coupling constant, observed Debye temperature, and reported T_c are all consistent with phonon mediated Cooper pairing [69]. So, while the low T_c of BaNi₂As₂ is does not preclude all possibility of it being an unconventional superconductor, evidence suggests this compound has both a fully gapped s-wave order parameter (with no sign change) and Cooper pairing is mediated by the exchange of phonons.

BaNi₂As₂, much like BaFe₂As₂, exhibits a structural transition at around 135 K. This transition is strongly first order in BaNi₂As₂, however, and is to a low temperature triclinic (space group $\overline{P1}$) rather than orthorhombic structure (Fig. 1.6). In the triclinic phase the nickel atoms no longer all reside in the same two dimensional plane, and instead form quasi one dimensional zig-zag chains (Fig. 1.7) [66]. Unlike BaFe₂As₂, no magnetic order has been reported at the structural transition [70]. Optical measurements show a modest reduction (about 10%) in carrier density within the low temperature phase, consistent with Fermi surface gapping at the Γ -point demonstrated in density functional theory (DFT) calculations and ARPES measurements [71, 72]. This reduction is not readily apparent in the reported Hall effect however, which shows only a minimal temperature dependence [65]. Early reports suggested the microscopic origin of this structural transition was likely conventional (*i.e.* due to lattice softening), though some predictions have been made that orbital order may instead drive the structural transition [73].

While the effects of chemical substitution and physical pressure are well documented in BaFe₂As₂, much less effort has been undertaken to investigate BaNi₂As₂. Reported pressure measurements extend only to 25 kbar [74]. These pressures



Figure 1.5: Picture of calculated Fermi surface of BaFe₂As₂ (a) and BaNi₂As₂ (b) compounds. Dashed lines indicate a proposed location for nodal planes in the superconducting order parameter. Significantly, any nodal plane will intersect the Fermi surface in BaNi₂As₂, which, combined with a vanishing thermal conductivity at T = 0, suggests BaNi₂As₂ will not have the proposed s_{+-} symmetry of the iron-based superconductors. Figure from Ref. [68].



Figure 1.6: Signatures of the triclinic transition in $BaNi_2As_2$. Main figure shows the resistance anamoly associated with the structural transition, while the insets display magnetic (a) and heat capacity (b) signatures of the transition. Figure is from Ref. [2].



Figure 1.7: Schematic of the $BaNi_2As_2$ triclinic structure. Left panel shows the in-plane nickel lattice in the triclinic phase, highlighted by the formation of zig-zag chains of atoms. Right panel displays the new triclinic unit cell. This figure is from Ref. [66].

broaden both the structural and superconducting transitions, but are insufficient to fully suppress the triclinic distortion and explore any dynamics at the structural quantum phase transition.

Substitution of P for As in the BaNi₂(As_{1-x}P_x)₂ series was reported to suppress the structural distortion, and promote a large superconducting enhancement from 0.7 to 3.3 K at the phase boundary [75]. The observation of a concurrent decrease in Debye temperature was seen as evidence that phonon softening may cause the enhanced T_c . The BaNi₂P₂ end-member of this series has a reported T_c ranging between 2.6 and 3.2 K, however, raising the doubt that this enhancement is perhaps correlated with the tetragonal structure, rather than arising from dynamics at the structural phase boundary.

1.6 This Work

In this thesis, I describe the synthesis and characterization of $BaNi_2As_2$, $Ba_{1-x}Sr_xNi_2As_2$, and $Ba(Ni_{1-x}Co_x)_2As_2$ single crystals, and their potential as a platform to study the effects of nematicity on superconductivity.

In Chapter 2, I discuss the methods I used to grow and characterize substituted BaNi₂As₂ single crystals. This includes a description of techniques used to probe properties such as heat capacity, magnetization, and electrical resistivity. In Chapter 3, I provide a description of a home-built nematic susceptibility experiment and the theory behind its operation.

Chapter 4 discusses my findings in the pure $BaNi_2As_2$ system, which suggest

the previous understanding of the structural transition in this compound was incomplete. Namely, through elastoresistivity experiments I observe a B_{1g} symmetry breaking nematic order *above* the triclinic structural transition. X-ray scattering experiments performed by collaborators in the group of Dr. Peter Abbamonte at the University of Illinois confirming that this nematic order coincides with the onset of a unidirectional charge density wave will also be discussed. I will then conclude this chapter with a phenomenological model for a tetragonal-orthorhombic-triclinic structural phase transition inspired by experimental results. This model was developed by Dr. Rafael Fernandes and Dr. Morten Christensen at the University of Minnesota.

In Chapter 5, I detail the impact of Co substitution for Ni in the $Ba(Ni_{1-x}Co_x)_2As_2$ series. In this work, Co substitution is observed to suppress the structural phase transition seen in the x = 0 endmember, and I observe a dramatic enhancement of superconducting critical temperature from 0.7 to 2.3 K when crossing the zero temperature structural phase boundary. Here the smooth emergence of a superconducting dome with varying x evokes consideration of a fluctuation mediated pairing enhancement.

In Chapter 6, I discuss the evolution of superconductivity, structure, charge order, and nematicity in the $Ba_{1-x}Sr_xNi_2As_2$ substitution series. Notably, this series exhibits a crossover between structural and electronically driven rotational point group symmetry breaking. Remarkably, near a quantum phase transition where nematic fluctuations are peaked, a nearly sixfold enhancement in superconducting T_c when compared with either series end member is observed. This behavior marks one of the strongest pieces of evidence to date for nematic fluctuation enhanced superconducting pairing.

Finally, in Chapter 7, I summarize my main findings and discuss some possible topics for future research.

Chapter 2: Methods

The results I present in this thesis were acquired through the synthesis and characterization of superconducting samples. All materials were grown at the University of Maryland in the Center for Nanophysics and Advanced Materials (CNAM) and most of my data was gathered using the facilities of the Center. In this chapter, I describe the synthesis and experimental techniques used to compile this work.

2.1 Flux Crystal Growth

Macroscopic single crystals provide a uniform crystal lattice that is unbroken to the boundaries of the material. Such samples are generally required for measurements of tensor properties or other characteristics sensitive to grain boundaries (such as electrical conductivity). Among the class of measurements requiring single crystal specimens are symmetry based analyses that seek to probe anisotropic material properties. For these reasons, all the data I present were collected on single crystals, unless otherwise noted.

The single crystals I examined were grown exclusively through a flux technique [76]. This method involves the dissolution of growth materials in a liquid metal solvent. For growing intermetallic compounds, the solvent often takes the form of a metal with a relatively low melting temperature. Common fluxes include In, Sb, Sn, Pb, Zn, Ga, Al, and Bi, though it must be noted that this list is nowhere near comprehensive, and more complex compounds rather than individual elements may be used as fluxes. The choice of flux is guided by how efficiently it dissolves growth materials, and is often informed by studying reported binary and ternary phase diagrams. The ideal flux will dissolve growth materials at relatively low temperatures and will not form competing phases that may disrupt the growth.

To grow a material, I combined elements in relative atomic ratios determined by consideration of previous reports, available phase diagrams, and the target crystal stoichiometry. These mixtures were combined in an alumina (Al_2O_3) crucible, commonly referred to as the growth crucible, which would then be loaded into a flatbottomed quartz tube. Quartz wool was placed below the growth crucible in the tube as a cushion to prevent the ampule from cracking. Often an additional crucible, known as the catch crucible, would be filled with quartz wool and loaded into the quartz tube above the growth crucible. A final amount of quartz wool would then be placed above the catch crucible. The whole tube would then be attached to a gas handling manifold where it would be pumped and purged using ultra-high purity argon gas. Once this procedure was repeated several times, the tubes were sealed using a hydrogen-oxygen torch in an inert environment of about 1/4 atmosphere of argon gas. A typical ampule produced in this fashion (see Fig. 2.1) would have an outer diameter of nearly one inch and a length of four to five inches. Alumina and quartz were both used for their relative stability. All the crystals I grew were sealed in ampules of this nature. However, it is worth mentioning that alternative environments are available when working with volatile materials that will interact with or destroy alumina/quartz.

Once prepared, I would place sealed ampules into a furnace, where they were heated until all starting materials were dissolved in solution. The quartz tubes themselves will begin softening near 1200 °C, so it is essential to choose a flux such that heating beyond this temperature is not required. At high temperatures, the Ar gas will produce an internal pressure within the sealed quartz of approximately 1 atmosphere, which helps to stabilize the ampule.

Once the ampule dwelt at high temperatures for a sufficiently long time, such that all growth materials dissolved and were integrated homogeneously into solution, the temperature of the growth would be slowly reduced. Upon cooling, the solubility of growth materials in the flux would reduce and the liquid solution would become less thermodynamically stable than the solid phase. Material would then begin to precipitate from solution, forming high quality single crystals in the successful growth.

Upon further cooling, ideally a temperature would be reached that was cool enough that sizeable single crystal were precipitated from solution but still hot enough to maintain a molten flux. At this temperature, I proceeded with either of two possible courses of action to separate crystals from the solution. The first option was to turn off the furnace, and allow the ampule to cool naturally to room temperature while still within the furnace. The resulting product would have crystals embedded in the solidified flux. Crystals were extracted from the flux through mechanical means or by chemically etching the flux away. Alternatively, the cru-



Figure 2.1: Photograph of a sealed quartz ampule containing a growth. Features such as the packing quartz wool and growth and catch crucibles are labelled.



Figure 2.2: Photographs showing the gas handling manifold used in sealing tubes (a), a N_2 glovebox for the storage of toxic/air sensitive materials (b), and box furnaces employed for crystal growth (c).

cible would be rapidly removed from the furnace while still hot and inverted in a centrifuge. Spinning the growth in this manner will decant the molten flux from the growth crucible into the catch crucible. The quartz wool that packed the catch crucible would act as a sieve to separate crystals from the decanted liquid. The additional quartz wool placed above the catch crucible as shown in Fig. 2.1 prevented

the top of the quartz tube from shattering under pressure during the spin.

2.1.1 Synthesis of BaNi₂As₂

The synthesis of BaNi₂As₂ crystals was complicated by the presence of arsenic. In addition to being highly toxic, elemental arsenic sublimates at approximately 615 °C. Sublimation limits the amount of arsenic dissolved in a molten metal solution, disrupting the growth. Additionally, the sublimation of a substantial amount of material originally in the solid phase will dramatically increase the pressure within the quartz ampule which may then fail catastrophically. An explosion of this nature will contaminate and possibly cause physical damage to a furnace, while also potentially releasing a toxic substance into the lab. To avoid these concerns, BaNi₂As₂ crystal growth did not involve elemental arsenic, but rather a less volatile prereacted binary compound NiAs. The binary was formed through a simple solid state reaction in which Ni and As powders are combined in ratios of 1.01:1 Ni:As. The excess nickel was included to minimize the risk of remnant unreacted arsenic. The powders were well mixed in a glovebox using a mortar and pestle, placed directly into a quartz ampule, and sealed under a partial pressure of argon gas. The sealed ampule was heated to 300 °C where it then dwelt for 12 hours. Following this dwell, the temperature was set to 600 °C for 24 hours, and finally 650 °C for an additional 24 hours. At this point, the furnace power was turned off, and allowed to cool to room temperature. The resulting NiAs product would emerge as a solid rust-colored lump. This lump was ground into a powder using mortar and pestle, and was confirmed to be the desired phase using x-ray diffraction. The NiAs binary does not sublimate, and has a melting temperature of 950 $^{\circ}$ C.

Ba(Ni_{1-x}Co_x)₂As₂ crystals, were synthesized from Pb flux, using a procedure originally reported by Ronning *et al.* [65]. In this technique, Ba pieces, prereacted NiAs powder, prereacted CoAs powder, and Pb shot are combined in atomic ratios of 1 : 2(1 - x) : 2x : 20. The resulting mixture was sealed in a quartz ampule under partial argon pressure and then was heated to 1000 °C at 50 °C/hour. It was allowed to dwell at 1000 °C for 12 hours, and was then subsequently slowly cooled to 600 °C over 200 hours. At 600 °C the excess Pb flux was decanted in a centrifuge at approximately 1000 RPM for a duration of 5 to 7 seconds.

Crystals in the Ba_{1-x}Sr_xNi₂As₂ substitution series were grown using an alternative "self-flux" technique where the flux is incorporated into the growth itself. In this method, I used the NiAs binary compound as a flux, and a growth technique similar to that reported by Sefat, *et al.* [66]. For these growths, I mixed Ba pieces, Sr pieces, and prereacted NiAs powder in ratios of 1 - x : x : 4. These solutions were heated in a quartz ampule at 750 °C for 12 hours to react any previously unreacted As. The melt was then heated to 1150 °C, stabilizing there for 6 hours. The ampule was then cooled to 950 °C over the course of 72 hours, following which the furnace was turned off, and cooled to room temperature over periods of approximately 24 hours. This technique was preferred over centrifuge decanting due to the high melting temperature of the NiAs. Once cooled, single crystals were isolated from the remaining NiAs flux using a razor blade.

Both growth techniques produced high quality single crystals. It is worth

noting that the NiAs self-flux technique grew to become my preferred method. This technique had the advantages of both producing much larger single crystals, up to several mm across, and avoiding lead contamination in the resulting product (Fig. 2.3).

2.1.2 BaNi₂As₂ Crystal Morphology and Properties

BaNi₂As₂ crystals have some distinct crystal properties that differentiate them from the more widely studied BaFe₂As₂ compound. BaFe₂As₂ is quite stable in air and can be stored in a dry, oxygen rich environment for over a year without deteriorating significantly. In contrast, BaNi₂As₂ is far less stable, decomposing over periods of approximately 24 hours in the laboratory environment. Alloying Sr with Ba in $Ba_{1-x}Sr_xNi_2As_2$ solutions improves the stability of these crystals, to the point that samples stored in ambient conditions may remain physically intact for several days or even weeks in very heavily substituted crystals (Fig. 2.4). Out of precaution, however, all of the $Ba_{1-x}Sr_xNi_2As_2$ and $Ba(Ni_{1-x}Co_x)_2As_2$ single crystals prepared for this thesis were stored in a nitrogen glovebox when not being handled. When preparing specimens for measurements, crystals would be removed from the glovebox and handled in air for periods of up to two hours. This limited exposure to air did not appear to effect crystal properties in the short-term. However, samples that were repeatedly handled did begin to show signs of decomposition, necessitating their replacement over time.

Additionally, $BaNi_2As_2$ and $BaFe_2As_2$ single crystals have different mechanical



Figure 2.3: Top panel: Graph showing the different temperature profiles used in the Pb and NiAs flux growth techniques for BaNi₂As₂. Bottom panel: Image of representative crystals extracted from the two growth processes, taken on mm grid paper. Notice that sample grown from NiAs self flux is significantly larger than the Pb grown crystal.



Figure 2.4: Images displaying the decomposition of $\text{Ba}_{1-x}\text{Sr}_x\text{Ni}_2\text{As}_2$ crystals in air. Samples were adhered to a piece of paper and left in the laboratory environment for two days. A clear degradation in samples with $x \leq 0.60$ is observed during this time.

properties that complicate sample preparation in the $BaNi_2As_2$ family of compounds. In particular, $BaNi_2As_2$ samples tended to shatter rather than exfoliate when cleaved along the *ab* plane, requiring more careful preparation than $BaFe_2As_2$.

2.2 Chemical and Structural Characterization

Thoroughly characterizing the chemical composition and structure of newly synthesized materials is of fundamental importance for materials research. An otherwise thorough characterization of a material has very little value if the identity of the material is itself unknown. In this section I describe the structural and chemical techniques used to characterize my samples.

2.2.1 X-ray diffraction

Structural characterization was carried out using x-ray scattering techniques. A detailed descriptions of these techniques and the theory behind them is beyond the scope of this work but further information may rather be found in many publications, including Refs. [77, 78].

Powder diffraction patterns were collected using a Rigaku Miniflex Benchtop X-ray Diffractometer. This apparatus was used to acquire full powder patterns over a period of only several minutes. This data was not of ideal resolution for the performance of full Rietveld-refinement, however, so single crystal x-ray diffraction experiments were also performed for more detailed structural studies.

Single crystal x-ray refinements were obtained on samples mounted in a trans-

mission geometry using a Bruker APEX-II CCD system equipped with a graphite monochromator and a MoK_{α} sealed tube ($\lambda = 0.71073$ Å). The resulting high quality pattern was refined using the Bruker SHELXTL Software Package. These data provided an accurate refinement of the lattice, as well as the elemental occupations, where possible. All such measurement were performed by Dr. Peter Zavalij, a crystallographer in the Chemistry Department at the University of Maryland.

Finally, scattering data taken over a wide temperature range were collected using a Xenocs GeniX 3D MoK_{α} microspot x-ray source with multilayer focusing optics and a Mar345 image plate detector. Single crystal samples were cooled with a closed-cycle cyrostat and mounted to a Huber four-circle diffractometer affording temperature control from 300 K to 8 K. The wide temperature range and high resolution of the apparatus allowed for a thorough study of the dynamics of BaNi₂As₂ near the structural transition. This data proved crucial for understanding this system. Measurements of this nature were performed by the group of Dr. Peter Abbamonte at the University of Illinois, Urbana-Champaign.

2.2.2 EDS and WDS

Chemical composition was determined primarily through energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS) techniques. Both of these techniques generate characteristic photons through bombarding the surface of a material with high energy electrons. They differ only in their photon measurement/analysis technique. In EDS, the entire characteristic spectrum of the material is measured simultaneously. These experiments require less of the operator and were generally preferred. EDS experiments were conducted using a Hitachi S-3400 Variable Pressure Scanning Electron Microscope and a 10-15 keV beam of high energy electrons.

WDS measurements, meanwhile, diffract the resulting spectrum, isolating specific wavelengths for measurement. WDS experiments afford a greater experimental resolution. This proved crucial in the $Ba(Ni_{1-x}Co_x)_2As_2$ series as the nickel and cobalt characteristic photons are of comparable energy, and accurate determination of their relative composition proved challenging using EDS alone. WDS experiments were performed by Dr. Philip Piccoli in the Geology Department at the University of Maryland.

2.3 Cryogenic Technologies

For many of the measurements, I needed an experimental environment that could be tuned dramatically in temperature. To that end, the majority of resistivity, heat capacity, and magnetization measurements I obtained were conducted in commercially available cryostats manufactured by Quantum Design, and offering, generally, a temperature range between 1.8 K and 400 K.

In the Quantum Design systems, the sample is loaded into a chamber under a relatively low partial helium pressure (about 10 torr) at room temperature. Cold helium gas, from either a liquid helium bath or a closed circuit refrigeration loop depending on the system, is pulled past the sample chamber allowing for accurate



Figure 2.5: Photographs of two Quantum Design ⁴He cryogenic measurement systems. The left image displays a Quantum Design Physical Property Measurement System (PPMS) equipped with a 9 Tesla superconducting magnet. I used this model, and others like it, to perform transport, heat capacity, and *ac* susceptibility measurements. The right image is a photograph of a Quantum Design Magnetic Property Measurement System (MPMS) SQUID Magnetometer used to collect *dc* magnetization data.

temperature control between 10 and 300 K. Below 10 K, liquid helium is transferred to a 1 K pot. Helium vapor is pumped from the pot, evaporatively cooling the helium liquid to temperatures below its 4.2 K boiling point. Helium-3 and adiabatic demagnetization refrigerator inserts were used in some experiments to extend measurements down to 350 mK and 100 mK, respectively.

The Quantum Design Physical Property Measurement System (PPMS) cryostats feature 12 concentric pins at the base of their sample space. Twisted pairs of copper wires soldered to these pins run up the length of the sample space and are fed through a vacuum feed-through. The PPMS used custom pucks that plug into these pins, allowing for low frequency electrical measurements of samples mounted to the pucks. General transport measurements are conducted using electronics provided with the PPMS system and controlled using a Quantum Design software (MultiVu) that integrates both the cryostat and measurement operations. Custom experiments, such as elastoresistivity, required the use of other commercial measurement electronics, however, and the creation of custom software to automate.

2.4 Resistivity Measurement

Much of the data I obtained were from variations on standard electrical transport measurements. To motivate these measurements, I first discuss a simple theory of electrical transport developed by Paul Drude [79]. I then provide details of the measurement technique I used.

2.4.1 Drude Model

A metal can be treated as a system in which charge carriers are free to move, while scattering with some characteristic relaxation time τ . Using these assumption, the classical equation of motion for a charge carrier in a metal subjected to external electric fields, **E**, and magnetic fields, **B**, can be written as:

$$\frac{d}{dt}\left(\mathbf{p}(t)\right) = q\left(\mathbf{E} + \frac{\mathbf{p}(t) \times \mathbf{B}}{m}\right) - \frac{\mathbf{p}(t)}{\tau}$$
(2.1)

where \mathbf{p} is the momentum of the charge carrier, m is its mass, and q is its charge. Assuming a zero magnetic field, the expectation value for the carrier momentum in Eqn. 2.1 becomes:

$$\langle \mathbf{p} \rangle = q \mathbf{E} \tau \tag{2.2}$$

Using this result, the current density \mathbf{J} as a function of the free carrier concentration n is found to be:

$$\mathbf{J} = \left(\frac{nq^2\tau}{m}\right)\mathbf{E} \tag{2.3}$$

Note in Eqn. 2.3 current density scales linearly with the electric field. This linear relationship is known as Ohm's law. Although the above argument is classical, this same linear relationship is found for a quantum free electron model with a Fermi-Dirac distribution [80]. In a real crystal, quantities such as the effective mass and scattering time will become anisotropic due to the lattice. Therefore, the constant relating the current density and electric field in a crystalline solid is not in general a scalar but rather a rank two conductivity tensor σ_{ij} , which is the matrix inverse of the resistivity tensor ρ_{ij} . The values of the ρ_{ij} tensor are determined by dynamics at the Fermi surface. This makes electrical transport measurements sensitive to many types of order, including magnetic, superconducting, and structural phase transitions. While valuable information may be extracted from the individual components of the resistivity tensor, mapping it in its entirety is arduous in most materials. Fortunately, the material properties of interest for this thesis (i.e. the location of phase transitions and magnitude of in-plane anisotropies) only required measurements within the basal plane of tetragonal crystals. Thus, the transport data I present in this work only probed ρ_{xx} , ρ_{yy} , and ρ_{xy} , where x and y denote the equivalent a and b lattice directions of the tetragonal cell.

2.4.2 Experimental Details

Extending Eqn. 2.3 to a bulk crystal, values of resistivity tensor components ρ_{ij} for a given material may be extracted by passing a current through a sample in the appropriate direction and measuring the resulting voltage drop. In principle, this experiment may be performed by attaching two wires to a sample, sourcing a current through these wires, and measuring the voltage drop across them. Indeed, this is the technique applied by a simple hand-held multimeter in the measurement of material resistance. However, such a measurement will return the the full resistance of the circuit, including the sample resistance as well as the resistance of the wires and the wire-sample contacts. For materials with a large resistance, the extrinsic contributions from the circuit and contacts may prove inconsequential. However,

for my metallic samples the contact and wire resistances may be several times if not orders of magnitude larger than the sample resistance, and may entirely mask the crystal contribution.

To eliminate the contamination of contact and wire resistance to the overall signal, I used a four-wire geometry when conducting transport measurements. In this measurement technique, current is sourced to the sample using two contacts placed at its edges, and voltage is measured across two inner wires. An example of this experimental configuration is shown in Fig. 2.6. Ideally, no current will pass through the voltage wires in this measurement configuration, and the voltage drop measured is only across the sample. The resistance R is found from the relationship R = V/I and depends on the geometry of the sample in question. Longitudinal resistivity tensor components, a material intrinsic property, can then be extracted from the raw resistance value, a sample dependent property, using the following relation:

$$\rho_{ii} = R_{ii} \frac{wt}{l} \tag{2.4}$$

where l, w, and t are geometric parameters of the physical sample (Fig. 2.6).

In practice, when preparing crystals for such measurements the as grown sample is polished or cleaved to minimize the ratio wt/l (and, in turn, maximize the sample resistance). I used gold wires for the electrical contacts, which I applied using either Dupont 4929N silver conducting paste or EPO-TEK H20E silver epoxy. When using Dupont 4929N to make sample contacts, 2-butoxyethyl acetate was first mixed with a small amount of paste to thin it to a proper consistency. A gold wire



Figure 2.6: Top panel: Illustration of a four-terminal longitudinal resistivity ρ_{ii} measurement. Geometric parameters l, w, and t are marked in image. Bottom panel: Image of an Sb₂Te₃ single crystal wired for the performance of a four-terminal measurement.

was then coated in a thin layer of paste and transferred to the surface of the wire. As the 2-butoxyethyl acetate solvent evaporated, and the paste mixture dried, it would adhere to the surface of the crystal producing, generally, a low resistance electrical contact. The silver epoxy had two components. When using the epoxy to create electrical contacts, these components were mixed in equal ratios. A gold wire was coated in this mixture and applied to the surface of a sample. Silver epoxy does not cure rapidly in ambient conditions, however, and is instead heated to 100°C for 12 minutes to cure. The silver epoxy has the benefit of providing a stronger mechanical contact and was preferred for measurements where the electrical contacts might be under greater stress. Generally I found that silver paste gave a higher quality electrical contact to the various transition metal-arsenide 122 intermetallic compounds, however.

2.5 Bulk Characterization Techniques

Electrical current tends to traverse the path of least electrical resistance. For this reason, transport measurements are particularly sensitive to sample inhomogeneity and, in the extreme case, the sample current may be shorted through regions with lower resistance, providing a misleading result. Any evidence for a phase transition observed in an electrical transport measurement must be confirmed using other measurement that probe bulk properties more directly. To this end, I used experimental techniques to measure bulk magnetic and thermodynamic properties as outlined below.

2.5.1 Heat Capacity

Heat capacity C relates the heat transferred from or to a material and the resulting change in the materials temperature. Crucially, heat capacity relates to the entropy (S) and temperature (T) of a material as:

$$C = T \frac{dS}{dT} \tag{2.5}$$

making heat capacity responsive to any effect (such as a phase transition) that impacts material entropy.

Heat can be stored in various degrees of freedom of a material. In a simple metal, the dominant contributions to the heat capacity at low temperatures will be from the vibrational modes of the lattice and the electronic degrees of freedom. The total heat capacity of the metal can be written as:

$$C = C_{el} + C_{phn} \tag{2.6}$$

where C_{el} and C_{phn} are the electronic and phononic contributions to heat capacity respectively. Electrons will be distributed across allowed energy levels according to the Fermi-Dirac distribution. The total energy that may be stored in the electronic degrees of freedom at low temperatures yields an approximately T^2 temperature dependence. The electronic heat capacity, as a temperature derivative of the internal energy of the system, will then obey a linear in T temperature dependence near T = 0, i.e.:

$$C_{el} = \gamma T \tag{2.7}$$

Here $\gamma = \frac{\pi^2}{3} k_B^2 N(E_F)$ where $N(E_F)$ in this instance is the electronic density of states at the Fermi energy. This parameter γ is a material specific property known as the Sommerfeld coefficient.

The phonon contribution to heat capacity may also be found as the temperature derivative of the internal energy of the phonon system. Phonons, as bosonic excitations, obey Bose statistics, producing differences between the internal energies of the electrons and lattice. The temperature dependence of the phonon contribution to heat capacity at low temperatures will be:

$$C_{phonon} = \frac{12Nk_B\pi^4}{5} \left(\frac{T^3}{\Theta_D^3}\right) \tag{2.8}$$

Where N is the number of atoms in the substance, k_B is Boltzmann's constant, and Θ_D is the material's Debye temperature. The Debye temperature is the lowest temperature at which the highest energy phonon mode in a material will be excited, and is a proxy for lattice rigidity. It is worth noting Eqn. 2.8 is only approximate, and assumes a simple phonon density of states and $T \ll \Theta_D$

Combining these results yields a total heat capacity for the system with temperature dependence:

$$C = \gamma T + \frac{12Nk\pi^4}{5} \left(\frac{T^3}{\Theta_D^3}\right) \tag{2.9}$$

The low temperature heat capacity of a system is often presented in graphs as C/T vs T^2 . Such a formulation is useful, as the data will be linear, assuming no contributions to the heat capacity other than those in Eqn. 2.9. Such linear plots are generally easier to interpret by eye. Additionally, the slope of the line will go as the inverse cube root of the Debye temperature and the *y*-intercepts will be the

material's Sommerfeld coefficient.

I measured the heat capacity of my samples using a pulse-relaxation technique [81]. In this method, samples are mounted on a sapphire stage suspended from a thermal bath using platinum wires under vacuum (approximately 10^{-4} Torr). The stage has a heater and thermometer. All heat transferred to and from the sample/sapphire stage system is either generated by the heater, or conducted through the platinum wires to the bath. Prior to measuring a sample's heat capacity, the thermal conductivity of the wires and the heat capacity of the sapphire stage are calibrated over the range of temperature capability of the cryostat. If a power is applied to the heater, the temperature of the sapphire stage and sample will then obey:

$$C_{tot}\frac{dT}{dt} = -\kappa(T - T_B) + P(t)$$
(2.10)

Here C_{tot} is the total heat capacity of the stage and sample, P(t) is any power applied to the stage, κ is the thermal conductivity of the wires, T is the sample stage temperature, T_B is the bath temperature, and t is time. If the system begins at T_B at t = 0 and a constant power P is applied, one finds:

$$T = (-P/\kappa)e^{-t\kappa/C_{tot}} + T_B + P/\kappa$$
(2.11)

By applying a nonzero power P for a finite time the temperature of the sample will climb to a maximum temperature T_{max} . If the power is turned off once the temperature has reached T_{max} the sample temperature will then decay exponentially according to:

$$T = (T_{max} - T_B)e^{-t\kappa/C_{tot}} + T_B$$
(2.12)

In practice, heat capacity measurements are then performed by applying a heat pulse to the sample, warming it to a temperature above that of the bath. The heat is then removed, and the temperature is allowed to decay back to equilibrium. The growth and decay of the temperature in time is measured and fit to Eqns. 2.11 and 2.12. The fits provide the time constant C_{tot}/κ from which the heat capacity can be extracted.

For measurements of the heat capacity of a crystal, I adhered specimens to the sample stage using Apiezon N-grease. N-grease has favorable cryogenic properties and serves the vital roles of both physically securing the sample, and providing a path for heat conduction between the sample and the stage. Typically the heat pulse was calibrated to produce a 2% increase in the overall temperature of the sample stage. As the grease contributes to the total heat capacity of the sample/stage system, I would perform preliminary measurements prior to mounting the sample to quantify this contribution. The addenda heat capacities were then subtracted from the total heat capacity to isolate their contribution from that of the crystal.

The model provided in Eqn. 2.10 assumes 100% efficiency in the heat transmission between the sample and stage. In the event the sample and sapphire are poorly coupled, the temperature versus time curve becomes more complex, no longer tracking a simple exponential growth and decay. This less ideal scenario is often modelled assuming a thermal link between the stage and bath as before, and an additional thermal link of finite thermal conductivity between the sample and stage. Data that do not show a clean exponential evolution of the temperature in time are fit using the predictions of this model. Finally, BaNi₂As₂, the material of interest in my work, features a strongly first order and temperature hysteretic structural transition. As the data collection method outlined above requires setting a temperature, applying a heat pulse, and tracking the temperature relaxation of the system to equilibrium, it is evident that this measurement will be sensitive to both warming and cooling first order transitions only if they both fall within the temperature range of the heat pulse. As the pulse applied in a standard measurement is only 2% of the temperature, however, this is generally not the case. To fully observe first order phase transitions then, heat capacity measurements were modified to be sensitive to both warming and cooling transitions. I took these measurements using an extended pulse, and analyzed the results using a local derivative approach through the post-processing feature in the Quantum Design software MultiVu. Figure 2.7 shows an example of a temperature versus time profile from such an experiment, as well as the sample heat capacity extracted from it.

2.5.2 *Dc* Magnetic Susceptibility

I measured dc magnetization of crystals using two common techniques. The first, vibrating sample magnetometry (VSM) extracts sample magnetization through a simple application of Faraday's law of induction. A magnetic field is applied to a sample, which is then rapidly oscillated within a conducting coil. If the sample is magnetized, it produces a changing flux through the coil, which produces an *ac* voltage. The amplitude of this voltage is directly related to the magnetization of



Figure 2.7: Example of the temperature versus time profile measured in a heat capacity experiment using an extended heat pulse technique (a). While a typical relaxation measurement features a temperature rise of at most several Kelvin, in this case a 3 mW pulse is applied to the sample stage between t = 0 s and t = 25 s to create a temperature rise of almost 50 K. The warming and cooling structural transitions of the $Ba_{1-x}Sr_xNi_2As_2$ crystal are clearly visible in the raw temperature versus time data. Heat capacity data extracted from the raw curve by taking local derivatives are shown in (b). The sharp jumps in heat capacity at 33 K and 60 K are indicative of the latent heat associated with the first order transition.

the sample. VSM measurements were conducted in a Quantum Design Dynacool system equipped with a VSM motor and a 14 T superconducting magnet.

The second technique, Superconducting Quantum Interference Device (SQUID) magnetometry, has the benefit of being significantly more sensitive. The system I used has sensitivity of 10^{-7} emu compared to a sensitivity of approximately 10^{-5} emu for the VSM. A SQUID device has two Josephson junctions that form the branches of a closed loop. Screening currents within the loop and, consequentially, the voltage drop across the device are highly sensitive to the magnetic flux threading the device pickup loop. By translating a magnetic sample through the SQUID, the voltage across the SQUID will rise and fall with the changing flux. The voltage across the device is measured as a function of the position of the sample and the magnetization of the material is extracted from this data. SQUID magnetometry experiments were conducted in a Quantum Design Magnetic Property Measurement System (MPMS) equipped with a 7 T magnet.

2.5.3 Ac Magnetic Susceptibility

Many of the materials I measured had superconducting transitions at temperatures below 1.8 K, a common though not absolute temperature limit for pumped ⁴He cryostats. The methods of measuring dc magnetic susceptibility that have been mentioned are generally challenging to adapt to temperatures below the 1.8 K limit, however. Thus, an alternative susceptibility probe was required to observe the Meissner effect in these samples. For temperatures below 1.8 K, a home-built ac susceptibility coil inspired by Ref. [82] was used to observe the magnetic signatures of superconductivity.

The *ac* susceptibility measurement, much like VSM magnetometry, operates through the application of electromagnetic induction. In this technique, rather than vibrating a sample the sample is held in a stationary position within a pickup coil, and an alternating magnetic field is applied. The magnetization of the sample will oscillate with the field, inducing an electromotive force within the pickup coil. The measured output in both *ac* susceptibility and VSM techniques will be an *ac* voltage. In the *ac* susceptibility technique, however, the *ac* voltage originates from a changing magnetization of the sample and dynamic properties of a material's magnetization may be probed. Knowledge of this dynamic contribution can be used to characterize ferromagnetic and spin glass systems, where domain formation provides a dissipative contribution to the *ac* susceptibility at T_c due to the onset of magnetic irreversibility.

Figure 2.8 shows an illustration of the basic principle of the *ac* susceptibility measurement. The pickup coil is actually composed of two counterwound coils separated in space, and is fully contained in the larger, drive coil. An *ac* current is sourced in the drive coil, producing the time varying magnetic field. The counterwound pickup coil will yield a measured voltage only due to the effects from the sample in the lower portion of the coil.



Figure 2.8: Illustration of basic principle of *ac* susceptibility technique. In this technique a sample is placed within a counterwound pickup coil. This coil is itself placed within a larger drive coil. By applying an *ac* current in the drive, an *ac* magnetic response will be induced in the sample, and the magnitude and relative phase of this response is measured in the pickup coil.
The measured voltage in the pickup coil of the *ac* susceptibility circuit is:

$$V_{ac} = -\frac{d\Phi}{dt} \tag{2.13}$$

where Φ is the difference in the magnetic flux between the two counterwound coils. Ideally Φ is simply the flux contribution from the sample, and can be expressed as:

$$\Phi = \alpha M \tag{2.14}$$

Here the constant α is determined by the volume filling fraction of the sample and geometry of the coil, while M is the sample magnetization. Given an ac drive field of the functional form $H_{ac} = Hsin(\omega t)$, the sample magnetization is:

$$M = H(\chi' sin(\omega t) + \chi'' cos(\omega t))$$
(2.15)

where χ' and χ'' are the real and dynamic susceptibilities respectively. The resulting voltage signal produced in the pickup coil is then presented in Eqn. 2.16

$$V_{ac} = \alpha H \omega (\chi'' sin(\omega t) - \chi' cos(\omega t))$$
(2.16)

A photograph of the homemade coil I used for these measurements is shown in Fig. 2.9. The coil was adapted for both ³He and ADR inserts for the Quantum Design refrigeration systems. When performing experiments, the drive coil was driven by a Stanford Research Systems SR830 lockin amplifier and the pickup coil voltage was measured using the same lockin. The lockin amplifier is a phase sensitive detector, and can be used to directly measure χ' and χ'' . In most measurements a frequency of 19.997 kHz was used, with a drive current of 100 μ A, equating to a driving field with a maximum amplitude of approximately 0.25 Oe. Using this coil it was possible to observe superconducting transitions in samples with masses less than 0.1 mg.

My *ac* susceptibility measurements had some complications, however. First, the counterwound coils were not exactly balanced so there was pickup from the self inductance of the coil. This produced a large temperature dependent background in all measurements. The technique was therefore applied only to samples with T_c below 5 K, where the background signal was temperature independent and easily subtracted from the measured signal.

Additionally, my measurements often showed some admixture of the real and complex parts of the susceptibility. To decouple the two, the data $(V_x \text{ and } V_y)$ had to be rotated by an angle θ to a new vector $(V'_x \text{ and } V'_y)$ by applying a rotation matrix as shown below:

$$\begin{bmatrix} V'_x \\ V'_y \end{bmatrix} = \begin{bmatrix} V_x \\ V_y \end{bmatrix} \begin{bmatrix} \cos(\theta) & \sin(\theta) \\ -\sin(\theta) & \cos(\theta) \end{bmatrix}$$
(2.17)

Knowing the correct value of θ , such that V'_x and V'_y will reflect the true real and dynamic susceptibilities of the material can be quite challenging in principle. I typically assumed that the dynamic susceptibility should have virtually constant values at temperatures significantly above and below the superconducting transition temperature, a reasonable assumption for a nonmagnetic metal at these frequencies. θ was then chosen, such that the normal state and base temperature dynamic susceptibilities for the system were equal. Figure 2.10 shows data to which such a procedure has been applied.



Figure 2.9: Photographs of *ac* susceptibility coil set. The device consists of two components, a top plate containing the drive and pick up coils and a mounting plate machined from high conductivity copper. Samples are fixed to this mounting plate using GE varnish.



Figure 2.10: Example of rotated *ac* susceptibility data. Data were taken on a 3.6 mg piece of elemental zirconium. The raw data collected using the homemade *ac* susceptibility coilset is shown in (a). V_y and V_x correspond to the strength of the signal out of phase and in phase with the driving current respectively. Therefore V_y is directly proportional to material χ' while V_x is directly proportional to χ'' . The offset in the V_x data between 1 and 0.1 K is believed to originate from some convolution between the measured in and out of phase response. Rotated data believed to reflect the true real and dynamic susceptibility are presented in (b). Data were rotated by 0.02 radians. The finite voltage values observed in the normal state represent the background signal intrinsic to the coilset.

Chapter 3: Nematic Susceptibility

Measurements of nematic susceptibility plays a central role in my studies of $BaNi_2As_2$. I measured nematic susceptibilities using an elastoresistivity technique developed by the group of Ian Fisher at Stanford University [59, 83, 84]. Here I describe the basic group theory considerations underlying these measurements and the Ginzburg-Landau theory that motivated their study. Both group theory and the Ginzburg-Landau formalism are well known, and will only be discussed to the extent needed to understand my experimental results. I finish this chapter with a discussion of the experimental apparatus I used to measure nematic susceptibility. For a more complete discussion of point groups see Refs. [85–87]

3.1 Point Groups

A mathematical group is a set equipped with an operation. The set and operation must satisfy four axioms; closure, invertibility, identity, and associativity. For a generic group G with operation \times these are defined as follows:

- Closure: $\forall g_i, g_j \in G; g_i \times g_j \in G$
- Identity: $\exists e \in G$ such that $\forall g_i \in G$; $g_i \times e = e \times g_i = g_i$

- Invertibility: $\forall g_i \in G, \exists g_j \in G$ such that $g_i \times g_j = e$
- Associativity: $\forall g_i, g_j, g_k \in G, (g_i \times g_j) \times g_k = g_i \times (g_j \times g_k)$

A point group is a collection of geometric symmetries of a system that keep at least a single point fixed. The collection of all such symmetries for a physical structure form a mathematical group.

Within applications of group theory to physics, and particularly the point group theory of structural transitions, a construction known as an irreducible representation (irrep) may provide valuable insight into the physical system. For the purposes of this discussion, a representation of a group will be defined as a mapping of the group from one space to another, such that the products of any two mapped elements is equal to the mapping of the product of the same two elements (*i.e.* a homomorphism). I note that this definition is slightly simplified, but adequately captures most of the essential physics and mathematics of group representations. A given group then will have a number of possible representations. These representations may feature a reduced dimensionality compared to the original group. For instance, a trivial representation of a given group will map all elements of the original group to the identity element of a one dimensional group. A representation is then said to be irreducible if it may only be dimensionally reduced further as the trivial representation.

An example of reducibility of representations may be found in the C_{2v} point group (the point group of nonlinear two dimensional molecules such as H₂O). This point group has four unique symmetry elements: the identity E, a two fold rotational axis of symmetry C_2 , and two mirror planes σ_v and σ'_v . That these elements satisfy the requirements of a group can be seen by examining Table 3.1.

Table 3.1: Multiplication table for C_{2v} point group. Row and column labels indicate the symmetry operations of the group, while entries in the body of the table denote their products. Through examining the entries of this table, it can be clearly seen that C_{2v} satisfies the four axioms of a mathematical group.

C_{2v}	E	C_2	σ_v	σ'_v
E	E	C_2	σ_v	σ'_v
C_2	C_2	E	σ'_v	σ_v
σ_v	σ_v	σ'_v	E	C_2
σ'_v	σ'_v	σ_v	C_2	E

The group elements of the C_{2v} point group can be thought of as symmetry operations for a structure in 3-dimensional Euclidean space. These four elements may then be represented by 3×3 matrices reflecting how these symmetry operations will transform a point in space as shown in Eqn. 3.1.

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \sigma_v = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \sigma'_v = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$
(3.1)

Now consider a transformation f_x from the above matrix representation to the group $\{1, -1\}$ with group operation of numerical multiplication, such that f_x maps every element of the original group to the entry in the upper left hand corner of its matrix representation. The effect of this mapping on the individual group elements is shown below:

$$f_x(E) = 1$$

$$f_x(C_2) = -1$$

$$f_x(\sigma_v) = 1$$

$$f_x(\sigma'_v) = -1$$
(3.2)

Such a transformation preserves the structure of the original group and is a homomorphism to a new representation. This new representation is reduced, showing that the matrix representation was not irreducible. This new representation cannot be further reduced, except to the trivial representation, and is one of the irreps of the C_{2v} point group.

There are an infinite number of point groups in three-dimensions. However, crystallographic constraints result in their being only 32 possible crystallographic point groups. These groups are well documented and their basic properties are frequently presented in a distilled form known as a character table. For reference, table 3.2 provides the character table for C_{2v} . The rows of the character table are the irreps, Γ_i , of the point group, while the columns represent the different elements of C_{2v} . The irreps are presented in the notation of Mulliken symbols. The body of the table provides the character of each operation in the given representation of the point group. The far right column, meanwhile, provides functions that operate as a basis for the given irrep. These functions are useful, in that they provide symmetry allowed normal modes that are active in infrared or Raman spectroscopy, and indicate the quadrupolar nematic order parameter symmetries allowed in the given point group.

Γ_i	E	C_2	σ_v	σ'_v	
A_1	1	1	1	1	x^2, y^2, z^2
A_2	1	1	-1	-1	xy
B_1	1	-1	1	-1	xz
B_2	1	-1	-1	1	yz

Table 3.2: C_{2v} character table.

3.2 The D_{4h} Point Group

BaNi₂As₂ and BaFe₂As₂ crystallize in a tetragonal structure; *i.e.* $a = b \neq c$ and $\alpha = \beta = \gamma = 90$. The point group of interest in my work is therefore the point group of the inversion symmetric tetragonal system D_{4h} .

The D_{4h} point group features 16 unique symmetry operations: the identity, two 90° rotations, five 180° rotations, five reflections, two improper rotations, and an inversion operation. Table 3.3 provides a partial character table for the D_{4h} point group ¹.

In the D_{4h} point group, there are four irreps that are relevant to the physics of electronic nematicity and structural transitions: A_{1g} , B_{1g} , B_{2g} , and E_g . The A_{1g} irrep is the totally symmetric representation, and a physical distortion that is symmetrically equivalent to the A_{1g} representation conserves the symmetries of the point group. A generic transition breaking the four fold rotational symmetry of the tetrag-

¹This character table has been truncated to display only irreps that are symmetric with respect to the symmetry center of the point group as these are the only irreps relevant to the physics of nematicity and structural distortions in this system.

Γ_i	E	$2C_4$	C_2	$2C'_2$	$2C_{2}''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(xz, yz)

Table 3.3: D_{4h} character table.

onal structure can be described as a physical distortion of shared symmetry with the B_{1g} , B_{2g} , and E_g irreps. A quadrupolar nematic order in these three symmetry channels would appear with form factors $x^2 - y^2$, xy, and (xz, yz), respectively. In terms of lattice degrees of freedom, a crystallographic distortion in the B_{1g} or B_{2g} channels corresponds to an orthorhombic transition, while E_g symmetric strain will correspond to a monoclinic distortion of the tetragonal lattice. A visualization of A_{1g} , B_{1g} , B_{2g} , and E_g symmetric distortions illustrating this point is provided in Fig. 3.1. In the BaFe₂As₂ system, electronic nematic order and the structural distortion break B_{2g} symmetry. On the other hand, the triclinic transition of BaNi₂As₂ will require B_{1g} , B_{2g} , and E_g symmetric distortions. The symmetry isolated magnitude of the structural distortion for both BaNi₂As₂ and BaFe₂As₂ compounds is provided in Table 3.4.



Figure 3.1: Symmetry isolated visualization of distortions to the D_{4h} point group. The black solid line displays the initial structure of the tetragonal cell, while the dashed red line shows the impact of a distortion transforming as the different irreps of the D_{4h} point group. Notice that an A_{1g} symmetric distortion responds to changes in cell volume that maintain all of the symmetries of the point group. B_{1g} , B_{2g} , and E_g symmetric distortions, meanwhile, all break the four-fold in plane rotational symmetry of the system.

Table 3.4: A decomposition of effective strain associated with crystal distortion between high and low temperatures in BaNi₂As₂ and BaFe₂As₂ crystals. These decompositions were carried out using lattice parameters reported in Reference [66] for BaNi₂As₂ and [49] for BaFe₂As₂ and strains were separated into symmetries reflective of the irreducible representations Γ_i of D_{4h} [83].

Γ_i	Strain	$BaNi_2As_2$	$BaFe_2As_2$
$\begin{bmatrix} A_{1g,1} \\ A_{1g,2} \end{bmatrix}$	$\frac{\frac{1}{2}(\epsilon_{xx} + \epsilon_{yy})}{\epsilon_{zz}}$	$0.0043 \\ 0.0061$	$0.0004 \\ 0.0020$
$\begin{array}{c} B_{1g} \\ B_{2g} \end{array}$	$\frac{\frac{1}{2}(\epsilon_{xx} - \epsilon_{yy})}{\epsilon_{xy}}$	-0.0015 -0.0008	0 0.0040
E_g	$\begin{pmatrix} \epsilon_{xz} \\ \epsilon_{yz} \end{pmatrix}$	$\begin{pmatrix} -0.0081\\ -0.0017 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \end{pmatrix}$

3.3 Nematic Susceptibility

Observation of electronically driven rotational symmetry breaking in high T_c superconductors has spawned significant interest in this phenomenon. In an electronic nematic system, rotational symmetries of the electronic system are broken due to an instability in the Fermi sea. Such a transition will necessarily lead to broken rotational symmetry in the structural and magnetic degrees of freedom as well, as these properties are coupled in a material. Thus, in some materials, such as BaFe₂As₂, a symmetry reducing structural transition is observed even though the lattice is not itself unstable. The reverse process, where electronic anisotropy develops at a structural transition driven by a softening phonon, is also expected. The observation of a broken electronic rotational symmetry is thus not conclusive evidence for an electronic nematic phase, as a nonzero electronic nematic order parameter can arise even if there is no electronically driven rotational symmetry breaking. This ambiguity may be removed through the observation of a diverging

nematic susceptibility, however, as I will describe in this next section.

3.3.1 Theory

The free energy \mathcal{F} of a nematic system will vary as a function of many external tuning parameters of the system such as pressure, temperature, magnetic field, *etc.* It will also depend on the magnitude of the symmetry-breaking crystal strain and the electronic nematic order parameter. Assuming the free energy is an analytic function at all temperatures, it is possible to expand \mathcal{F} as a polynomial in both the electronic nematic order parameter ψ and the anisotropic crystal strain (the structural nematic order parameter) ϵ . In principle, there will be a nematic and structural order parameter of shared symmetry with each of the irreps of the material point group. For simplicity, the free energy expansion to fourth order in ψ and ϵ shown below only features a single ψ and ϵ , both of shared symmetry with irrep Γ_i .

$$\mathcal{F}(\psi_{\Gamma_i}, \epsilon_{\Gamma_i}) \approx F_0 + \frac{a}{2}\psi_{\Gamma_i}^2 + \frac{b}{4}\psi_{\Gamma_i}^4 + \frac{c}{2}\epsilon_{\Gamma_i}^2 + \frac{d}{4}\epsilon_{\Gamma_i}^4 - \lambda\psi_{\Gamma_i}\epsilon_{\Gamma_i}$$
(3.3)

Here the coefficients a, b, c, d, and λ are positive in the disordered phase (*i.e.* above the nematic transition), and will depend on temperature, magnetic field, pressure, *etc.* The first order terms are not included as they would cause the order parameter to assume a nonzero value at all temperatures. The third order term, however, is disregarded here only for simplicity. The bilinearly coupled term in Eqn. 3.3, $\lambda \psi_{\Gamma_i} \epsilon_{\Gamma_i}$, can only be included if ψ and ϵ transform as the same irrep. If ψ and ϵ transform as different irreps they will couple only trivially in higher order terms in the free energy expansion. The bilinear coupling is consequential, as a finite value of ϵ will guarantee finite ψ (or vice versa). ϵ is then said to be a conjugate field to the nematic order.

This ambiguity is circumvented through measurements of nematic susceptibility. A system at thermal equillibrium will always occupy a local minimum in the free energy. For the free energy to exhibit a minima at a nonzero value of ψ and a rotational symmetry breaking transition to occur, one of the coefficients in the free energy expansion must become unstable (*i.e.* negative). In the simplest case, we can imagine the parameter a as the unstable coefficient. If the system undergoes an electronically driven nematic transition at T_{nem} , a may be expanded to first order in temperature as:

$$a = a_0(T - T_{nem}) \tag{3.4}$$

where a_0 is simply a constant. Inserting this temperature dependence into Eqn. 3.3 and minimizing the free energy with respect to ψ and ϵ yields:

$$\begin{cases} \psi_{\Gamma_i} = 0, & T \ge T_{nem} \\ \psi_{\Gamma_i} = \sqrt{\frac{a_0(T_{nem} - T)}{b}}, & T \le T_{nem} \end{cases}$$
(3.5)

As mentioned, the bilinear coupling between ψ_{Γ_i} and ϵ_{Γ_i} guarantees that both will become nonzero at the same temperature. Practically speaking, this requires a structural distortion to occur at the electronic nematic transition temperature. Concurrently, if a softening elastic modulus drives a lattice distortion, the electronic nematic order parameter will become nonzero as alluded to in the introduction to this section. This complicates interpreting the source of an electronic nematic phase transition, as the observation of a transition to a nonzero electronic nematic order parameter does not guarantee that electronic degrees of freedom have driven the transition.

The thermodynamic susceptibility of an ordered phase is defined as the derivative of the order parameter derivative with respect to its conjugate field. For my experiments, I was interested in the electronic nematic susceptibility, *i.e.* $\chi_{\text{nem}}^{\Gamma_i} \equiv \partial \psi_{\Gamma_i} / \partial \epsilon_{\Gamma_i}$. The mean field expectation for the nematic susceptibility may be found from Eqn. 3.3. Differentiating \mathcal{F} with respect to ψ_{Γ_i} one finds the free energy is minimized under the condition

$$a\psi_{\Gamma_i} + b\psi_{\Gamma_i}^3 - \lambda\epsilon_{\Gamma_i} = 0 \tag{3.6}$$

Differentiating again with respect to ϵ_{Γ_i} yields the expected nematic susceptibility.

$$\frac{\partial \psi_{\Gamma_i}}{\partial \epsilon_{\Gamma_i}} \approx \frac{\lambda}{a} \tag{3.7}$$

Where I have ignored higher order terms in ψ . Notice, that if *a* follows the temperature dependence given in Eqn. 3.4 *i.e.* electronic degrees of freedom drive a nematic transition in the system, the susceptibility will diverge at T_{nem} (Fig. 3.2).

A diverging nematic susceptibility then reflects a zero crossing in the coefficient a, and is a hallmark of an electronically driven, rotational symmetry breaking phase transition. In contrast, for a lattice driven transition, the constant c will become negative as the lattice softens. In this case we would expect that a will likely not evolve dramatically in temperature, and, the nematic susceptibility will not diverge at T_{nem} . Therefore, the observation of a diverging nematic susceptibility provides direct evidence for electronically driven symmetry breaking.



Figure 3.2: Mean-field predictions for free energy (left) and thermodynamic susceptibility (right) approaching a continuous phase transition. Minima in the free energy appear at nonzero order parameter at temperatures below the transition temperature T_{nem} . Meanwhile, a diverging susceptibility is predicted approaching the transition temperature from both above and below.

3.3.2 Experiment

The electronic nematic order parameter ψ is not a uniquely defined physical quantity. Therefore, the nematic susceptibility may be probed using a number of different techniques. I chose to measure nematic susceptibility of single crystals through an elastoresistivity technique due to the ease with which existing infrastructure in CNAM could be adapted to perform such experiments.

Electronic resistivity ρ provides powerful probe of some electronic properties, including changing symmetries at the Fermi surface. The crystal strain field, meanwhile, is conjugate to an electronic nematic order parameter of the same symmetry. When the applied strain is vanishingly small, and the system is in the linear response regime, the resistance anisotropy will be directly proportional to the electronic nematic order parameter. Taken with proper symmetry considerations, components of the dimensionless elastoresistivity tensor:

$$m_{ij,kl} = \lim_{\epsilon \to 0} \frac{\partial ((\rho(\epsilon) - \rho(\epsilon = 0)) / \rho(\epsilon = 0))_{ij}}{\partial \epsilon_{kl}}$$
(3.8)

are directly proportional to the electronic nematic susceptibility of a system. Here ρ_{ij} is a component of the resistivity tensor and ϵ_{kl} is a component of the strain tensor. For the D_{4h} point group, three nematic susceptibilities may be measured, corresponding to B_{1g} , B_{2g} , and E_g symmetry breaking. The definition of these susceptibilities is provided in Eqn. 3.9.

$$\chi_{\text{nem}}^{B_{1g}} \equiv m_{11} - m_{12}$$

$$\chi_{\text{nem}}^{B_{2g}} \equiv m_{66}$$

$$\chi_{\text{nem}}^{E_g} \equiv m_{44}$$
(3.9)

Here, and throughout the rest of this thesis, elastoresistive indices are expressed in the compactifed Voigt notation (*i.e.* 1 = xx, 2 = yy, 3 = zz, 4 = yz, 5 = xz, 6 = xy).

To characterize the elastoresistivity tensor, I applied strain to samples by anchoring them directly to a lead-zirconium-titanate PZT actuator stack. By loading the sample/actuator system into a cryogenic refrigerator and applying a voltage to the stack it was possible to vary strain *in-situ* and measure elastoresistivity over a wide temperature range. When voltage is applied to the stack it will expand along its poling direction and contract in the orthogonal axis. By mounting crystals with different orientations with respect to the piezo principle axis, and measuring different components of the resistivity tensor, I isolated different components of the elastoresistivity tensor. I note that only $m_{11} - m_{12}$ and m_{66} elastoresistivity coefficients are presented in this thesis.

3.3.2.1 B_{1g} Susceptibility

Figure 3.3 shows the technique I used to measure the $\chi_{\text{nem}}^{B_{1g}} \equiv m_{12} - m_{11}$ elastoresistivity coefficient. In this experiment, two nominally identical samples were mounted orthogonally on the top surface of the PZT stack. Both crystals were shaped into long rectangular bars oriented along the crystallographic *a*-axis, and the longitudinal resistivity is measured. Here the sample with current along the poling direction of the stack will be referred to as R_1 , while the orthogonal sample will be referred to as R_2 . The stack applies a voltage dependent strain along its poling direction of $\epsilon_{xx}(V)$ and an orthogonal strain of $-\epsilon_{yy}(V)$. Assuming the sample is in the regime of linear response, and utilizing the definition of the elastoresistivity tensor (Eqn. 3.8), one can calculate the change in resistance ($\Delta R = R(\epsilon) - R(\epsilon = 0)$) for the sample mounted along the poling direction of the actuator as:

$$\frac{\Delta R_1}{R_1} = \epsilon_{xx}(V)m_{11} - \epsilon_{yy}(V)m_{12}$$
(3.10)

The orthogonal sample will meanwhile show a normalized resistance change of:

$$\frac{\Delta R_2}{R_2} = -\epsilon_{yy}(V)m_{11} + \epsilon_{xx}(V)m_{12}$$
(3.11)

Therefore,

$$\frac{\Delta R_1}{R_1} - \frac{\Delta R_2}{R_2} = (\epsilon_{xx}(V) + \epsilon_{yy}(V))(m_{11} - m_{12})$$
(3.12)

Equation 3.12 relates the relative changes in sample resistance and crystal strain to the $m_{11} - m_{12}$ elastoresistivity coefficients. In the experimental procedure, R_1 and R_2 are measured over a wide range of applied strains by sweeping the driving voltage for the piezo at a constant temperature. The slope of the linear relationship between $\frac{\Delta R_1}{R_1} - \frac{\Delta R_2}{R_2}$ and $\epsilon_{xx}(V) + \epsilon_{yy}(V)$ is then extracted as the B_{1g} nematic susceptibility.

3.3.2.2 B_{2g} Susceptibility

Figure 3.4 shows the configuration I used to measure the $\chi_{\text{nem}}^{B_{2g}} \equiv m_{66}$ elastoresistivity coefficients. These experiments were conducted using a single sample wired in a transverse geometry, as described by Shapiro, *et al.* [84]. Generally, the transverse component of resistivity (ρ_{xy}) will be zero in the absence of magnetic field. A distortion breaking the in-plane mirror symmetries along the principle axes (*i.e.* a B_{2g} distortion) may promote a nonzero transverse resistivity proportional to the magnitude of the m_{66} elastoresistivity coefficient, however.

For measurement of $\chi_{\text{nem}}^{B_{2g}}$, I would mount a single crystal at a 45° with respect to the principal axis of the stack. The current contacts to the crystal are oriented along the crystallographic *a*-axis. With the crystal mounted at a 45° angle with respect to the poling direction of the piezoelectric actuator, the ϵ_{xx} and orthogonal $-\epsilon_{yy}$ strains of the stack are now along the (1 1 0) and (1 $\overline{1}$ 0) directions of the sample. Though the induced transverse resistance is of interest, sample contacts of finite size applied to a crystal by hand will always feature some amount of



Figure 3.3: Schematic of B_{1g} symmetric nematic susceptibility measurement. In this experiment two samples that were prepared along the crystallographic (1 0 0) axis were placed orthogonally on the piezoelectric stack. Top image displays an illustration of the experiment. The bottom image is a photograph of the actual experimental apparatus.

longitudinal contribution to a nominally transverse measurement. To quantify the magnitude of this longitudinal contribution, I used a five wire geometry for these measurements, simultaneously measuring both R_{xx} and R_{xy} . At zero magnetic field and zero strain, any measured voltage in the transverse coordination will originate from R_{xx} contamination. Therefore, at zero applied strain, R_{xy} and R_{xx} will scale according to $R_{xy} = \gamma R_{xx}$, where γ is a constant. For a sample with length l and width w the change in sample resistance ($\Delta R = R(\epsilon) - R(\epsilon = 0)$) with respect to applied strain will follow the relation below:

$$\frac{l}{w}\left(\frac{\Delta R_{xy}}{R_{xx}} - \gamma \frac{\Delta R_{xx}}{R_{xx}}\right) = (\epsilon_{xx} + \epsilon_{yy})m_{66} \tag{3.13}$$

Using Eqn. 3.13, I extracted the m_{66} elastoresistivity tensor component from the physically observable variables R_{xy} , R_{xx} , l, w, ϵ_{xx} , and ϵ_{yy} .

3.4 Experimental Details

When performing elastoresistivity measurements, I mounted crystals to a Piezomechanik PSt150/55/7 PZT stack using Devcon brand 5-minute epoxy. The stack and sample were mounted on a bare PPMS puck outfit with a custom machined sample stage and cooled using a Quantum Design PPMS system.

The applied strain was measured using a strain gauge mounted on the reverse side of the stack (opposite the side that the samples were mounted on). The strain gauge was a model WK-05-062TT-350 gauge produced by Vishay electronics. This model is composed of two mutually orthogonal gauges, allowing for the simultaneous measurement of both ϵ_{xx} and ϵ_{yy} . I used the temperature dependence of the strain



Figure 3.4: Schematic of B_{2g} symmetric nematic susceptibility measurement. In this experiment a transverse voltage is measured on a single sample mounted at a 45° angle to the poling direction of the stack. Top image displays an illustration of the experiment. The bottom image is a photograph of the actual experimental apparatus.

gauge's gauge factor (provided by Vishay) when calculating the strain at cryogenic temperatures. The motion of the piezo stack is voltage hysteretic, requiring a direct measurement of the strain gauge during every experiment. The Poisson's ratio of the stack ($\nu_p = -\epsilon_{xx}/\epsilon_{yy}$) was observed to remain effectively constant across different voltages and temperatures, however. Thus, in most experiments only ϵ_{xx} was directly measured, with ϵ_{yy} being calculated using the known Poisson's ratio of the stack.

The experiment requires electrical contacts to measure the resistance of the sample(s), source a voltage to the PZT stack, and measure the resistance of the strain gauge. Six wires were used to measure the sample resistance². A four terminal resistance measurement was simultaneously conducted to extract changes in the strain gauge resistance, and infer the strain experienced by the samples. These ten electrical connections are made to the pins in the PPMS sample space, and take advantage of the built in PPMS wiring. Sample resistances were measured using either an SR830 lockin amplifier or LS372 resistance bridge. The SR830 was preferred due to its reduced noise and faster measuring time. When measuring sample resistances using the SR830, two lockin amplifiers were used to measure the two different output signals. In this experiment I used a 1-2 V excitation and a 1 k Ω limiting resistor was wired in parallel with the current circuit to source a

²For the B_{1g} geometry, samples are wired in parallel requiring only six total wires for the two four terminal measurements. B_{2g} susceptibility is taken on a single sample with five electrical contacts. Six wires are used nontheless, so that all voltage measurements are taken across twisted pairs, minimizing inductive pickup in the voltage circuit.



Figure 3.5: Schematic of the experimental electronics configuration in nematic susceptibility measurements. The left panel displays the measurement configuration for the crystal circuit. The right panel displays the piezoelectric actuator circuit incorporating an Omron G5V-2 electrical relay to control the polarity of the voltage sourced to the piezo stack.

constant current of 1-2 mA. The output of the first lockin was fed into the reference of the second, and measurement frequencies of about a hundred Hz were used. The strain gauge resistance was measured using a dc current sourced by a Lakeshore 120 Current Source, while voltage was measured using a Kiethley 2182A nanovoltmeter.

The PZT stack was rated for voltages in the range of +150 V to -50 V at room temperature. Although I never pushed beyond this limit, this range is expected to grow at cryogenic temperatures. The high voltage was sourced using a Thorlabs TPZ001 power supply. The power supply was connected to a homebuilt electrical relay circuit that allowed me to switch the polarity of the voltage applied to the stack. This circuit uses an Omron brand G5V-2 relay, the schematic for which is provided in Fig. 3.5. While the operating voltage applied to the PZT stack may be as high as 150 V, the internal wiring of the PPMS is only rated to 50 V. Furthermore, the helium gas pressure in the PPMS sample chamber will be in the corona region, where the voltage required for the formation of electric arcs as determined using Paschen's law is minimized. While the formation of an arc is unlikely, as it depends strongly on the separation between cathode and anode as well as the helium pressure, it may still prove possible above 100 V, and would risk damaging the experiment as well as potentially the sample chamber. To avoid arcing and prevent damage to the internal PPMS wiring, a custom feed through was made, running well insulated wiring through the top flange of the sample space to drive the piezo (Fig. 3.6).

Careful sample preparation played a crucial role in my measurements. Systematic experimental errors may arise from sample misorientation, imperfect strain transmission due to finite sample thickness, and, in the case of mutually orthogonal sample measurement, inhomogeneity between samples. As most of my measurements were taken using mutually orthogonal samples I needed to consider all three sources of error.

The sample orientation is crucial in elastoresistivity experiments, and deviations from the sample configuration presented in Figs. 3.3 and 3.4 will produce additional contaminating signals. Fortunately, identifying in plane sample orientation in both the $Ba_{1-x}Sr_xNi_2As_2$ and $BaFe_2As_2$ compounds is relatively straightforward as thin specimens of both materials tend to naturally cleave along the crystallographic (1 0 0) axis. To confirm that cleaved crystals do indeed break along the *a* axis I performed Laue x-ray scattering experiments on a number of samples (Fig.



Figure 3.6: Photograph of elastoresistivity probe is provided in (a). A photograph of a homemade electrical feed-through, a KF-flange outfitted with hermetically sealed SMA and BNC adapters, is shown in (b). Many experiments were also conducted with an alternative feed-through constructed using Henkel Loctite STYCAST 2850FT. Photograph of electronics used to conduct elastoresistivity experiments are displayed in (c).



Figure 3.7: Laue x-ray diffraction pattern taken on $BaNi_2As_2$ single crystal. White dots show regions of high x-ray scattering intensity, while the green dots denote a fit to a tetragonal crystal cell. These measurements indicate good crystallinity in measured samples. They also confirm that samples naturally cleave along the crystallographic (1 0 0) direction.

3.7). While it is also possible to cleave $BaFe_2As_2$ crystals along other high symmetry axes, such as the (1 1 0) direction, using a razorblade, attempts to prepare $Ba_{1-x}Sr_xNi_2As_2$ samples rotated within the *ab* plane were unsuccessful. I found that even very thin $Ba_{1-x}Sr_xNi_2As_2$ crystals generally shatter rather than cleave along (1 1 0).

In addition to simplifying the process of sample cleaving, crystal thickness had to be minimized to promote complete and homogeneous strain transmission through samples. For this thesis, all elastoresistive experiments were performed on samples of thicknesses between 20 and 60 μ m. Previous work in BaFe₂As₂ suggests that samples as thick as 100 μ m may also be suitable, however [59]. While BaFe₂As₂ specimens are easily exfoliated to a desirable thickness, the interlayer bonding is stronger in the $Ba_{1-x}Sr_xNi_2As_2$ class of compounds, making it challenging to apply the same method for sample preparation. $BaNi_2As_2$ crystals were therefore mechanically polished rather than cleaved to the desired thickness. Polishing was done exclusively with P4000 grade sandpaper purchased from Buehler. Polishing with such a fine abrasive can be tedious, particularly when beginning with a thick sample. Experience suggests, however, that cracks developed with rougher sandpaper may affect the elastoresistivity measurement, and samples polished more roughly appeared to be more prone to snapping under strain. Broken samples produce resistance values that are discontinuous and hysteretic in both temperature and strain. Intrinsically hysteretic elastoresistance may also be manifested in samples with some nematic order, as I will discuss in Chapter 4.

The procedure used to prepare $Ba_{1-x}Sr_xNi_2As_2$ elastoresistivity measurements then typically went as follows. Large single crystals (approximately 2 mm × 2 mm × 0.2 mm) were polished to a thicknesses of approximately 60 μ m. I then used a razor blade to cleave the crystal into bars with a desirable aspect ratio for transport measurements. As samples only cleaved cleanly along the (1 0 0) direction, no further indicators were required to properly orient crystals. In experiments conducted on pairs of orthogonally mounted crystals, two bars were cut from the same initial crystal piece to minimize the risks of sample inhomogeneity. Electrical contacts were then applied to the samples using a two component EPO-TEK silver epoxy. Samples with contacts were adhered to the piezoelectric stack, using 5-minute Devcon epoxy. The 5-minute epoxy was allowed to cure for approximately 24 hours at room temperature before measurements were performed.

Chapter 4: BaNi₂As₂: Structural Transition, CDW, and Nematicity

Portions of this chapter have been summarized or, in places, lifted largely verbatim from Refs. [1, 3]. Low temperature x-ray diffraction studies presented in this chapter were performed at the University of Illinois and phenomenological modeling was performed by collaborators at the University of Minnesota.

4.1 Introduction

High-temperature superconductivity in both cuprate [21, 22] and iron-based materials [23–25] emerges from a notably complex normal state. Although magnetic spin fluctuations are believed to drive Cooper pairing in these materials, the common occurrence of a rotational symmetry-breaking nematic phase has captured increasing attention in recent years [43,88]. In contrast to a conventional structural transition, considerable evidence suggests that the nematic phase in these compounds is due to an electronic instability rather than lattice softening [59,89].

Theoretical analysis has shown that fluctuations associated with such an electronic nematic phase, particularly near a putative quantum critical point, can significantly enhance superconductivity [60–63,90]. Being peaked at zero wave-vector, nematic fluctuations favor pairing instabilities in several symmetry channels, in contrast to the case of magnetic fluctuations. Experiments have indeed shown a striking enhancement of nematic fluctuations centered at optimal tuning of superconductivity in a number of iron-based superconductors [59, 89], and a strong tendency towards nematicity in high T_c cuprate materials [53,91,92]. However, the overarching presence of magnetic fluctuations emanating from proximate antiferromagnetic instabilities makes it challenging to draw firm conclusions about the relationship between enhanced pairing and nematicity in these nematic materials. The FeSe_{1-x}S_x substitution series is an important exception, where the system exhibits both superconductivity and nematicity in the absence of magnetic order [93]. However, in this series the superconducting transition temperature is virtually unaffected by tuning through the nematic quantum critical point [93, 94], leaving open questions about the influence of nematic fluctuations.

The nickel-pnictide intermetallic BaNi₂As₂ provides an interesting candidate material to further pursue the interaction between nematic and superconducting phases. The BaNi₂As₂ compound exhibits a rotational symmetry breaking tetragonaltriclinic structural distortion at transition temperature $T_S = 135$ K and superconducts at critical temperature $T_c = 0.7$ K [65, 66]. Superconductivity in BaNi₂As₂ is predicted to be of conventional origin, and experimental results confirm a BCSlike evolution of thermodynamic properties [67, 69]. Furthermore, neutron diffraction measurements in BaNi₂As₂ single crystals provide no evidence for long range magnetic order in either the high or low symmetry crystal structures of this compound [70]. Thus, in contrast to the Fe-based superconductors in which magnetic order along the crystallographic (1 1 0) direction breaks the B_{2g} symmetry of the tetragonal cell, the structural distortion in BaNi₂As₂ is likely not driven by spin degrees of freedom. Although there are apparently no experimental results that indicate the structural transition is of unconventional origins, predictions of orbital order in the triclinic phase [73] suggest that the tetragonal-triclinic distortion inBaNi₂As₂ may originate from an electronic instability.

In an effort to further elucidate the origin of the structural distortion in $BaNi_2As_2$, x-ray diffraction measurements were performed over a wide temperature range and electronic nematic susceptibilities were measured via elastoresistivity experiments. Scattering experiments revealed the existence of a previously unreported long range unidirectional charge density wave (CDW) order in both the tetragonal and triclinic crystal structures. The CDW in the tetragonal structure was observed with an incommensurate wave vector of $(0.28\ 0\ 0)$, with an onset temperature of 148 K. While no orthorhombicity was observed in the temperature range of the charge order, the CDW notably breaks the B_{1g} symmetry of the tetragonal cell. Correspondingly, a B_{1g} symmetric electronic order was observed in elastoresistivity below 148 K. In contrast to the Fe-based superconductors, however, the B_{1g} and B_{2g} electronic nematic susceptibilities exhibit only a very modest temperature dependence above the onset of CDW order; indicating the CDW and the tetragonal-triclinic structural transition in $BaNi_2As_2$ is driven by structural rather than electronic degrees of freedom.

In this chapter I discuss in detail elastoresistivity and x-ray scattering results of BaNi₂As₂, and conclude with a phenomenological Ginzburg-Landau model for the tetragonal-triclinic structural transition.

4.2 Methods

Temperature dependent x-ray diffraction measurements were carried out using a Xenocs GeniX 3D MoK_{α} microspot x-ray source with multilayer focusing optics and a Mar345 image plate detector. Single crystal samples were cooled with a closed-cycle cyrostat and mounted to a Huber four-circle diffractometer. These measurements and their analyses were performed by the group of Dr. Peter Abbamonte at the University of Illinois.

To investigate whether triclinicity in BaNi₂As₂ is driven by electronic, rather than lattice degrees of freedom, I measured symmetry isolated components of the elastoresistivity tensor in tetragonal BaNi₂As₂. These measurements were performed using the piezoelectric elastoresistance technique of Refs. [84, 89], and discussed in Chapter 3. Although, $m_{12} - m_{11} (\chi^{B_{1g}}_{nem})$, $m_{44} (\chi^{E_g}_{nem})$, and $m_{66} (\chi^{B_{2g}}_{nem})$ are all of interest, only the $m_{12} - m_{11}$ and m_{66} values are reported here. Crystal properties, specifically tendencies towards formation of a narrow cross section in the *ac* plane and cleaving along the crystallographic *a*-axis, made it prohibitively challenging to fabricate a sample suitable for an experimental characterization of m_{44} in BaNi₂As₂.

4.3 CDW Order

The x-ray results presented in this section were collected at the University of Illinois by Sangjun Lee, Gilberto A. de la Pena, Stella X.-L. Sun, Yizhi Fang, Matteo Mitrano, and Dr. Peter Abbamonte.

To characterize the BaNi₂As₂ tetragonal-triclinic structural transition, a series of detailed, temperature-dependent x-ray diffraction measurements were taken. It was found that structural Bragg peaks were indexed to the expected I4/mmmand $\overline{P1}$ space groups in the tetragonal and triclinic structures respectively. Data collected when cooling showed an abrupt transition between the two structure types, with only a narrow region of coexistence, confirming the strongly first order nature of the triclinic structural transition.

Notably, upon cooling below 148 K additional Bragg reflections appear at propagation vector $(0.28 \ 0 \ 0)_{tet}$ [Fig. 4.1 (a,c)] (here the "tet" subscript denotes $(H \ K \ L)$ indices are derived from the tetragonal unit cell). These reflections are observed across several Brillioun zones, confirming they originate from a coherent structure and are not errant or sample extrinsic reflections. The intensity associated with these reflections strengthens rapidly with cooling, before vanishing entirely at the structural phase boundary. They are replaced by a new set of superstructure peaks propagating along q-vector $(0.31 \ 0 \ 0)_{tri}$ [Fig. 4.1 (b,c)] (where the "tri" subscript indicates these reflections index to the triclinic cell). Upon cooling deeper within the triclinic structure these peaks move within the $(H \ K)$ plane, eventually locking in on a $(0.33 \ 0 \ 0)_{tri}$ wave vector, commensurate with the triclinic cell.

As these reflections are not observed at room temperature, have non-integer indices, and appear only below 148 K, they are attributed to CDW order in $BaNi_2As_2$. To my knowledge this was the first such observation in a pnictide superconductor with the $ThCr_2Si_2$ structure type. In addition, the width of the reflections associ-



Figure 4.1: $(H \ L)$ reciprocal space mapping at 142 K (a) and 15 K (b) in BaNi₂As₂ crystals. Peaks associated with the CDW superstructures occur at non-integer Miller indices, and are marked by dashed circles. (c) A line momentum scan showing the sharp scattering peaks emanating from I-CDW and C-CDW superstructures. Inset is a schematic of the momentum scan. Plot from Ref. [3].

ated with both the incommensurate charge density wave (I-CDW) and commensurate charged density wave (C-CDW) orders are within the resolution limits of the experiment, indicating they are both long range. They are also notably unidirectional, appearing along ($H \ 0 \ 0$), but never in the orthogonal ($0 \ K \ 0$) direction. The (0.28 0 0) superstructure therefore breaks the B_{1g} symmetry of the tetragonal system. Surprisingly, no structural orthorhombicity can be observed in this region, however.

Within the triclinic phase, the CDW wave-vector nests hole-like pockets that form around the Γ point, suggesting that they may be connected to the CDW formation. No evidence for band folding or an emerging energy gap as would be expected in a generic Peierls distortion has been observed, however.

4.4 Elastoresistivity

Figure 4.2 shows the elastoresistance $m_{12} - m_{11}$ in stoichiometric BaNi₂As₂, which is proportional to $\chi_{\text{nem}}^{B_{1g}}$. While $m_{12} - m_{11}$ is negative at temperatures well above the structural transition, it becomes positive and grows rapidly in magnitude near $T_S \approx 135$ K [Fig. 4.2(a,b)]. Before it peaks at T_S , however, $m_{12} - m_{11}$ starts displaying strain-hysteretic behavior at a temperature of about 148 K [Fig. 4.2(a),(b)]. This temperature coincides with the emergence of the CDW peaks at incommensurate wave vector (0.28 0 0).

Although it may appear natural to fit a Curie-Weiss model to this $m_{12} - m_{11}$ versus temperature data near T_S , such a fit would be inappropriate. The thermo-
dynamic susceptibility is defined in the limit of vanishing field. In the temperature range where hysteresis is present, the nematic order parameter is not a single-valued function of the strain in the zero strain limit, and the slopes of these curves are therefore no longer well defined material susceptibilities. Rather, in analogy to hysteresis in the more familiar magnetic susceptibility, the observation of a strain-hysteretic nematic order parameter in BaNi₂As₂ indicates a static B_{1g} symmetry-breaking phase at a temperature T_{nem} that is higher than T_S . Crucially, the electronic nematic susceptibility, proportional to $m_{12} - m_{11}$, does not seem to diverge near T_{nem} – in fact, it is nearly temperature-independent above T_{nem} and far removed from the strong 1/T divergence predicted by Ginzburg-Landau phenomenology and observed in BaFe₂As₂. This strongly suggests that this transition (*i.e.* I-CDW order) is driven primarily not by electronic, but rather by lattice degrees of freedom.

While $m_{12} - m_{11}$ exhibits a relatively rich evolution in temperature, m_{66} ($\chi^{B_{1g}}_{\text{nem}}$) shows little temperature dependence (Fig 4.3) and no visible hysteresis in the resistance versus strain isotherms. The discrepancy between B_{2g} and B_{1g} elastoresistivities confirms that symmetry breaking at T_{nem} is limited to the B_{1g} symmetry channel. Figure 4.4 illustrates how deformations in each symmetry channel distort the transition metal sublattice of the ThCr₂Si₂ system. Notice, that the transition metal sublattice is rotated 45° from the principal axes of the tetragonal cell. This means the B_{1g} symmetric CDW and nematic orders are along the directions of the Ni-Ni next nearest neighbors in BaNi₂As₂. This also happens to be along the direction of the zigzag Ni chains observed in the triclinic cell. In the BaFe₂As₂ system, meanwhile, the diverging nematic susceptibility (Fig. 4.3) and structural distortions



Figure 4.2: Electronic nematic susceptibility measurement in BaNi₂As₂. A strongly temperature-dependent elastoresistivity is seen in the straindependent resistance isotherms for single crystals mounted parallel (a) and perpendicular (b) to the poling direction of the piezo stack. Panel (c) shows the nematic susceptibility, $m_{12} - m_{11}$, is completely flat at high temperatures before growing in magnitude upon approach to the incommensurate charge-density wave (I-CDW) ordered phase (light grey region), and then peaking at the structural transition into the triclinic phase (dark grey region). Black symbols include error bars representing 90% confidence intervals of data. The I-CDW phase is also accompanied by a nematic order observed in hysteresis in the strain-dependent resistance isotherms shown in (a) and (b). Inset shows (*H K*) map of reciprocal space at 142 K, displaying a reflection from the superstructure at wave vector (0.28 1 7).



Figure 4.3: Electronic nematic susceptibility measurements in BaNi₂As₂ and BaFe₂As₂ compounds. $\chi^{B_{2g}}_{\text{nem}}$ measurements in BaFe₂As₂ (blue) display a clear, 1/T temperature divergence over a wide temperature range near the nematic transition $(T/T\mathcal{N} = 1)$. Neither $\chi^{B_{1g}}_{\text{nem}}$ (black) nor $\chi^{B_{2g}}_{\text{nem}}$ (blue) diverge approaching T_{nem} in BaNi₂As₂, however. Below T_{nem} (in the CDW phase) the $m_{12}-m_{11}$ elastoresistivity coefficient grows rapidly, while m_{66} shows only a slight anomaly. Error bars represent 90% confidence intervals for data.

are in the B_{2g} channel (*i.e.* along the direction of Fe-Fe nearest neighbors).

4.5 Phenomenology of a Tetragonal-Triclinic Phase Transition

Diffraction and elastoresistivity studies yield several main findings in BaNi₂As₂. Including:

- A B_{1g} symmetry breaking I-CDW superstructure at temperatures above the triclinic transition.
- A B_{1g} symmetry breaking electronic order concurrent with the I-CDW phase.
- A strengthening of both CDW and nematic orders approaching the triclinic transition.
- Evidence that the nematic and CDW orders are not driven by electronic correlations, as indicated by the absence of a diverging nematic susceptibility.

A faithful description of the structural distortion in BaNi₂As₂ must capture all of these features, and in this section I will provide a model attempting to capture these phenomena. The phenomenological model is based largely on work developed originally by Dr. Morten Christensen and Dr. Rafael Fernandes at the University of Minnesota. It has been modified slightly for this work. The model will be itself divided into two main subdivisions. First, I discuss a proposed relationship between the observations in the x-ray and elastoresistivity experiments. I then describe a mechanism that produces a tetragonal-triclinic structural distortion, and show how a B_{1g} symmetric order may contribute to such a transition.



Figure 4.4: Visualization of B_{1g} and B_{2g} symmetric distortions of the transition metal sublattice. Black structures denote the disordered ThCr₂Si₂ cell, while the images in red correspond to the tetragonal cell following a B_{1g} or B_{2g} symmetric distortion. The Ni/Fe transition metal sites are denoted by closed circles, while the unit cell boundary is marked by a line. Note, that as the square transition metal sublattice is rotated at a 45° angle from the crystal unit cell, the B_{1g} (B_{2g}) distortion is along the direction of transition metal next nearest (nearest) neighbors.

A possible phenomenological model for the relationship between CDW and nematic order has been proposed for the cuprate superconductors [58] and URu₂Si₂ [95]. In this model, a bidirectional CDW in a tetragonal system is described using a two component order parameter $\Psi = (\Psi_x, \Psi_y)$, with the two components representing the CDW strength in the orthogonal x- and y-directions. The CDW can not only break translational symmetry, but in the case of Ψ_x and Ψ_y of unequal magnitude will additionally break the rotational point group symmetry. The symmetry determined free energy expansion in terms of electronic nematic order ($\psi_{B_{1g}}$), CDW order, and crystallographic strain ($\epsilon_{B_{1g}}$) will be as follows:

$$\mathcal{F} = a\psi_{B_{1g}}^2 + b(\Psi_x^2 + \Psi_y^2) + c\epsilon_{B_{1g}}^2 + \lambda_1\psi_{B_{1g}}(\Psi_x^2 - \Psi_y^2) + \lambda_2\epsilon_{B_{1g}}(\Psi_x^2 - \Psi_y^2) + \lambda_3\epsilon_{B_{1g}}\psi_{B_{1g}} \quad (4.1)$$

Here, as in Eqn. 3.3, a, b, c, and λ_i depend on temperature, pressure, *etc.* Note, in the case of a purely unidirectional CDW ($\Psi_y = 0$) the strength of the electronic nematic order parameter ψ couples directly with the square of the CDW strength Ψ_x^2 in addition to crystal strain ϵ .

Returning to the experimental results, the dimensionless width of the $\Delta R/R$ hysteresis loop can serve as a proxy for the strength of electronic nematic order, just as residual magnetization quantifies the strength of the magnetic order parameter in a ferromagnet. The x-ray scattering intensity of an I-CDW peak is a direct probe of the strength of the CDW order parameter. Plotting the symmetry coupled values versus temperature (Fig. 4.5) I find that the two order parameters feature the same temperature evolution.

The scattering and elastoresistivity results taken together suggest that the



Figure 4.5: A comparison of the squared peak intensity of a $(0.28\ 0\ 0)$ I-CDW superstructure reflection [the $(-1.72\ 1\ 7)$ peak; red symbols] and the elastoresistive hysteresis width (blue symbols). These data scale linearly, indicating an intimate relationship between nematic and CDW orders. Strain-dependent isotherms were repeated three times at each temperature, and hysteresis widths were measured at the widest point. Error bars represent extremal values of the hysteresis width between separate measurements.

electronic nematic and CDW order are intimately linked. Whether the elastoresistivity is directly measuring changes in resistance due to the charge order itself or a more true nematic order (*i.e.* orbital order) driven by coupling to the rotational symmetry breaking CDW cannot be determined from this data. When considering whether or not the electronic structure is unstable to rotational symmetry breaking, however, the answer to this question is perhaps inconsequential. Whether or not charge order coexists with an additional rotational symmetry breaking electronic phase, or is itself the source of the hysteretic elastoresistivity, the lack of diverging susceptibility above the CDW onset indicates the CDW is driven by structural considerations. Therefore, in BaNi₂As₂, the I-CDW order above the triclinic transition is apparently driven by electron-phonon coupling, as expected in a Peierls system. This is unlike the cuprate compounds wherein charge order is unconventional and the energies of softening phonon modes never approach 0 in the CDW phase [96].

Elastoresistivity and x-ray scattering measurements confirm that I-CDW and electronic nematic order are directly correlated, if not existing as one and the same, in the tetragonal phase. A complete understanding of the structural transition in BaNi₂As₂ must capture the cascading broken symmetries, lead first by the B_{1g} symmetry at 148 K, and then later by the simultaneous breaking of B_{2g} and E_g symmetries at $T_S = 135$ K.

To model these transitions, I first consider the structural free energy of a tetragonal crystal using the harmonic approximation [97]. This formulation uses an effective strain tensor μ_i (Eqn. 4.2). The entries of this effective strain tensor are

composed of weighted sums of the more conventional crystallographic strains, ϵ_{ij} :

$$\mu = \begin{pmatrix} \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} \\ \frac{1}{6}(\epsilon_{xx} + \epsilon_{yy} - 2\epsilon_{zz}) \\ \frac{1}{\sqrt{2}}(\epsilon_{xx} - \epsilon_{yy}) \\ 2\epsilon_{xz} \\ 2\epsilon_{yz} \\ 2\epsilon_{yz} \\ 2\epsilon_{xy} \end{pmatrix}$$
(4.2)

An expansion of the free energy in terms of the effective strain tensor μ_i is preferred over a similar expansion in ϵ_{ij} because μ_i is already partitioned into elements that transform as irreducible representations of the D_{4h} point group. For instance, μ_3 corresponds to B_{1g} symmetry breaking strain, μ_4 and μ_5 break E_g symmetries, and a nonzero μ_6 breaks B_{2g} symmetry. Within the harmonic approximation the elastic free energy \mathcal{F} in terms of nontrivial (point-group breaking) strains can be expressed as:

$$\mathcal{F} = \frac{1}{2}(C_{11} - C_{12})\mu_3^2 + \frac{1}{2}C_{66}\mu_6^2 + \frac{1}{2}C_{44}(\mu_4^2 + \mu_5^2)$$
(4.3)

From this form it is evident that a continuous tetragonal-triclinic phase transition, is not permitted, as there are no second order terms in the free energy coupling μ_3 , μ_4 , μ_5 , and μ_6 (all of which must become nonzero in the triclinic phase). This is consistent with the strongly first order transition observed in the real system. An alternative expansion to third order that also includes contributions from a unidirectional, B_{1g} symmetry breaking CDW phase $\Psi = (\Psi_x, 0)$ as is seen in the scattering experiment is provided below:

$$\mathcal{F} = \frac{1}{2} (C_{11} - C_{12}) \mu_3^2 + \frac{1}{2} C_{66} \mu_6^2 + \frac{1}{2} C_{44} (\mu_4^2 + \mu_5^2) + \frac{1}{2} a \Psi_x^2 + \lambda_1 \mu_3 \Psi_x + \lambda_2 \mu_4 \mu_5 \mu_6 + \frac{\lambda_3}{2} (\mu_4^2 - \mu_5^2) (\mu_3 + \lambda_4 \Psi_x)$$
(4.4)

Here the coupling parameters λ_1 , λ_2 , and λ_3 are in principle small. This is not necessarily the case for λ_4 .

In BaNi₂As₂, a B_{1g} symmetry breaking CDW order parameter is observed in the vicinity of the triclinic transition. Though not observed in the experimental result, the bilinearly coupled terms in the free energy also imply a nonzero structural distortion in the same symmetry channel as the CDW onset. Therefore, at temperatures just above T_S , the CDW order will have nonzero strength $\overline{\Psi_x}$ and the B_{1g} symmetric strain will also condense to a nonzero value $\overline{\mu_3}$. In the presence of these finite orders the free energy becomes:

$$\mathcal{F} = \frac{1}{2}C_{66}\mu_6^2 + \mu_4^2(\frac{1}{2}C_{44} + \lambda_3\overline{\mu_3} + \lambda_3\lambda_4\overline{\Psi_x}) + \mu_5^2(\frac{1}{2}C_{44} - \lambda_3\overline{\mu_3} - \lambda_3\lambda_4\overline{\Psi_x}) + \lambda_2\mu_4\mu_5\mu_6$$
(4.5)

Minimizing this equation with respect to μ_6 yields:

$$\mu_6 = \frac{-\lambda_2}{C_{66}} \mu_4 \mu_5 \tag{4.6}$$

which gives a free energy of:

$$\mathcal{F} = -\frac{3\lambda_2^2}{2C_{66}}\mu_4^2\mu_5^2 + \mu_4^2(\frac{1}{2}C_{44} + \lambda_3\overline{\mu_3} + \lambda_3\lambda_4\overline{\Psi_x}) + \mu_5^2(\frac{1}{2}C_{44} - \lambda_3\overline{\mu_3} - \lambda_3\lambda_4\overline{\Psi_x}) \quad (4.7)$$

The system is stable so long as the coefficients for both the μ_4^2 and μ_5^2 terms are positive. However, if $\frac{1}{2}C_{44} < |\lambda_3\overline{\mu_3} + \lambda_3\lambda_4\overline{\Psi_x}|$ either μ_4^2 or μ_5^2 will become unstable,

condensing to a nonzero value. Meanwhile, the negative coefficient of quartic term $-\frac{3\lambda_2^2}{2C_{66}}\mu_4^2\mu_5^2$ guarantees that μ_4^2 and μ_5^2 will simultaneously take on nonzero values¹.

A triclinic structural distortion of a tetragonal lattice, led by a B_{1g} symmetric charge order, then requires only an intrinsically soft C_{44} elastic modulus such that $\frac{1}{2}C_{44} < |\lambda_3\overline{\mu_3} + \lambda_3\lambda_4\overline{\Psi_x}|$. Though it is assumed here that this theory applies to BaNi₂As₂, confirming this belief requires further research quantifying the elastic moduli of BaNi₂As₂ crystals,

4.6 Conclusion

In this chapter, I present experimental results characterizing the BaNi₂As₂ compound and a theoretical model of the tetragonal-triclinic distortion observed therein. Notably, the results include a previously unobserved complexity to the structural transition, with emerging charge and nematic orders observed above T_S . Although nematic susceptibility measurements have revealed that electronic degrees of freedom do not drive rotational symmetry breaking in this material, the rich physics I observed suggests that BaNi₂As₂ deserves further study.

¹There will of course be another $\mu_4^2 \mu_5^2$ quartic term. The simultaneous condensation of nonzero μ_4 and μ_5 requires that $-\frac{3\lambda_2^2}{2C_{66}}$ is large enough that the net quartic contribution from both terms remains negative.

Chapter 5: $Ba(Ni_{1-x}Co_x)_2As_2$: Evolution of Structure and Superconductivity

Portions of this chapter are taken largely verbatim from published work Refs. [2,3]. Low temperature x-ray diffraction studies were performed at the University of Illinois.

5.1 Introduction

As I discuss in Chapter 4, diffraction and elastoresistive results established that there is rich physics near the triclinic transition in the BaNi₂As₂ system. Although triclinicity appears to be driven by structural degrees of freedom, observations of CDW reflections and an electronic nematic order suggest a previously unreported cascade of symmetry breaking in this system.

BaCo₂As₂ specimens, meanwhile, feature no observable structural or magnetic transitions, remaining in the ThCr₂Si₂ structure between room temperature and 1.8 K. Material properties, such as an enhanced Wilson's ratio, do indicate this compound is proximate to a ferromagnetic quantum critical point [98], however, and hole doping in the Ba_{1-x}K_xCo₂As₂ series yields long range ferromagnetic correlations [99]. Here I discuss the physical properties of Co-substituted BaNi₂As₂ single crystals, showing that the low temperature triclinic phase is smoothly suppressed with cobalt substitution before vanishing at critical concentration $x_c = 0.11$. A concomitant enhancement of T_c from 0.7 K to 2.3 K is observed approaching x_c . I find that, in contrast to other reported BaNi₂As₂ substitution studies [75, 100], and in a manner reminiscent of similar work in BaFe₂As₂ [101], Ba(Ni_{1-x}Co_x)₂As₂ exhibits a strong enhancement of T_c in both the triclinic and tetragonal low temperature phases. T_c decreases rapidly for $x > x_c$, and superconductivity vanishes entirely by x = 0.15. The observed superconducting dome is suggestive of a Cooper pairing enhancement reminiscent of superconductivity emerging from quantum criticality.

5.2 Methods

 $Ba(Ni_{1-x}Co_x)_2As_2$ crystals were grown out of Pb-flux using a solution growth technique originally reported by Ronning, *et al.* [65] and described in Chapter 2.

Elemental analysis in substituted samples was conducted using wavelength dispersive x-ray spectroscopy (WDS) by Dr. Philip Picolli of the Geology Department at UMD. This technique consistently determined $Ba(Ni_{1-x}Co_x)_2As_2$ crystals formed with the expected 1:2:2 stoichiometry, and was used to determine the xvalues for these samples. Detailed structural data were collected on single crystals using a Bruker APEX-II CCD system equipped with a graphite monochromator and a MoK_{α} sealed tube ($\lambda = 0.71073$ Å) by Dr. Peter Zavalij. Data were refined using the Bruker SHELXTL Software Package. Crystallographic information for $Ba(Ni_{1-x}Co_x)_2As_2$ single crystals collected in the tetragonal phase (250 K) are shown in Table 5.1. Atomic positions evolve monotonically across the phase diagram, while low conventional residual values R_1 confirm high crystal quality (Fig. 5.1).

Transport, heat capacity, and *ac* magnetic susceptibility data were taken using Quantum Design PPMS and DynaCool systems. In-plane transport data were taken using a four wire configuration. Au wires were attached to cleaved or polished (to remove Pb contamination) single crystals using DuPont 4929N silver paste. Single crystal *ac* magnetic susceptibility was measured using a homemade coil [82]. *Ac* magnetic susceptibility measurements between 0.1 and 3 K were taken with the coil mounted on a Quantum Design Adiabatic Demagnetization Refrigerator insert for the PPMS. Data were taken at a frequency of 19.997 kHz, in an *ac* field with an amplitude of approximately 0.25 Oe. DC magnetic susceptibility measurements were carried out in a Quantum Design Magnetic Property Measurement System (MPMS) SQUID magnetometer.

Heat capacity measurements were taken with a relaxation technique fit to a dual time constant model. The background heat capacity of the platform and grease were also measured and subtracted from the result. Experiments on Co substituted samples were complicated by the relatively small size of the crystals (< 0.1 mg). To circumvent this issue, heat capacity measurements were taken on collections of several samples pulled from the same growth. Sharp anomalies at the structural transitions in measurements taken on these collections of crystals, along with the high degree of growth homogeneity determined through WDS, suggest little if any



Figure 5.1: Structural and chemical characterization of $Ba(Ni_{1-x}Co_x)_2As_2$ single crystals grown from Pb-flux. (a) WDS chemical composition characterization for $Ba(Ni_{1-x}Co_x)_2As_2$ single crystals. $x_{wds} = x_{nominal}$ represented by black dashed line. (b) Lattice parameters in the $Ba(Ni_{1-x}Co_x)_2As_2$ series collected at 250 K. Data show a dependence of a and c axis length on x through x = 0.251. Note that some error bars are too small to be seen.

error in heat capacity data due to collection averaging.

Standard density functional theory calculations for pure BaNi₂As₂ were conducted using the WIEN2K [102] implementation of the full potential linearized augmented plane wave method in the local density approximation. The k-point mesh was taken to be $11 \times 11 \times 11$, with lattice constants taken from experimental measurements. Supercell calculations were implemented for Co-substituted cases, *i.e.* Ba₄Ni₇CoAs₈ for x = 0.125 and Ba₂Ni₃CoAs₄ for x = 0.250, and resultant electronic structures unfolded via recently developed first-principles unfolding methods [103]. All DFT calculations were performed by Dr. Limin Wang.

Table 5.1: $Ba(Ni_{1-x}Co_x)_2As_2$ crystallographic data determined through singlecrystal x-ray diffraction on crystals grown from Pb flux. All data were collected at 250 K.

x	0	0.083	0.133
Crystal system	Tetragonal	Tetragonal	Tetragonal
Space group	I4/mmm	I4/mmm	I4/mmm
a(Å)	4.144(2)	4.1256(5)	4.1140(7)
$b(\text{\AA})$	4.144(2)	4.1256(5)	4.1140(7)
$c(\text{\AA})$	11.656(6)	11.7486(15)	11.827(2)
$V^3(\text{\AA}^3)$	200.2(2)	199.97(5)	200.17(8)
Reflections	1737	1705	1776
R ₁	0.0140	0.0179	0.0156
Atomic parameters:			
Ba	2a (0,0,0)	2a (0,0,0)	2a (0,0,0)
Ni/Co	$4d \ (0,1/2,1/4)$	$4d \ (0,1/2,1/4)$	$4d \ (0,1/2,1/4)$
As	4e (0,0,z)	4e (0,0,z)	$4e (0,\!0,\!z)$
	0.34726(6)	0.34785(7)	0.34812(6)
Bond lengths (Å):			
Ba-As(Å)	3.4288(15)	3.4213(6)	3.4189(6)
Ni/Co-As(Å)	2.3619(11)	2.3615(5)	2.3618(5)
As-As(Å)	3.560(71)	3.575(0)	3.592(5)
Bond angles (deg):			
As-Ni/Co-As	103.32(2)	103.710(16)	103.971(15)
As-Ni/Co-As	122.63(5)	121.74(4)	121.14(3)

Temperature dependent x-ray diffraction measurements were carried out using

a Xenocs GeniX 3D MoK_{α} microspot x-ray source with multilayer focusing optics and a Mar345 image plate detector by the group of Dr. Peter Abbamonte at the University of Illinois. Single crystal samples were cooled with a closed-cycle cyrostat and mounted to a Huber four-circle diffractometer.

5.3 Physical Properties

Figure 5.2 shows a plot of the resistivity of Ba(Ni_{1-x}Co_x)₂As₂ crystals versus temperature collected upon heating and cooling. A hysteretic resistive jump/drop is clearly visible at small x values at the the tetragonal-triclinic structural phase transition, but this is quickly suppressed with increasing x. Extrapolating these data, I determined that the structural transition vanishes entirely at critical Co concentration $x_c \approx 0.11$. This observation is consistent with the evolution of the heat capacity anomaly associated with the structural distortion shown in Fig. 5.3, which also is absent by x = 0.133. The low temperature heat capacity displayed in the inset to Fig. 6.8 shows no dramatic changes in Debye temperature and a monotonically increasing Sommerfeld coefficient for the reported Co concentrations. The Sommerfeld coefficient is enhanced from 10 mJ/mol-K² to nearly 16 mJ/mol-K² between x = 0.013 and x = 0.083. The extracted Debye temperatures are $\omega_D = 236$ K, 218 K, and 225 K for x = 0.014, 0.083, and 0.133 respectively. Pure BaNi₂As₂ was observed to have a Debye temperature of 250 K, consistent with previous work [66].

Despite changes in the low temperature structure, superconductivity evolved continuously in the Ba(Ni_{1-x}Co_x)₂As₂ series (see Fig. 5.2 inset), with T_c increasing



Figure 5.2: Transport measurements in Ba $(Ni_{1-x}Co_x)_2As_2$ single crystals grown from Pb flux. Main figure displays resistance normalized to room temperature value, and vertically offset for clarity. Data show clear suppression of anomalies associated with the structural transition, which vanishes by x = 0.133. Inset displays low temperature resistance normalized to 3.5 K value. Samples display clear enhancement of T_c when approaching structural phase boundary. Data plotted in blue ($x \le 0.083$) feature a low temperature resistance anomaly consistent with the triclinic structural distortion. Curves plotted in red remain tetragonal down to the lowest measured temperature.

upon cobalt substitution from 0.7 K at x = 0 to 1.7 K at x = 0.014. T_c continues to increase with increasing x in the triclinic phase, eventually reaching a maximum of 2.3 K at x = 0.083. T_c then gradually decreases with increasing x beyond 0.083, until vanishing for $x \ge 0.251$. Though small crystal sizes complicate dc magnetization measurements in these samples, the observation of enhanced T_c rather than a rapid suppression for small x suggests that Co behaves as a nonmagnetic substituant in the Ba(Ni_{1-x}Co_x)₂As₂ series.

Figure 5.4 shows heat capacity (main), transport (a) and ac magnetization (b) measurements of the superconducting transition in the same single-crystal sample (crystal dimensions of 0.67 mm \times 0.83 mm \times 0.067 mm) with x = 0.063. Balancing the entropy in the observed heat capacity jump yields a T_c of 1.8 K for this sample. The red curve in Fig. 5.4 is the α -model prediction of heat capacity for a single band BCS superconductor [104]. This curve has been scaled by a constant value of 1.35 to match the observed heat capacity jump. This model describes data well near T_c , and deviations at low temperatures may be due to nuclear Schottky contributions as observed in the pure compound [67]. The modeled heat capacity jump $\Delta C_e/\gamma T$ is approximately 2.2, well above the weakly coupled BCS value of 1.43, indicating strongly coupled superconductivity at this Co concentration. This value is consistent with previous reports of enhanced normalized heat capacity jumps of approximately 1.9 in both $Ba(Ni_{1-x}Cu_x)_2As_2$ and $BaNi_2(As_{1-x}P_x)_2$ [75,100] and greatly exceeds the near-BCS value observed in pure BaNi₂As₂ [67]. While previous work on Cu- and P-substituted BaNi₂As₂ suggested that the enhancement in the tetragonal phase was consistent with a phonon softening picture, this is not the case here, as the



Figure 5.3: Heat capacity C_p versus temperature measurements collected on warming in Ba(Ni_{1-x}Co_x)₂As₂ crystals grown from Pb flux. Anomalies are indicative of structural transitions. Inset displays low temperature C_p/T data plotted versus T^2 .

Debye frequency exhibits little change through the entire Co substitution range, as noted above.

Both superconductivity and the structural transition in optimally substituted x = 0.083 samples were observed to be of bulk origin; *i.e.* the transitions yielded large anomalies in the heat capacity of the material (see Fig. 5.3 main and inset). Figure 5.5 shows the temperature dependence of the upper critical field in an optimally substituted sample, which exhibits an approximately three fold enhancement compared to the pure compound. As reported in BaNi₂As₂, superconductivity in optimally substituted Ba(Ni_{1-x}Co_x)₂As₂ is more robust when field is applied parallel to the crystal plane. At higher fields, resistance curves taken in this orientation begin to broaden, while data taken with field along the *c*-axis remain sharp over all measurements. The H_{c2} anisotropy Γ remains virtually constant at all temperatures, with $\Gamma = 1.50$, which is slightly below the value of 2.1 reported for the pure compound [65].

5.4 CDW Order

X-ray data in pristine BaNi₂As₂ samples display an abrupt transition between tetragonal and triclinic crystal structures consistent with a strongly first order structural phase transition. Despite heat capacity and resistive signatures indicative of a bulk tetragonal-triclinic structural transition, scattering experiments in Ba(Ni_{1-x}Co_x)₂As₂ crystals of cobalt concentration x = 0.07 and 0.08 did not show a clear first order structural transition. Rather, tetragonal and triclinic structures



Figure 5.4: Plot of measured heat capacity versus temperature showing the superconducting transition of a Ba(Ni_{1-x}Co_x)₂As₂ sample with near optimal substitution x = 0.063 grown from Pb flux. Electronic heat capacity C_e was determined by subtracting the phonon contribution βT^3 from the total heat capacity. Red curve is the α -model predictions for a BCS superconductor [104] ($\alpha = 1.764$) scaled vertically by a constant multiple to better match the data. Inset shows superconducting transition measured via four terminal resistance (a) and the real part of *ac* susceptibility measured using a homemade coil (b).



Figure 5.5: H_{c2} data collected on an optimally substituted Ba(Ni_{1-x}Co_x)₂As₂ sample of x = 0.083 grown from Pb flux. Isomagnetic resistance data collected with field parallel to crystal a-axis (a) and parallel to crystal c-axis (b). Data collected parallel to the c-axis were taken in 0.5 kOe increments (0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5 and 4 kOe), while measurements with H || a were taken in 1 kOe increments (0, 1, 2, 3, 4, 5, and 6 kOe). (c) H_{c2} vs T_c phase diagram in parallel and perpendicular configuration. Data are taken at the midpoint of the resistive transition, and "error bars" represent the range wherein resistance is between 90% and 10% the normal state value. Curves are fits to a model of a dirty BCS superconductor developed by Werthamer, Helfand, and Hohenberg [105]. Inset shows upper critical field anisotropy Γ determined using the midpoint criteria.

coexist over a wide temperature range at these concentrations, showing that Cosubstitution broadens the structural transition [3]. X-ray data do confirm, however, that samples with cobalt concentration $x \ge 0.12$ feature no triclinic domains [3].

Charge order, present in the unsubstituted $BaNi_2As_2$, is also suppressed with increasing Co in the $Ba(Ni_{1-x}Co_x)_2As_2$ series. While a unidirectional I-CDW is observed in the tetragonal structure of $BaNi_2As_2$, no such incommensurate superstructure is observed in any of the Co-substituted samples, showing that this order is fragile to Co substitution [3]. The CDW order observed in the triclinic phase is a robust feature of the $Ba(Ni_{1-x}Co_x)_2As_2$ phase diagram however, appearing with the emergence of triclinic domains in samples of both x = 0.07 and 0.08 [3]. In the pure compound, the triclinic CDW first appears at an incommensurate wavevector, eventually locking in to the commensurate structure $(0.33 \ 0 \ 0)_{tri}$ deeper within the triclinic phase [3]. While the incommensurability of the CDW increases in Co substituted samples, a similar pattern is observed, with the CDW eventually stabilizing at a commensurate wavevector in the triclinic phase [3].

Surprisingly, the orientation of the CDW wave vector in the triclinic phase is inconsistent across samples of variable x. While x = 0 and x = 0.08 both lockin to a $(0.33\ 0\ 0)_{tri}$ C-CDW structure, x = 0.07 orders instead in the orthogonal $(0\ 0.33\ 0)_{tri}$ orientation [3]. Alhough crystallographic a- and b-axis are inequivalent in the triclinic phase, the observation that CDW reorientation does not evolve systematically across the Ba $(Ni_{1-x}Co_x)_2As_2$ system suggests the CDW ordering vector is sensitive to extrinsic stresses, perhaps from sample mounting or the triclinic-tetragonal phase boundaries in the coexistence region. The revelation that the CDW is not pinned along a particular axis in the triclinic structure is particularly surprising, however, as the structure of the Ni lattice in the triclinic phase is highly anisotropic.

5.5 Discussion

 T_c evolves nearly identically in Cu [100] and P [75] substituted BaNi₂As₂ crystals. In both of these systems T_c is stagnant in the triclinic phase, and is abruptly enhanced crossing the zero temperature structural phase boundary suggesting that enhanced superconductivity may originate from the tetragonal structure rather than from dynamics at the structural critical point. However, Co substitution causes a strong enhancement of T_c within the triclinic phase and a smooth evolution through the triclinic-tetragonal T = 0 boundary. In fact, in Ba(Ni_{1-x}Co_x)₂As₂ we see a dome-shaped superconducting phase diagram (Fig. 5.6) hinting at the possibility of a different mechanism for superconducting enhancement.

Previous reports suggest the BaFe₂As₂, BaCo₂As₂, and BaNi₂As₂ electronic structures differ through only a rigid shift in the chemical potential [69,98]. Calculations in the Ba(Ni_{1-x}Co_x)₂As₂ series, however, show a monotonic enhancement in electronic density of states (DOS) at E_F with increasing Co (Fig. 5.7) due to a Co d-orbital component that smoothly adds to the total DOS rather than a rigid band shift. The calculated DOS(E_F) is 1.81, 2.02, and 2.09 states/eV for x = 0, 0.125, and 0.25 respectively. Although the DOS behavior in triclinic BaNi₂As₂ cannot be inferred from these calculations, calculations at x = 0.125 and 0.25 reflect the true ground state DOS. In a BCS superconductor, an enhancement of the electronic DOS



Figure 5.6: Phase diagram for $Ba(Ni_{1-x}Co_x)_2As_2$ as determined from my transport data in single crystals grown from Pb flux. Structural and superconducting critical temperatures were both determined using the midpoint of each resistive transition. Red (blue) symbols denote the tetragonal-triclinic transition on warming (cooling) as gathered from transport measurements. The plotted superconducting T_c has been multiplied by a factor of 10. Inset displays transport data for optimally substituted, x = 0.083, samples featuring both clear enhancement in T_c and structural transition anomaly.

could be expected to provide an environment more hospitable to superconductivity and vice versa. The observed suppression of T_c for x > 0.1 does not coincide with a suppression in the calculated DOS in this regime, suggesting that changes in DOS are likely not the predominant factor responsible for the evolution of T_c . Calculations also suggested no changes to Fermi surface topology that account for the rapid suppression of superconductivity in over-substituted Ba(Ni_{1-x}Co_x)₂As₂. While the enhanced Wilson ratio observed in the Co-based end-member BaCo₂As₂ [98] suggests that increasing Co concentration may ultimately invoke ferromagnetic correlations, the concentrations where T_c is suppressed in the Ba(Ni_{1-x}Co_x)₂As₂ series are far from x = 1, suggesting that it is also unlikely that the rapid suppression of T_c in the tetragonal phase results from proximity to ferromagnetism.

The Ba(Ni_{1-x}Cu_x)₂As₂ and BaNi₂(As_{1-x}P_x)₂ series also exhibit features associated with phonon softening in high T_c samples, including strong superconducting coupling and a dramatically reduced Debye temperature [75, 100]. While strong superconducting coupling is also observed in the Ba(Ni_{1-x}Co_x)₂As₂ series, the Debye temperature only changes minimally over the range of x studied here. While the effect of phonon softening on pairing cannot be ignored, the distinct behavior found in the Ba(Ni_{1-x}Co_x)₂As₂ series suggests another mechanism is responsible for the strengthening of superconductivity, which appears to be centered around x_c . The dome shaped superconducting phase diagram in Ba(Ni_{1-x}Co_x)₂As₂ is a provocative suggestion that fluctuation-driven superconducting enhancement is instead a possibility.



Figure 5.7: Simulated evolution of electronic density of states in $Ba(Ni_{1-x}Co_x)_2As_2$. All calculations were taken for samples in the tetragonal phase using experimentally determined lattice parameters. Plots are for x = 0 (top), 0.125 (center), and 0.25 (bottom).

5.6 Conclusion

In this chapter I present experimental results characterizing the Ba(Ni_{1-x}Co_x)₂As₂ series. The system features a strong enhancement in superconducting T_c when tuned across a zero temperature tetragonal-triclinic structural phase boundary. Unlike the related Ba(Ni_{1-x}Cu_x)₂As₂ [100] and BaNi₂(As_{1-x}P_x)₂ [75] series, Ba(Ni_{1-x}Co_x)₂As₂ samples exhibit a strong superconducting enhancement both in crystals that are triclinic and in crystals that are tetragonal at lowest temperatures. Additionally, Ba(Ni_{1-x}Co_x)₂As₂ crystals do not feature clear evidence for superconducting enhancement derived from a softening phonon mode as is reported in the Cu and P substitution series. Rather, the superconducting phase diagram, reminiscent of the dome shaped phase diagrams of quantum critical superconducting systems, suggests the possibility of fluctuation driven superconducting enhancement.

Chapter 6: $Ba_{1-x}Sr_xNi_2As_2$: Tuned Nematicity and Superconductivity

Portions of this chapter have been summarized or, in places, lifted largely verbatim from Ref. [1]. Low temperature x-ray diffraction studies presented in this chapter were performed at the University of Illinois and phenomenological modeling was performed by collaborators at the University of Minnesota.

6.1 Introduction

BaNi₂As₂, the nickel-based analog of iron-based superconductor parent BaFe₂As₂, is a metallic compound that exhibits a strongly first-order structural transition from a tetragonal to triclinic cell at $T_S = 135$ K on cooling. While magnetic order has not been found in BaNi₂As₂ to date [65, 66, 70], incommensurate and unidirectional charge density wave (CDW) order onsets at temperatures above T_S [3]. This incommensurate CDW (I-CDW) breaks the B_{1g} symmetry of the tetragonal cell and is accompanied by a corresponding electronic symmetry breaking that I have observed in elastoresistivity experiments (see Chapter 4). A commensurate CDW (C-CDW) order is also observed upon cooling into the triclinic phase [3]. In contrast, the SrNi₂As₂ compound remains in a tetragonal structure down to the lowest measured temperatures and no known CDW or magnetic orders exist in this material [106]. Additionally, BaNi₂As₂ and SrNi₂As₂ both superconduct below approximately 0.7 K. Thermodynamic experiments, as well as first-principle analyses, have indicated that superconductivity in each of these compounds is of conventional origin [67, 69].

Given the nearly identical T_c of both BaNi₂As₂ and SrNi₂As₂, the isoelectronically substituted Ba_{1-x}Sr_xNi₂As₂ series presents a platform to explore the interplay between structure, charge, nematic, and superconducting order. Here I discuss the evolution of physical properties in the Ba_{1-x}Sr_xNi₂As₂ system. Elastoresistivity measurements indicate that, while symmetry breaking is driven by structural degrees of freedom in BaNi₂As₂, Sr substitution rapidly strengthens electronic nematic correlations in this system. Additionally, the superconducting phase is found to be not only robust to substitution, but is dramatically enhanced near the zero temperature structural phase boundary. The nearly sixfold enhancement of T_c in the optimally substituted compound is observed to coincide with a strengthened electronic nematic susceptibility. The coincidence of strong nematic fluctuations and enhanced T_c , along with the absence of other apparent sources of strengthened pairing, suggests that superconducting enhancement in this series is driven by nematic correlations [1].

6.2 Methods

I synthesized $Ba_{1-x}Sr_xNi_2As_2$ single crystals in CNAM using the molten flux technique discussed in Chapter 2. Unlike my earlier discussion of Co substituted Ba(Ni_{1-x}Co_x)₂As₂, a NiAs self-flux was preferred for these studies. Although the residual resistivity ratio (RRR) of NiAs-grown crystals of 8 is slightly smaller than the RRR of 10 that I observed in Pb-grown samples, self-flux was preferred due to the larger crystals produced using the self-flux method. After synthesis, I determined the Sr content of individual single crystals by EDS measurements. The 250 K lattice parameters of a number of samples were determined through single crystal x-ray diffraction measurements performed by Dr. Peter Zavalij.

Temperature dependent x-ray diffraction measurements were carried out using a Xenocs GeniX 3D MoK_{α} microspot x-ray source with multilayer focusing optics and a Mar345 image plate detector. Single crystal samples were cooled with a closed-cycle cyrostat and mounted to a Huber four-circle diffractometer. These measurements and their analyses were performed by the group of Dr. Peter Abbamonte at the University of Illinois.

Resistivity measurements were obtained using a four wire technique. In preparation for these experiments, crystals were mechanically extracted from the flux and mechanically polished to an appropriate size ($\approx 1 \text{ mm} \times 0.25 \text{ mm} \times 0.06 \text{ mm}$). *Dc* magnetization data were collected using a SQUID-VSM technique in a Quantum Design MPMS3 system, while low temperature *ac* susceptibility was conducted using a homemade coil [82]. Heat capacity measurements were generally performed using a heat pulse-relaxation technique fit to a two-tau model. Heat capacity measurements capturing the first order structural phase transition were modified to be sensitive to both warming and cooling transitions by applying an extended heat pulse, and extracting the heat capacity using a local derivative approach. Finally, using a home-built elastoresistivity probe I performed elastoresistive experiments on $Ba_{1-x}Sr_xNi_2As_2$ samples of varying x to determine the x-dependence of nematic properties in this series. *In-situ* tunable biaxial strain was applied to single crystal specimens through adhering crystals directly to piezoelectric PZT stacks [84, 89] as described in Chapter 3. The change in resistivity was measured using a Stanford Research SRS830 lockin amplifier. B_{1g} symmetric susceptibilities were measured on pairs of crystals mounted in a mutually orthogonal configuration, while the B_{2g} susceptibility is extracted from a single crystal wired in a transverse geometry.

6.3 CDW Order

The results from 250 K lattice characterization presented in this section were obtained by Dr. Peter Zavalij. The low temperature scattering experiments presented in this section were collected at the University of Illinois by Sangjun Lee, Gilberto A. de la Pena, Stella X.-L. Sun, Yizhi Fang, Matteo Mitrano, and Dr. Peter Abbamonte.

Single crystal x-ray diffraction experiments performed at 250 K confirmed that $Ba_{1-x}Sr_xNi_2As_2$ crystals formed in the tetragonal ThCr₂Si₂ structure across the entire range of Sr content. As expected, replacing the larger Ba ion with Sr dramatically reduces the length of the crystallographic *c*-axis in samples with increasing *x*. A subtle feature is observed in the evolution of the *a*-axis lattice parameter and tetrahedral bond angles with respect to *x* in $Ba_{1-x}Sr_xNi_2As_2$ samples near $x_c = 0.7$ (Fig. 6.1). Comparing this behavior to that of the iron-based systems suggests this anomaly may be due to an interaction between interlayer arsenic atoms that is promoted by the shrinking unit cell. As-As interactions in the iron-based 122 compounds (as is observed in CaFe₂As₂ under pressure [107,108]) breaks no crystal symmetries and occurs as the interlayer As-As separation approaches 3 Å. Both of these behaviors are consistent with observations in Ba_{1-x}Sr_xNi₂As₂. However, in the iron-based compounds interlayer As atoms will form a dimer. This bond causes a dramatic collapse in the crystallographic *c*-axis, an abrupt reduction in As-As spacing, and an expansion of the transition metal-pnictogen layer, all of which are absent in the Ba_{1-x}Sr_xNi₂As₂ series. Thus, if an interaction between interlayer arsenic atoms is responsible for the structural anomaly in Ba_{1-x}Sr_xNi₂As₂ samples, it manifests in a fundamentally different manner than in other ThCr₂Si₂ species.

Additionally, low temperature x-ray diffraction measurements performed at the University of Illinois show that increasing x suppresses the structural transition, which vanishes abruptly near critical concentration $x_c = 0.7$. The coincidence of the complete suppression of the triclinic transition and the high temperature crystallographic anomalies mentioned previously is suggestive that near this concentration a relatively "small" crystallographic change renders the system inhospitable to the triclinic phase. These measurements also establish that, unlike the $Ba(Ni_{1-x}Co_x)_2As_2$ system I discussed in Chapter 5, the triclinic and tetragonal structures do not coexist over a wide temperature range in the $Ba_{1-x}Sr_xNi_2As_2$ series.

Figure 6.2 shows the x-ray diffraction $(H \ K)$ mappings of reciprocal space,



Figure 6.1: Structural and chemical properties of $\operatorname{Ba}_{1-x}\operatorname{Sr}_x\operatorname{Ni}_2\operatorname{As}_2$ single crystals. (a) Crystal structure of tetragonal $\operatorname{BaNi}_2\operatorname{As}_2$. (b) Evolution of actual Sr content (determined via EDS) versus nominal value included in the growth. (c-e) x dependence of a and c lattice parameters (c), As-As spacing (d), and tetrahedral bond angles (e) in $\operatorname{Ba}_{1-x}\operatorname{Sr}_x\operatorname{Ni}_2\operatorname{As}_2$ single crystals. All data are collected at 250 K. The dashed line running vertically through panels (c), (d), and (e) denotes the critical concentration, x_c , where the system undergoes a zero temperature structural phase transition.

illustrating a representative I-CDW x-ray scattering peak in $Ba_{1-x}Sr_xNi_2As_2$ single crystals. Appearing with a $(0.28 \ 0 \ 0)_{tet}$ periodicity in BaNi₂As₂, the I-CDW superstructure wave vector appears to have a slight substitution dependence, appearing closer to $(0.27 \ 0 \ 0)_{tet}$ in samples with x = 0.4. Estimates derived from peak full width at half maximum values suggest a correlation length of approximately 330 Å at x = 0.4. I-CDW peak widths in x = 0 samples, meanwhile, are limited by the resolution of the experimental apparatus, placing a lower bound on the correlation length of nearly 1000 Å in pristine BaNi₂As₂. In x = 0.4 specimens, as in the pure compound, superstructure reflections are unidirectional, observed only along $(H \ 0 \ 0)$ and not in the orthogonal $(0 \ K \ 0)$ direction, breaking B_{1g} symmetry of the tetragonal phase. In more heavily substituted Ba_{0.35}Sr_{0.65}Ni₂As₂ samples, the incommensurate peaks are not visible in the measured temperature range. While only a single representative peak is displayed in Fig. 6.2, I-CDW reflections have been observed across several Brillioun zones in BaNi₂As₂ and Ba_{0.6}Sr_{0.4}Ni₂As₂, and are absent in the entirety of visible k-space at all temperatures in Ba_{0.35}Sr_{0.65}Ni₂As₂ and $Ba_{0.28}Sr_{0.72}Ni_2As_2$.

Additionally, all samples with an observable structural distortion (x < 0.7) exhibit C-CDW peaks in the triclinic phase. These peaks are observed at wavevector $(0.33\ 0\ 0)_{tri}$ in unsubstituted BaNi₂As₂. Samples of x = 0.4 also exhibited this same $(0.33\ 0\ 0)_{tri}$ periodic superstructure when first entering the triclinic phase. Deep within the triclinic phase, however, another commensurate CDW with wavevector $(0.5\ 0\ 0)_{tri}$ is observed. At the onset of this second commensurate CDW, the scattering intensity associated with the $(0.33\ 0\ 0)_{tri}$ CDW decreases dramatically,


Figure 6.2: $(H \ K)$ k-space mapping of x-ray scattering intensity in $Ba_{1-x}Sr_xNi_2As_2$ single crystals in the neighborhood of $(H \ K \ L)$ coordinates (0.28 1 7) are presented for samples of x = 0 (a), 0.4 (b), 0.65 (c), and 0.72 (d). Top panels show k-space mapping at 300 K, where no superstructure reflections are visible for all x. The lower panels show data collected at temperatures just above the tetragonal-triclinic structural transition temperature for x = 0, 0.4, and 0.65. Specimens with x = 0.72 exhibit no structural transition, and the lower panel of (d) displays the k-space intensity map collected at the base temperature of the experiment, 8 K.

but does not vanish. In samples of x = 0.65, however, the $(0.33 \ 0 \ 0)_{tri}$ scattering peaks are entirely absent, and only a $(0.5 \ 0 \ 0)_{tri}$ periodic superstructure is observed. Combining all of this information yields the CDW phase diagram shown in Fig. 6.3.

6.4 Resistivity, Magnetization, and Specific Heat

In Fig. 6.4, I show the results of basic magnetic and transport measurements in $Ba_{1-x}Sr_xNi_2As_2$ single crystals. Temperature hysteretic anomalies in the high temperature transport measurements [Fig. 6.4 (a)] occur at the first order tetragonal-



Figure 6.3: CDW phase diagram for the $Ba_{1-x}Sr_xNi_2As_2$ system developed from low temperature x-ray scattering experiments.

triclinic structural transition. With increasing x this transition is smoothly suppressed, before abruptly vanishing near $x_c = 0.70$. The location of these anomalies was used to construct the structural phase diagram for the Ba_{1-x}Sr_xNi₂As₂ series (Fig. 6.5), and are consistent with the observed tetragonal-triclinic transition temperatures found using x-rays. Magnetization data [Fig. 6.4 (c)] similarly can be used to track the evolution of the structural distortion, as a sharp decrease in susceptibility is observed entering the triclinic phase.

Resistivity anomalies at the triclinic distortion are also observed to change in character across the Ba_{1-x}Sr_xNi₂As₂ phase diagram. While resistivity increases sharply in the BaNi₂As₂ parent when cooling through the structural transition, a decrease in resistivity is observed entering the triclinic phase in samples near x = 0.6. This development coincides with the change in C-CDW wave vector from $(0.33 \ 0 \ 0)_{tri}$ to $(0.5 \ 0 \ 0)_{tri}$, suggesting the CDW may dictate the nature of these low temperature transport anomalies. A similar evolution of the resistivity anomaly is observed with increasing x in the BaNi₂(As_{1-x}P_x)₂ [75], but is not seen in either the Cu or Co substituted compounds [2, 100].

Figures 6.4(b,d) show the low temperature resistivity and *ac* susceptibility behavior of $Ba_{1-x}Sr_xNi_2As_2$ crystals, including signatures of superconductivity. Samples with less than 40% Sr substitution exhibit virtually constant T_c . The location of superconducting signatures in the transport and magnetic measurements of $Ba_{1-x}Sr_xNi_2As_2$ single crystals with Sr concentrations in the range 0.4 < x < 0.7are observed to increase significantly in temperature, however, reaching values as high as 2.5 K.



Figure 6.4: Temperature dependent normalized resistivity data for $\operatorname{Ba}_{1-x}\operatorname{Sr}_x\operatorname{Ni}_2\operatorname{As}_2$ single crystals at high (a) and low (b) temperatures. Successive curves in (a) are vertically offset for clarity. Temperature hysteretic anomalies in (a) coincide with the tetragonal-triclinic distortion. *Dc* magnetization data collected at 10 kOe with $H \parallel a$ are presented in (c). Sharp, temperature hysteretic anomalies at high temperature indicate structural transition, while divergence at low temperature likely originates from paramagnetic impurities. (d) Low temperature ac magnetic susceptibility χ' showing superconducting transitions. In all panels samples plotted in red (blue) are triclinic (tetragonal) at lowest temperatures.



Figure 6.5: Structural phase diagram of $\text{Ba}_{1-x}\text{Sr}_x\text{Ni}_2\text{As}_2$, displaying the x dependence of the tetragonal-triclinic structural phase transition upon cooling. Transition temperatures were determined through resistivity measurements. The triclinic distortion is smoothly suppressed with increasing Sr content until $x_c = 0.70 \pm 0.02$ beyond which the triclinic phase abruptly vanishes.

Resistivity, heat capacity, and magnetization data are presented for a single representative x = 0.68 crystal in Fig. 6.6. Heat capacity and transport measurements confirm a bulk hysteretic tetragonal to triclinic structural transition [Fig. 6.6(a)] between 35 and 60 K. Measurement below 5 K exhibit broad resistive and magnetic superconducting signatures at temperatures of approximately 2 K. Heat capacity data, however, shows a sharp anomaly at a much lower temperature, 0.5 K [Fig. 6.6(d)]. This separation of resistive and heat capacity signatures of superconductivity provides strong evidence that the increased T_c extracted from the former is due to a filamentary superconducting phase. Though the origins of filamentary superconductivity is unknown, that such filamentary superconductivity is only observed near the tetragonal-triclinic phase boundary is suggestive that the filamentary phase may be due to a small volume of the nominally triclinic sample remaining in the tetragonal structure down to zero temperature. I conclude, that the observed heat capacity anomalies track the bulk superconducting T_c , which remains virtually constant for x in the range $0 < x < x_c$.

While the data presented in Fig. 6.6 are collected from a single specimen, they are consistent with measurements taken across a number of samples in this range of x. I did not find any crystals in which both the triclinic structural distortion and bulk enhancement of superconducting T_c were observed.

An abrupt, enhancement of the bulk T_c was observed in $\text{Ba}_{1-x}\text{Sr}_x\text{Ni}_2\text{As}_2$ samples with $x > x_c$. A maximum T_c of 3.55 K was observed in crystals of Sr content x = 0.71. Increasing Sr content beyond this value smoothly suppressed superconductivity, towards the x = 1 end member T_c of 0.7 K. The abrupt enhancement of



Figure 6.6: Physical properties of a single $Ba_{1-x}Sr_xNi_2As_2$ crystal with Sr content x = 0.68. (a) Transport data are taken between 1.8 and 300 K in a $Ba_{0.32}Sr_{0.68}Ni_2As_2$ sample. Inset shows heat capacity measurements of the tetragonal-triclinic structural transition in the same crystal specimen. Anomalies associated with the structural transition are observed in heat capacity, showing it is of bulk origin and is strongly first order. (b-d) Magnetization (b), transport (c), and heat capacity (d) measurements show superconducting transitions, observed in the same single crystal. While magnetization and transport signatures suggest a T_c of approximately 2 K, a heat capacity anomaly is only observed near 0.5 K, indicating the bulk superconducting T_c is virtually identical to the BaNi₂As₂ end-member.



Figure 6.7: Superconducting phase diagram of $Ba_{1-x}Sr_xNi_2As_2$, displaying the x dependence of superconducting T_c . The dark blue regions indicate an area of bulk superconductivity in the crystals, while the light blue region is indicative of an area of filamentary superconductivity. Black squares indicate superconducting critical temperatures extracted from resistivity measurements. Red circles indicate superconducting critical temperatures extracted from magnetization measurements. Blue triangles indicate superconducting critical temperatures extracted from heat capacity measurements.

superconductivity at the structural phase boundary is consistent with observations in both the phosphorous [75] and copper [100] substituted BaNi₂As₂ series, and indicates the triclinic transition interferes with the mechanism that produces enhanced superconductivity. The superconducting phase diagram for the Ba_{1-x}Sr_xNi₂As₂ series gathered from transport, magnetic, and thermodynamic experiments is presented in Fig. 6.7.

Finally, Debye temperatures extracted from low temperature heat capacity measurements in $Ba_{1-x}Sr_xNi_2As_2$ crystals show a clear discontinuity when crossing the zero temperature structural phase boundary [Fig. 6.8(c)]. In the oversubstituted samples, the Debye temperature remains effectively constant between x = 0.7 and x = 0.87 before increasing in the SrNi₂As₂ end member. As Fig. 6.8(b) shows, the Sommerfeld coefficient (γ) exhibits little dependence on x across the phase diagram, decreasing modestly between x = 0 and x = 1. Both the Debye temperature and Sommerfeld coefficient are extracted from heat capacity data [Fig. 6.8(a)] using the method discussed in Chapter 2.

6.5 Elastoresistivity

I performed elastoresistivity measurements across the $Ba_{1-x}Sr_xNi_2As_2$ series; investigating the evolving role of electronic degrees of freedom in rotational symmetry breaking. In the case of tetragonal $Ba_{1-x}Sr_xNi_2As_2$, as in the pure $BaNi_2As_2$, there are three symmetry-distinct channels of rotational symmetry breaking, corresponding to the B_{1g} , B_{2g} , and E_g irreducible representations of the D_{4h} point group. The breaking of the crystal symmetry in all three channels at the triclinic transition suggests that one or more of the three nematic susceptibilities $\chi^{B_{1g}}_{nem}$, $\chi^{B_{2g}}_{nem}$, or $\chi^{E_g}_{nem}$ may be diverging above T_S in the Sr substituted $Ba_{1-x}Sr_xNi_2As_2$.

Figures 6.9 and 6.10 show my measurements of the B_{1g} symmetric elastoresistivity in substituted $Ba_{1-x}Sr_xNi_2As_2$ crystals. Figure 6.9 shows a clear suppression in temperature and broadening of the peak in $m_{12} - m_{11}$ elastoresistivity with increasing x. Increasing x beyond x = 0.75 rapidly suppresses $m_{12} - m_{11}$ values, however, which become effectively temperature independent as x approaches 1.

Strain hysteretic resistance indicative of a B_{1g} symmetric electronic nematic order is observed at a temperature T_{nem} that is larger than T_S in lightly substi-



Figure 6.8: (a) C_p/T vs T^2 for several x in the Ba_{1-x}Sr_xNi₂As₂ series are presented. Red (blue) symbols indicate that samples of this concentration favor a triclinic (tetragonal) structure at lowest temperature. Evolution of the Sommerfeld coefficient (b) and Debye temperature (c) are included as a function of x. Dashed vertical line at $x_c = 0.7$ denotes the critical Sr concentration when the system transitions from triclinic to tetragonal crystal symmetries at lowest temperature.



Figure 6.9: B_{1g} symmetric elastoresistivity of $\text{Ba}_{1-x}\text{Sr}_x\text{Ni}_2\text{As}_2$ single crystals with successive vertical offsets applied to the data. The magnitude of the vertical spacing between adjacent data sets is 20. The peaks in the temperature dependent $m_{12} - m_{11}$ curves tracks the triclinic transition temperature for samples with $x < x_c$. Interestingly, this peak broadens but persists in samples with x = 0.75 that feature no structural phase transition.

tuted $Ba_{1-x}Sr_xNi_2As_2$ crystals. This strain hysteretic transport coincides with the emergence of the B_{1g} symmetry breaking I-CDW. The onset of strain-hysteretic behavior at T_{nem} , indicated by the light-gray shaded area in Fig. 6.10, moves closer to the triclinic structural transition T_S , with increasing x, however, and eventually merges with the latter for x = 0.63. Additionally, the modest temperature dependence of $m_{12} - m_{11}$ above T_{nem} observed in stoichiometric $BaNi_2As_2$ (see Chapter 4), is not reflected in more heavily-substituted samples. Indeed, $m_{12} - m_{11}$ starts displaying a diverging behavior above T_{nem} over a wide temperature range in $Ba_{1-x}Sr_xNi_2As_2$ samples with increasing x. These data may be reasonably fit to a modified Curie-Weiss function ($\chi_{nem}^{B_{1g}} = \frac{\lambda}{a_0(T-T_{nem})} + \chi_0$) above T_{nem} (bottom panel in Fig. 6.10), indicating diverging susceptibilities reminiscent of electronically driven nematic order.

Thus, my elastoresistivity data shows a change in the character of the tetragonal symmetry-breaking transition from lattice-driven for small x to electronicallydriven for x near optimal doping. A more detailed discussion of how predictions for such a crossover compare to the observed experimental results is included in Appendix A.

While increasing x promotes a divergence in the B_{1g} nematic susceptibility, the B_{2g} susceptibility is only very weakly temperature dependent in samples with x = 0 and x = 0.63 (Fig. 6.11). The stagnant B_{2g} susceptibility indicates an absence of strengthening electronic nematic fluctuations in the B_{2g} symmetry channel. This contrasts with the structurally related Fe-based superconductors, where ubiquitous signatures of nematicity in the B_{2g} channel are reported [59]. Unfortunately, as



Figure 6.10: Nematic susceptibilities of $\text{Ba}_{1-x}\text{Sr}_x\text{Ni}_2\text{As}_2$ single crystals. Dark grey regions indicate triclinic structural phases in x = 0, 0.40 and 0.63, and light grey regions (only in x = 0 and 0.40) indicate temperatures where elastoresistive hysteresis is observed in the tetragonal structure. Lower panels display the inverse susceptibilities $[(m_{12} - m_{11}) - \chi_0]^{-1}$, truncated at the onset of nematic order. The constant χ_0 is a temperature independent component of the elastoresistance, coming from factors unrelated to nematic order, including changing sample geometry. χ_0 is determined through fitting data to the modified Curie-Weiss functional form; $m_{12} - m_{11} = \lambda/(a_0(T - T_{nem}) + \chi_0)$. Black dashed lines show results of this fitting. No fit is presented for samples with x = 0 or x = 1, as neither of these show Curie-Weiss behavior. The dotted black line in the lower panel of (a) is a guide to the eye, indicating incipient nematic fluctuations in the vicinity of T_{nem} .



Figure 6.11: B_{1g} and B_{2g} symmetric nematic susceptibility for $Ba_{1-x}Sr_xNi_2As_2$ samples with x = 0.63. Data exhibits a Curie-Weiss type divergence in the B_{1g} channel, while B_{2g} symmetric susceptibility does not diverge.

in stoichiometric BaNi₂As₂, sample geometry of as grown $Ba_{1-x}Sr_xNi_2As_2$ crystals does not allow for measurements of the E_g nematic susceptibility.

 $Ba_{1-x}Sr_xNi_2As_2$ specimens of x = 0.75 show a large and diverging $m_{12} - m_{11}$ elastoresistive response, reaching a maximum value of nearly 35. X-ray diffraction measurements show no structural distortion or superstructure reflections between room temperature and 8 K, while transport measurements show no indication of a phase transition [Fig. 6.12(a,b)]. Despite the absence of any apparent transition, $m_{12} - m_{11}$ coefficients display a clear peak and subsequent downturn near 25 K [Fig. 6.12(c)]. Such a nematic susceptibility peak, in the absence of any apparent order, is unprecedented in its observation. However, it may simply be an indication of a freezing *nematic glass*, or possibly an artifact of quenched disorder subverting long-range nematic correlations.

6.6 Analysis

In Fig. 6.13 I present my global phase diagram for the $\text{Ba}_{1-x}\text{Sr}_x\text{Ni}_2\text{As}_2$ system, combining structural order, charge order, nematic susceptibility, and superconducting transition temperatures. As I discussed, structural and C-CDW transition temperatures remain pinned to each other, but decrease in temperature with increasing x until they are suppressed to T = 0 at a critical Sr concentration of $x_c = 0.70$. The I-CDW phase, which has an onset above T_S and is denoted by upright red triangles in Fig. 6.13, is also suppressed with increasing x until it merges with T_S and disappears altogether.

In parallel, superconductivity in $Ba_{1-x}Sr_xNi_2As_2$ single crystals evolves dramatically across the phase diagram [Fig. 6.13(b)]. The "bulk" signature of T_c , as determined by specific heat measurements (c.f. Fig. 6.14), remains relatively constant versus x until it abruptly jumps upon crossing the zero-temperature structural phase boundary, from approximately 0.5 K in x = 0.68 samples to near 3.5 K at x = 0.71. Optimally substituted x = 0.71 presents a very robust superconducting transition as measured by resistivity, diamagnetism, and specific heat anomaly, and is well fit by a single band model with a BCS gap [Fig. 6.14 inset]. Remarkably,



Figure 6.12: Evolution of a and c crystallographic lattice parameters (a), resistivity (b), and elastoresistivity (c) as a function of temperature in optimally substituted $Ba_{1-x}Sr_xNi_2As_2$. While elastoresistivity displays a peak, no sign of an apparent phase transition is observed in either transport or structural measurements.



Figure 6.13: Evolution of structural, charge and nematic orders in $Ba_{1-x}Sr_xNi_2As_2.(a)$ Single-crystal measurements yield a phase diagram showing incommensurate charge-density wave (I-CDW) order (upright red triangles), elastoresistive strain-hysteresis (open black squares), commensurate charge-density wave (C-CDW) order (inverted red triangles), and the cooling transition of the first-order triclinic structural distortion (closed blue circles). Black asterisks mark the peak position of nematic susceptibilities, which extend beyond the disappearance (vertical dashed line) of the triclinic phase at $x_c = 0.70$. The color scale represents interpolated values of the nematic susceptibility $m_{12} - m_{11}$ generated from data taken in $Ba_{1-x}Sr_xNi_2As_2$ single crystals with x = 0, 0.2, 0.4, 0.5, 0.63, 0.75, 0.87, and 1.0. (b) Superconducting transition temperatures T_c in $\operatorname{Ba}_{1-x}\operatorname{Sr}_x\operatorname{Ni}_2\operatorname{As}_2$ single crystals determined by transport (black squares), magnetization (red circles), and heat capacity (blue triangles) measurements. Dark blue shading reflects regions of bulk superconductivity (as confirmed via heat capacity, magnetization and transport transitions) while the light blue region indicates filamentary superconductivity observed as broad transitions in transport and magnetic measurements, but absent in heat capacity.

this optimal T_c of 3.5 K at x = 0.71 marks a nearly sixfold enhancement compared to both the Sr- and Ba-based end members. Moving away from x = 0.71, the superconducting transition decreases continuously with increasing x toward that of SrNi₂As₂, passing through a regime with no notable change in structure or appearance of charge-ordered phases. Moreover, this dramatic change in pairing strength occurs while the Sommerfeld coefficients remains virtually unchanged [Fig. 6.14 main], suggesting that the T_c enhancement cannot be explained by changes in the electronic density of states.

Consistent with prior studies [2,75,100], the Ba_{1-x}Sr_xNi₂As₂ system exhibits a discontinuity in the Debye temperature Θ_D at x_c . However, Θ_D remains approximately constant between x = 0.71 ($\Theta_D = 198$ K) and x = 0.86 ($\Theta_D = 188$ K), despite a nearly two-fold difference in the superconducting T_c . This contrast indicates that, like the electronic density of states, changes in lattice stiffness do not come close to capturing the enhancement in the pairing potential. Rather, the smooth increase in critical temperature upon approaching x_c from above is reminiscent of a fluctuation-driven superconducting enhancement.

Returning to Fig. 6.13, the amplitude of the B_{1g} nematic susceptibility is overlaid with the triclinc and CDW phase boundaries as a color scale. Beginning from the SrNi₂As₂ end member, a smooth enhancement of electronic nematic fluctuations is observed at the lowest temperatures. In stark contrast to the stagnant behavior of other thermodynamic quantities, such as specific heat, dramatic strengthening nematic fluctuations grow concurrently with rapidly enhancing superconducting T_c , with an over ten-fold enhancement of $m_{12} - m_{11}$ from x = 1 to x_c . Having ruled out



Figure 6.14: Heat capacity measurements in over-substituted $Ba_{1-x}Sr_xNi_2As_2$ single crystals with x = 0.71, 0.80, and 0.86 show a dramatic enhancement of T_c . The Debye temperatures and density of states of these samples are all comprable. (inset) The superconducting transition in the same x = 0.71 single-crystal specimen, measured by magnetization (upper panel), electronic heat capacity (center panel), and transport (lower panel) are consistent with a strongly enhanced T_c of 3.5 K, far above the values at either series end member. The dashed line in the heat capacity data indicates the predicted electronic heat capacity anomaly for a single band, s-wave superconductor, with a BCS gap [104].

the usual sources of T_c increase expected for a conventional phonon-mediated superconductor (density of states and Debye frequency), I propose that superconducting enhancement in this system is driven by nematic fluctuations. This conclusion is supported by a decrease in the size of the normalized jump in the electronic heat capacity approaching optimal T_c (Fig. 6.15). This decrease in the magnitude of the superconducting heat capacity signature is consistent with increasingly "hot" and "cold" regions in the superconducting gap structure [60] as the nematic contribution to pairing increases. The strength of this enhancement establishes nematic fluctuations as a promising mechanism for dramatically enhancing Cooper pairing, even in a conventional superconductor such as, presumably, the one studied here.

The origin of nematic order cannot be inferred solely from elastoresistance measurements. In the structurally and chemically similar BaFe₂As₂ compounds, the B_{2g} electronic nematic order has been proposed to be driven by magnetic degrees of freedom, since the stripe magnetic ground state breaks the tetragonal symmetry in the same channel [109–111]. The Ba_{1-x}Sr_xNi₂As₂ series, in contrast, exhibits no known magnetic order. However, it does exhibit unidirectional CDW order that also breaks the tetragonal symmetry in the B_{1g} channel. It is therefore tempting to attribute the nematic instability in Ba_{1-x}Sr_xNi₂As₂ to charge fluctuations. This provides a compelling scenario to explain the phase diagram of Ba_{1-x}Sr_xNi₂As₂ in terms of two cooperative ordered states: a charge-driven electronic nematic phase and a lattice-driven triclinic phase. While both break the tetragonal symmetry in the B_{1g} channel, the latter also breaks additional symmetries. The elastoresistance measurements show that the symmetry breaking in the triclinic phase cannot be



Figure 6.15: Plot of normalized electronic heat capacity measurements $C_e/\gamma T$ vs T^2 for slightly over-substituted Ba_{1-x}Sr_xNi₂As₂ single crystals with x = 0.71, 0.80, and 0.86. Approaching the optimal substitution, the size of the normalized heat capacity jump is seen to decrease.

accounted for solely by electronic degrees of freedom, as evidenced by the lack of divergence of the B_{2g} nematic susceptibility.

6.7 Conclusion

In this chapter I describe my characterization of $Ba_{1-x}Sr_xNi_2As_2$ single crystals. Like the $Ba(Ni_{1-x}Co_x)_2As_2$ series presented in Chapter 5, $Ba_{1-x}Sr_xNi_2As_2$ single crystals exhibit a large superconducting enhancement near the zero temperature tetragonal-triclinic structural phase boundary. This superconducting enhancement does not appear to be explained by obvious changes in the Debye temperature or the electronic density of states.

I measured the B_{1g} and B_{2g} symmetric elastoresistivity in $Ba_{1-x}Sr_xNi_2As_2$ single crystals of varying x and observed an increasingly divergent B_{1g} symmetric nematic susceptibility with increasing x. A large nematic susceptibility persists into heavily substituted samples that exhibit no tetragonal-triclinic structural phase transition. Due to the coexistence of enhanced T_c and a large nematic susceptibility ity at optimal substitution I propose that the superconducting enhancement in this system is due to coupling to strong nematic fluctuations as has been proposed in Refs. [60–64].

Chapter 7: Conclusions

7.1 Summary of Main Results

In this thesis I described my studies of the nickel-pnictide superconducting compound BaNi₂As₂. The crystals used to conduct these studies were synthesized in CNAM, and the vast majority of physical characterization was similarly conducted at the University of Maryland. The structural and superconducting phase diagrams were constructed for both $Ba_{1-x}Sr_xNi_2As_2$ and $Ba(Ni_{1-x}Co_x)_2As_2$ substituted variants of parent $BaNi_2As_2$. Furthermore, careful characterization of the electronic nematic properties of the $Ba_{1-x}Sr_xNi_2As_2$ system was performed.

My work began with a more careful investigation of the BaNi₂As₂ parent compound. This involved growing single crystals and providing them to collaborators at the University of Illinois for the performance of variable temperature single crystal x-ray diffraction measurements. I also performed elastoresistivity measurements to characterize the nematic character of BaNi₂As₂. Through these studies, I determined that a structurally driven B_{1g} symmetry breaking order manifests in BaNi₂As₂ at a temperature T_{nem} that is higher than the structural transition temperature. This symmetry breaking transition was driven by the formation of long range and unidirectional CDW order incommensurate with the tetragonal unit cell propagating with wave vector $(0.28 \ 0 \ 0)_{tet}$. Charge order appears to drive a concurrent electronic nematic order, as determined by a linear scaling between the symmetry coupled CDW order parameter and nematic order parameter.

The electronic and structural behavior of the Ba(Ni_{1-x}Co_x)₂As₂ series was then examined. In order to construct the structural and electronic phase diagram for this system, single crystals were synthesized from Pb flux, and characterized through a combination of four-terminal electrical transport, *ac* magnetic susceptibility, heat capacity measurements, and x-ray scattering studies. I observed a smooth suppression of the tetragonal-triclinic of the BaNi₂As₂ compound, terminating near the 10% replacement of Co for Ni. A strong enhancement in superconducting T_c was observed, with a maximum T_c at the zero temperature structural phase transition. T_c diminished rapidly away from optimal substitution. Near optimal substitution a small decrease in Debye temperature was observed, although neither this change, nor monotonically evolving DOS calculated through supercell calculations appear to capture the increased pairing. Rather, this enhancement in T_c from 0.7 to 2.3 K forms a continuous dome in the temperature-substitution phase diagram, suggestive of some other mechanism causing enhanced pairing.

Finally, I synthesized $Ba_{1-x}Sr_xNi_2As_2$ single crystals using NiAs self-flux and examined their material properties. Through a combination of electrical transport, heat capacity, dc and ac magnetization, and variable temperature x-ray diffraction measurements, I constructed the global phase diagram for this series. Additionally, B_{1g} and B_{2g} symmetric electronic nematic susceptibilities were measured across the phase diagram. Increasing Sr content produced a strengthening B_{1g} nematic susceptibility, well fit by a modified Curie-Weiss model. This strengthened nematic susceptibility persists into heavily substituted samples wherein no tetragonal-triclinic transition is observed. Concurrently, when the triclinic transition temperature is tuned to absolute zero, a sixfold enhancement of superconducting T_c is observed. This strengthened pairing appears to originate from coupling to strengthened electronic nematic fluctuations emanating from the tuned quantum phase transition.

Overall my results represents a re-examination of the BaNi₂As₂ compound, uncovering previously unreported charge order and nematic phases. I argue that BaNi₂As₂ represents an interesting model system, wherein the interaction of phases crucial to numerous high T_c compounds may be explored in the absence of magnetism and unconventional Cooper pairing.

7.2 Future Work

My results in $BaNi_2As_2$ raise several questions that are worth further exploration.

First, theoretical predictions of nematic fluctuation enhanced superconductivity suggest the emergence of hot and cold spots along the superconducting gap as a consequence of the symmetry of the nematic fluctuations [60]. A comprehensive study of the superconducting gap structure across the $Ba_{1-x}Sr_xNi_2As_2$ phase diagram, or, in particular the over-substituted regime, could provide important experimental insight into the degree with which nematic fluctuations may be distorting the superconducting gap structure. This may be performed most readily in thermodynamic experiments such as thermal conductivity and heat capacity measurements, but one may also expect signatures of increasing gap anisotropy to manifest in tunneling measurements as well as quasi-particle interference experiments.

Additionally, one of the most notable outstanding experimental mysteries is the I-CDW emerging in the tetragonal phase of pristine $BaNi_2As_2$. The absence of an induced orthorhombicity despite C_4 symmetry breaking charge order should not be allowed due to symmetry. It is currently assumed that a very slight orthorhombicity is indeed induced in the region of I-CDW, and this distortion is simply below the resolution of the experimental apparatus. If this suspicion is true, diffraction experiments conducted on specimens mounted to an *in-situ* tunable strain apparatus should prove the I-CDW is extremely sensitive to applied strain. Beyond the novelty of a readily strain tuned charge order, such experiments would play a crucial role in confirming or disproving the current understanding of the intertwining charge and nematic order in $BaNi_2As_2$.

Appendix A: Ginzburg-Landau Model of $Ba_{1-x}Sr_xNi_2As_2$ Series

The observed crossover between structural and electronically driven nematicity in $Ba_{1-x}Sr_xNi_2As_2$ is apparently unlike any other previously reported system. In this Appendix I discuss a simple model for this crossover and show that the experimental results are consistent with the predictions of this model. This model was developed by Dr. Morten Christensen and Dr. Rafael Fernandes at the University of Minnesota.

To explain the crossover between structurally and electronically driven symmetry breaking in $Ba_{1-x}Sr_xNi_2As_2$, I write the free energy expansion for the generic nematic system as:

$$\mathcal{F}(\psi_{\Gamma_i}, \epsilon_{\Gamma_i}) \approx F_0 + \frac{a_n}{2}\psi_{\Gamma_i}^2 + \frac{b_n}{4}\psi_{\Gamma_i}^4 + \frac{a_s}{2}\epsilon_{\Gamma_i}^2 + \frac{b_s}{4}\epsilon_{\Gamma_i}^4 - \lambda\psi_{\Gamma_i}\epsilon_{\Gamma_i}$$
(A.1)

Motivated by the experimental results, I introduce an instability in both the structural and electronic channels by assigning the following temperature dependencies to a_n and a_s :

$$a_n = a_{n0} \left(T - T_{nem} \right)$$

 $a_s = a_{s0} (T - T_S)$ (A.2)

where, for simplicity, $a_{n0} = a_{s0} = 1$ and where T_{nem} and T_S , meanwhile, represent the temperatures at which the bare electronic and structural systems become unstable

to rotational symmetry breaking.

A lattice driven structural transition is observed if $T_{nem} \ll T_S$, while an electronically driven transition is observed if $T_S \ll T_{nem}$. Motivated by the chemical substitution induced crossover observed in the physical system (see Chapter 6) I assume:

$$T_{nem} = T_0 (1 + \delta)$$

$$T_S = T_0 (1 - \delta)$$
(A.3)

where δ represents a system tuning parameter, such as chemical substitution.

The structural phase diagram generated from this model is shown in Fig. A.1. Although the theoretical phase diagram doesn't capture the behavior of the $Ba_{1-x}Sr_xNi_2As_2$ system, the predicted nematic susceptibility provided in Fig. A.2 is consistent with the elastoresistivity experiments.

Examining Fig. A.2, we see that increasing δ induces a crossover between weakly and strongly diverging susceptibilities. This is consistent with the observed x dependence of the nematic susceptibility of the Ba_{1-x}Sr_xNi₂As₂ series (Fig. 6.10). This supports the notion that the system features B_{1g} symmetry breaking instabilities of both electronic and structural origin. Increasing x suppresses the bare structural transition temperature more rapidly than the bare electronic transition temperature, promoting an increasingly divergent electronic nematic susceptibility.



Figure A.1: Simulated phase diagram for the coupled structural-nematic transition. The symmetry breaking transition temperature for the system (solid line) is shown as a function of temperature and the "substitution" parameter δ . The dashed lines represent the bare electronic and structural transition temperatures T_{nem} and T_S . The curve is generated using a structural-nematic coupling of $\lambda = 0.10$ in Eqn. A.1. For $\lambda = 0$, the transition temperature is given by the dashed lines.



Figure A.2: Simulated nematic susceptibility in structurally-driven ($\delta < 0$) and electronically-driven ($\delta > 0$) regimes. Here δ ranges from $\delta = -0.20$ to $\delta = 0.20$. A sharp peak is evident in the electronically driven case. These curves are generated using a structural-nematic coupling of $\lambda = 0.10$ in Eqn. A.1.

List of Growths

Throughout the course of my research, I synthesized a number of different materials unrelated to BaNi₂As₂. A comprehensive list of materials I have synthesized (or attempted to synthesize) is provided below.

Target Material	Growth Notes	Result	Material Notes
CeCoIn ₅	In self-flux growth	Synthesized single crystals	Superconductor, $T_c=2.3$ K
YbCoGa ₅	Ga self-flux growth	Unsuccessful	
$CeCo_{1-x}Fe_xIn_5$	In self-flux growth $(x=0.01, 0.03)$	Synthesized $CeCoIn_5$ single crystals	Superconductor, $T_c=2.3$ K
$CeFeIn_5$	Pb flux growth	Unsuccessful	
$CeNiIn_5$	Pb flux growth	Unsuccessful	
$CeCo_{1-x}Ni_xIn_5$	In self-flux growth $(x=0.01, 0.03)$	Synthesized $CeCoIn_5$ single crystals	Superconductor, $T_c=2.3$ K
$\operatorname{Ce}_{1-x}\operatorname{Yb}_{x}\operatorname{CoIn}_{5}$	In self-flux growth $(x=0.2, 0.3, 0.4)$	Synthesized single crystals	Superconductor
$\mathrm{Ba}(\mathrm{Fe}_{1-x}\mathrm{Co}_x)_2\mathrm{As}_2$	(Fe,Co)As self-flux growth $(x=0, 0.08)$	Synthesized single crystals	Superconductor, $T_c=20$ K
$\operatorname{Ba}_{1-x}\operatorname{Sr}_x\operatorname{Ni}_2\operatorname{As}_2$	Pb flux growth $(x=0.1, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8)$	Synthesized single crystals	Superconductor, maximum $T_c=3.5$ K
$\mathrm{Ba}_{1-x}\mathrm{Sr}_x\mathrm{Ni}_2\mathrm{As}_2$	NiAsself-fluxgrowth $(x=0, 0.1, 0.2, 0.3, 0.33, 0.36, 0.4, 0.425, 0.45, 0.475, 0.5, 0.53, 0.475, 0.5, 0.53, 0.56, 0.6, 0.7, 1)$	Synthesized single crystals	Superconductor, maximum $T_c=3.5$ K

$\mathrm{Ba}(\mathrm{Ni}_{1-x}\mathrm{Co}_x)_2\mathrm{As}_2$	$\begin{array}{llllllllllllllllllllllllllllllllllll$	Synthesized single crystals	Superconductor, maximum T_c =3.5 K
$BaFeNiAs_2$	(Fe,Ni)As self-flux growth	Synthesized single crystals	Non Fermi liquid behavior
${\rm Ba}({\rm Fe}_{1/3}{\rm Ni}_{1/3}{\rm Co}_{1/3})_2{\rm As}_2$	(Fe,Ni,Co)As self- flux growth	Synthesized single crystals	Non Fermi liquid behavior
${\rm Ba}({\rm Cr}_{1/3}{\rm Ni}_{1/3}{\rm Co}_{1/3})_2{\rm As}_2$	(Cr,Ni,Co)As self- flux growth	Synthesized single crystals	Non Fermi liquid behavior
$BaFe_2Bi_2$	Al flux growth	Unsuccessful	
$BaFe_2Bi_2$	Sn flux growth	Unsuccessful	
$CaFe_2Bi_2$	Sn flux growth	Unsuccessful	
$SrFe_2Bi_2$	Sn flux growth	Unsuccessful	
$BaCo_2As_2$	CoAs self-flux growth	Synthesized single crystals	Proximate to fer- romagnetism
$CaNi_2Ge_2$	Pb flux growth	Unsuccessful	
FeAs	Sn flux growth	Synthesized single crystals	SDW, $\mathrm{T}_{N}{=}70~\mathrm{K}$
$\operatorname{Fe}_{1-x}\operatorname{Co}_x\operatorname{As}$	Sn flux growth (x=0.1)	Synthesized single crystals	
Ce_2InSi_2	In self-flux growth	Unsuccessful	
CeAlSi	Al self-flux growth	Synthesized single crystals	Ferromagnet

CeAlSi	In flux growth	Synthesized single crystals	Ferromagnet
CeAlGe	Al self-flux growth	Synthesized single crystals	Antiferromagnet
CeAlGe	In flux growth	Synthesized single crystals	Antiferromagnet
LaAlGe	Al self-flux growth	Synthesized single crystals	Superconductor, $T_c=0.7$ K
LaAlGe	In flux growth	Synthesized single crystals	Superconductor, $T_c=0.9$ K
$YbBi_2$	Bi self-flux growth	Unsuccessful	
$YbPb_2$	Pb self-flux growth	Unsuccessful	
YbAu ₂	Pb flux growth	Synthesized single crystals	Several low tem- perature (presum- ably magnetic) transitions
LuAu ₂	Pb flux growth	Unsuccessful	Several low tem- perature (presum- ably magnetic) transitions
$CeAuBi_2$	Bi self-flux growth	Synthesized single crystals	Antiferromagnet, $T_N=12 \text{ K}$
$Ce_3Au_3Bi_4$	Pb flux growth	Unsuccessful	
$Ce_{1-x}La_xAuBi_2$	Bi self-flux growth $(x=0.25, 0.5)$	Synthesized single crystals	
$LaAuBi_2$	Solid state reaction	Unsuccessful	
$CeAu_2In$	Zn flux growth	Unsuccessful	

$\mathrm{Sb}_{2}\mathrm{Te}_{3}$	Te self-flux growth	Synthesized single crystals	Topological lator	Insu-
$\mathrm{Bi}_2\mathrm{Se}_3$	Se self-flux growth	Synthesized single crystals	Topological lator	Insu-

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