

Studies Of Strongly Correlated Electron Systems Using Neutron Scattering

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"It's not what you gather but what you scatter that tells you what kind of life you have lived."

- Helen Walton

Abstract

The world presents many natural and man-made crises and challenges that require scientific solutions. Condensed matter physics is one of the most influential and solution oriented disciplines in science. The field saw a significant rise in popularity especially during the past century as mankind enters the Information Age, when energy and computing related technologies become ubiquitous. This technological progress has been driven by efforts from scientists and engineers, through the synthesis, understanding, and implementation of new materials. Condensed matter physicists strive to solve puzzles at the frontier of material research. In the 21st century we have many advance tools at our disposal to help evaluate and solve these puzzles. For this thesis we focus on the forefront techniques of neutron scattering, along with other experimental methods to explore three frontier problems in condensed matter physics. The first problem is the investigation of phase transitions in Ru/Fe [Ruthenium/Iron] substituted PrFeAsO [Praseodymium Iron Arsenic Oxide]. PrFeAsO belongs to the 1111 family of iron pnictides, in which superconductivity can usually be induced by suppressing the magnetic and structural transitions via carrier doping. We have used neutron powder diffraction to investigate the effect of isoelectronic substitution on these transitions in PrFeAsO. Second is the study of the helimagnetic ordering in Cr [Chromium] doped FeGe [Iron Germanide]. Both CrGe [Chromium Germanide] and FeGe are in the B20 cubic structure, where CrGe exhibits no long range magnetic order down to at least 2 K, FeGe orders helimagnetically at 280 K with a periodicity of 700 Angstroms. We use small

angle neutron scattering to study the Cr doping dependence of helimagnetism in FeGe. Finally, we examine the lattice dynamics in rocksalt structure compounds UC [Uranium Carbide] and US [Uranium Sulfide]. A recent inelastic neutron scattering experiment revealed quantum harmonic oscillator behavior of N [Nitrogen] atoms in UN [Uranium Nitride]. We deduce that other uranium rocksalts should also exhibit such behaviors. We use inelastic neutron scattering to extend the study on quantum harmonic oscillations in uranium rock salts.

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Chapter 1

Introduction

Throughout the history of mankind, from the invention of the Internet all the way back to the agricultural revolution, we, the human race, have been defined by our ability to learn, and to teach, to adapt, and to create. Be it driven by our survival instinct, our yearn for the general betterment of the future, or by pure curiosity, we have been able to identify or even invent problems and solutions, all for the continuous progress towards a better tomorrow. Today, we stand atop the shoulders of giants, with thousands of years of knowledge gifted to us from our ancestors. However the world is constantly changing and evolving, and with every passing second, new scenarios present themselves that demand new solutions.

Nowadays, scientific research is undertaken by a relative few and funded by the masses, and as a result, scientists and perhaps science in general have the duty to direct research towards the interest of the public. Time and time again, problems and challenges present themselves in the form of crises, for example global warming, overpopulation, new diseases, etc. The problems, often complex and multifaceted, can usually be broken down into smaller and more focused topics. Given this specific quality of forefront problems in science, the rest of this introduction will be dedicated to providing the necessary contexts for the research topics presented in this thesis, hopefully enough for the more casual readers to relate to.

At the forefront of condensed matter physics research is the study of materials, may it be materials that are abundant in nature, or ones that are artificially synthesized. The purpose of condensed matter physics is to understand the properties of these materials, particularly materials that have foreseeable applications, i.e. those that may lead to significant technological advances. Today some of the hottest research topics are related to energy generation and distribution, and digital storage and processing. Throughout this introduction we will provide segues from a broader point of view down to the more focused research topics .

1.1 Understanding the high T_C iron-based superconductors

Superconductivity was first discovered in 1911 by Kamerlingh Onnes in mercury, of which the resistance becomes zero below 4.2 K (1). Efforts to understand this newly discovered phenomenon immediately followed suit, and eventually led to the Ginzburg-Landau theory in 1950 and the BCS theory in 1957 by Bardeen, Cooper, and Schrieffer (1; 2). However, the theoretical limit for superconducting temperature T_C at the time was understood to be about 30 K (1; 2), far too low to be considered for most practical applications.

During the latter years of the 1980's, a series of copper containing compounds subsequently coined "cuprates" were found to have superconducting temperatures well above the formerly predicted limit. The first among the cuprates, Ba-La-Cu-O has a T_C of 35 K, was discovered by Bednorz and Müller in 1986 (3). During the following year, the highest T_C was quickly raised to 93 K in Yttrium Barium Copper Oxide, now commonly known as YBCO (4). Since the discovery of YBCO and other materials that superconduct at temperatures higher than the boiling point of liquid nitrogen (77 K), many applications using superconductors became economically and technologically feasible. Superconducting magnets and Superconducting Quantum

Interference Devices (SQUIDS) used in medical and scientific instruments are among some of these applications.

In 2008, a new group of high T_C superconductors was discovered, this time with iron being the common ingredient instead of copper (5; 6). This group of materials is now commonly referred to as “iron based superconductors” or “iron pnictides”. Following the discovery the scientific community dedicated much effort to study and decipher the laws that govern high temperature superconductivity in these materials. One of the main goals of the study of superconductivity is the hope to achieve a material that superconducts at room temperature. A room temperature superconductor will have an enormous impact on the modern world, from the design of power grids, to local power storage, to other applications such as magnetic levitation and magnetic refrigeration (7). The first sensible step for the rest of the journey to such a goal is to systematically investigate and understand the available superconducting materials, to take in and digest the data that has been freshly prepared and catered to us. For this, we study ties between multiple phase transitions and superconductivity for one member of the iron pnictide family, PrFeAsO . We focus on the structural and magnetic phase transitions found in Ru/Fe substituted $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$, and the reason behind the lack of expected superconductivity in the doped series. Systematic studies on the material are carried out using neutron powder diffraction, magnetic neutron diffraction, and accompanied by heat capacity and magnetic susceptibility measurements.

1.2 Synthesizing and characterizing skyrmionic materials

The computer is arguably the most important technological innovation in the past century. The perhaps self fulfilling prophecy of exponential advancement of computers over the past few decades is now famously known as Moore’s law (8). This exponential

advancement of computers is made possible through the constant research and development invested by both the public and private sector. In order to continue progress at this rate, the ongoing development in science and technology related to this field is essential.

This brings us to the forefront of computer storage and processing related technologies. Spintronics, a new technology that exploits the ability to manipulate magnetic moments through external magnetic fields as well as electrical fields, have shown promising capabilities that consistently outperform existing technologies. Skyrmions are 2D topological magnetic objects that form under certain temperature and magnetic field range in certain materials. The size of a skyrmion is in the order of nanometers and therefore making it an ideal candidate for spintronic data storage devices. Scientists are in the progress of learning how to manipulate, create, and eliminate skyrmions. Recent advancement such as an article published in 2013, titled “Writing and Deleting Single Magnetic Skyrmions” is one of the examples (9).

One group of materials where skyrmions can be induced, are the B20 cubic crystals, which includes MnSi, MnGe, FeSi, and FeGe. The skyrmions and other magnetic structures in these compounds originates from the lack of inversion symmetry in the crystal structure. We chose to study the helimagnetic behavior of Cr doped $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$, which also originates from the lack of inversion symmetry and is largely related to the existence of skyrmions.

1.3 Dynamics of next generation nuclear fuel Uranium rocksalts

The energy crisis of today can be attributed to many different factors, for example the unpredictable oil prices, the lack of non-fossil fuel based energy sources, etc. It is clear that something must be done in order to satisfy our ever increasing demand for

energy. According to data published by the U.S. Energy Information Administration (EIA) in 2012, more than 80% of the world’s energy is still being generated by fossil fuel (10). It is apparent that many of the energy related problems can be alleviated if cheaper and more reliable alternative energy sources are available.

One obvious candidate for non-fossil fuel based energy is nuclear power. Though not a sustainable source in theory, nuclear fuel is abundant enough to last for hundreds, if not thousands of years at the current consumption rate (11). With the limitations of other alternative energy sources, such as the relatively infancy of solar energy, or the geological restrictions of wind energy and hydroelectricity, nuclear energy can help bridging the gap between fossil fuels and alternative energy sources of the future. Indeed newer and better designs of nuclear power plants are constantly being researched. The research and designing of the next generation nuclear power plant, known as “Generation IV reactors”, focuses on cost effectiveness, safety, minimal waste, among other improvements over the plants of today (12).

Some members of uranium rocksalts are among the proposed candidates as high temperature fuel for the Generation IV reactors (13; 14). In 2009, Ref. (15) observed a series of even spaced energy modes in UN by neutron scattering. In addition to the obvious practical need to understand the dynamics of a potential nuclear fuel, the discovery is also scientifically intriguing. The even spaced energy modes observed is perhaps the best physical realization of a quantum harmonic oscillator (QHO) to our knowledge. In this thesis, we extend the investigation to other members from the uranium rocksalt family, UC, and US, mainly focus on the behavior of the QHO modes. The main tool used for this investigation is inelastic neutron scattering. The results will be presented and interpreted with the help of a well established model for a 3D QHO.

Chapter 2

Experimental Techniques

The step-by-step process in experimental Condensed Matter Physics is straightforward: (1) Obtain a physical sample of the material of interest; (2) Perform measurements on the sample; (3) Analyze and understand the data. However each of these steps is by no means straightforward itself. In this chapter we will provide some background on the first two steps relating to the research projects in this thesis, with emphasis on the second step: the experimental measurements. Although both steps are technically experimental technique, the sample synthesis for each of the studied materials are largely specific to each material and perhaps best left to be explained during each of its respective chapters. On the other hand since there are significant overlaps among the measurement methods used in each of the projects, this chapter will provide a background for the measurement techniques.

Various experimental measurements were performed for the research of this thesis, including heat capacity and magnetic susceptibility measurements, x-ray diffraction, muon spin spectroscopy, and various techniques of neutron scattering, which includes neutron powder diffraction, inelastic neutron scattering, and small angle neutron scattering experiments.

2.1 Preparation of samples

No scientific study can be possible without a subject of interest. In order to perform research in experimental condensed matter physics, a physical subject is almost always necessary. While many compounds can be readily purchased from chemical manufacturers such as Alfa Aesar or Sigma-Aldrich, more often than not scientists have to synthesize the materials themselves. This is expected since much of the frontier of condensed matter physics involve studying newly discovered materials, sometimes even with the synthesis of the material being the focus itself.

There are numerous methods of sample preparations, such as synthesis processes for single crystals like the Bridgman method (16), or the vapor transfer method (17), or synthesis processes for polycrystals that involve ball milling, or annealing, or arc melting, or processes for preparing nano-materials, or different methods of etching and purifying a certain compound from a mixture with contaminants. Each of these methods is unique to the specific material of interest. Due to the multi-subject nature of this thesis, multiple distinctive methods of sample synthesis were used. Detailed information regarding the preparation process for each of the materials is located under each material's respective chapter. Reader can refer to the sample description section under each chapter for more details.

2.2 Bulk properties characterizations

After one has acquire a piece of the sample, the next step is to perform simple and relatively quick measurements on the sample, for a number of reasons. If certain properties of the material is known, for example a para-ferromagnetic phase transition that occurs at a certain temperature, a quick magnetic susceptibility measurement can reveal the authenticity and the quality of the sample. On the other hand, if very little property is known about the sample, the same measurement may then reveal features at a certain temperature or magnetic field range, which can be then used for

the planning of further, perhaps more sophisticated and time consuming experiments, such as neutron scattering experiments at a large scale facility.

Some of the said “simple and relatively fast” measurements have been made easier and more user friendly by the advancement of lab instrument in recent decades. Manufacturers such as Quantum Design, Inc. sell prepackaged products such as the Physical Properties Measurement System (PPMSTM) and the Magnetic Properties Measurement System (MPMSTM) that enable users to perform temperature and field dependence measurements through programmable software interfaces. Properties characterization such as the temperature and field dependence of resistivity, magnetization, and heat capacity, are some of the measurements that can be done with these instruments.

2.2.1 Magnetic susceptibility

Magnetic susceptibility is the response in magnetization of a material due to an applied magnetic field. Magnetic susceptibility measurements reveal important information about the material, such as the temperature and field required for a magnetic phase transition to occur in the material. It is extremely rewarding to explore the magnetic phase diagram for an unknown material. Magnetic susceptibility measurements provide basic magnetic information about the material, reveal areas of interest near certain fields and temperatures. For instance the Curie-Weiss’s law states that the temperature dependent magnetization of a paramagnetic material obeys the following equation (1).

$$\chi = \frac{M}{H} = \frac{M\mu_0}{B} = \frac{C}{T} \quad (2.1)$$

Here M is the magnetization of the material; μ_0 is the permeability of free space ; $B = \mu_0 H$ is the magnetic field; C is the Curie constant of the material; and T is the temperature of the sample environment.

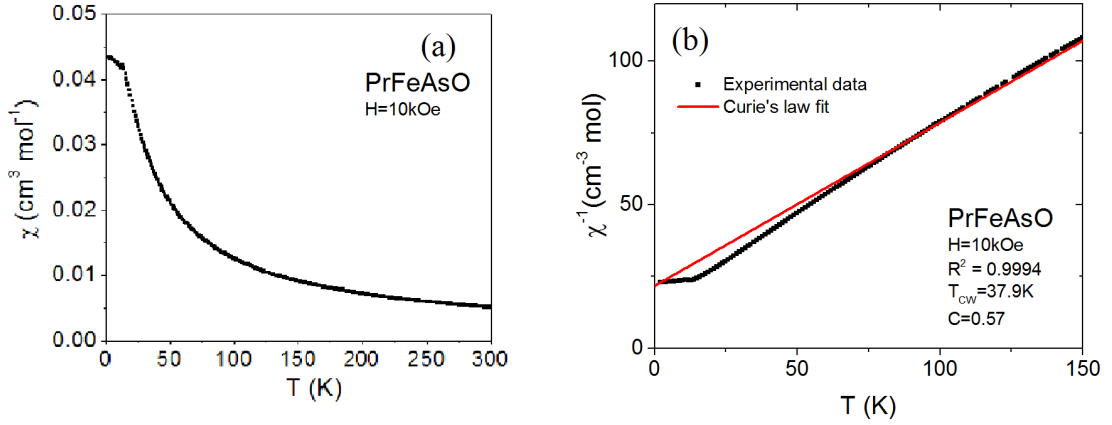


Figure 2.1: An example of temperature dependent magnetic susceptibility, collected for PrFeAsO, unpublished data.

For completion the total magnetic field has to be modified to include the Weiss field λM , so that the total magnetic field is $B + \lambda M$, and the last part of the last equation becomes the following (1).

$$\chi = \frac{M\mu_0}{B + \lambda M} = \frac{C}{T - T_C} \quad (2.2)$$

A simple linear fit can be easily done to a temperature dependent magnetic susceptibility dataset using this equation, and any deviation from the fit hints at a magnetic transition away from the paramagnetic state.

Fig.2.1(a) shows the temperature dependent magnetic susceptibility for PrFeAsO and (b) shows the inversed magnetic susceptibility from the same dataset. A simple linear fit is shown in Fig.2.1(b) as an example of the data analysis process described above, for which the Curie constant C and the Curie-Weiss temperature T_{CW} is determined to be 0.57 and 37.9K respectively. The data deviates from the linear fit around 70K, followed by an upturn around 14K. These features are later found to be indications of the critical fluctuation of the Pr magnetic moment, followed by the anti-ferromagnetic ordering of the Pr moment at 14K. The data presented here are

original unpublished work done during the $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ project. However, similar data can be found in Ref.(18).

2.2.2 Specific heat

Specific heat is another material property that can be measured relatively quickly. Specific heat measurements provide information about the lattice, electronic, and magnetic properties of a system. It is also one of the properties that can be compared rather directly to a theoretical model. Important magnetic information can be revealed if one can separate the lattice and electronic contribution from the magnetic contribution of the specific heat. The lattice specific heat at low enough temperature is proportional to T^3 , known as the Debye T^3 law, and the contribution from conduction electrons at low temperatures is proportional to T (1). As a result one can fit the measured specific heat of a metal to a function proportional to T and T^3 , such as $C = \lambda T + AT^3$, then subtract the fitted function from the overall specific heat to obtain the magnetic specific heat. The magnetic specific heat can then be used to calculate for the entropy of the interacting spins. This can be done by integrating the specific heat from 0 K, and the resulted value should approach the limit of $Nk_B \ln(2J + 1)$ at high enough temperature. (N is the Avogadro's number, k_B is the Boltzmann's constant, J is the total angular momentum.) Reader may refer to chapter 3 for an example of this exercise.

2.3 Neutron scattering

Neutron is a very useful probe for the investigations of materials. Since neutrons do not possess any electric charge, they can penetrate deep into a sample and interact with the internal environment of a physical system. Neutrons also possess an intrinsic magnetic moment of spin-1/2, as a result neutron scattering is capable of extracting not just structural and dynamical, but also magnetic information of materials. Much

Table 2.1: Neutron experiments performed for the each of the material reported in this thesis. NPD/MNS: Neutron powder diffraction/ Magnetic neutron diffraction; INS: Inelastic neutron scattering; SANS: Small angle neutron scattering.

	NPD/MNS	INS	SANS
PrFe _{1-x} Ru _x AsO	✓		
Fe _{1-x} Cr _x Ge	✓		✓
US/UC		✓	

of the fundamental techniques in neutron scattering were developed during the 40's through the 60's, notably by separate efforts led by Bertram Neville Brockhouse at Canada's Chalk River Nuclear Laboratory, and Clifford Shull at Oak Ridge National Laboratory. The two scientists shared the Nobel Prize in Physics of 1994 for "pioneering contributions to the development of neutron scattering techniques for studies of condensed matter" (19).

There are numerous neutron scattering instruments and facilities around the world, each designed to focus on a specific technique. These techniques can generally be divided into two main categories, elastic neutron scattering and inelastic neutron scattering. Elastic neutron scattering, as described by its name, focuses on the detection and analysis of neutrons elastically scattering by the sample. In elastic neutron scattering, neutrons are scattered by the nuclei of atoms or interactions with the magnetic moments of free electrons. In crystals where a regular lattice structure is present, the scattered angle and intensity of the neutrons can be modeled using existing theories to determine the lattice and magnetic structure of the material. Inelastic neutron scattering on the other hand, studies neutrons that are inelastically scattered by the sample. This technique reveals dynamical properties of the sample, such as phonon and magnon excitations. More details about the two techniques will be discussed during each topic's respectively sections below.

In the following sections we will focus on neutron scattering techniques that are relevant to the work reported in this thesis. Brief background and theory will be provided for each technique. Table 2.1 lists the neutron experiments performed on each material.

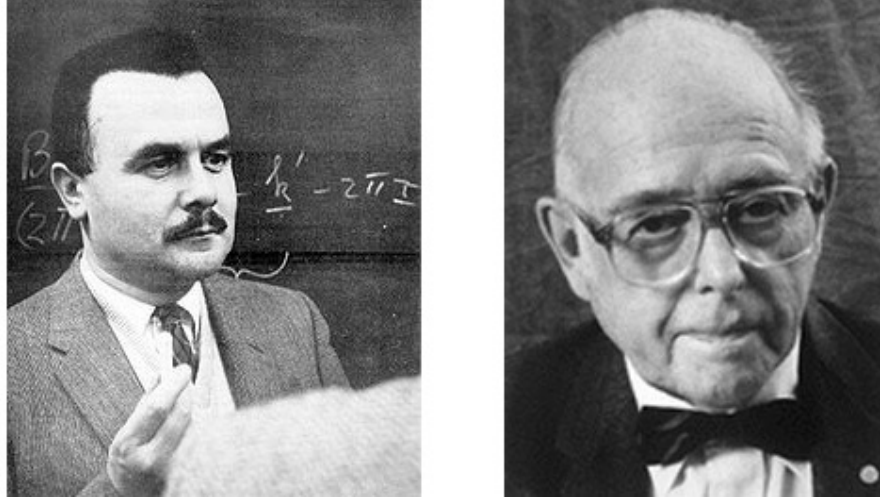


Figure 2.2: Bertram Neville Brockhouse (1918-2003) and Clifford Shull (1915-2001).

2.3.1 Elastic neutron scattering

Elastic neutron scattering, as described by its name, considers only elastically scattered neutrons, i.e. $|k_i| = |k_f|$. Shown in Fig.2.3 is the neutron diffraction pattern taken by Shull and Wollan for NaCl in 1946. Each of the peaks' position (2θ), intensity and width contains important information about the measured material.

Bragg's law relates the deflected angle 2θ of an elastically scattered wave on a crystalline material to the inter-planar distance d of the scattering plane by the following expression (1).

$$d = \frac{\lambda}{2\sin\theta} \quad (2.3)$$

Fig.5.4 is a geometric illustration of Bragg's law. The black horizontal lines represent the scattering planes formed by layers of atoms in the crystal. Therefore, by knowing the wavelength λ of the incoming neutrons, and measuring the 2θ of a series of individual peaks, one can determine inter-planar distances d between the layers. Together with the correct crystal structure, and Miller indices for each peak, one can refine the structural parameters of the measured crystal. For example, for

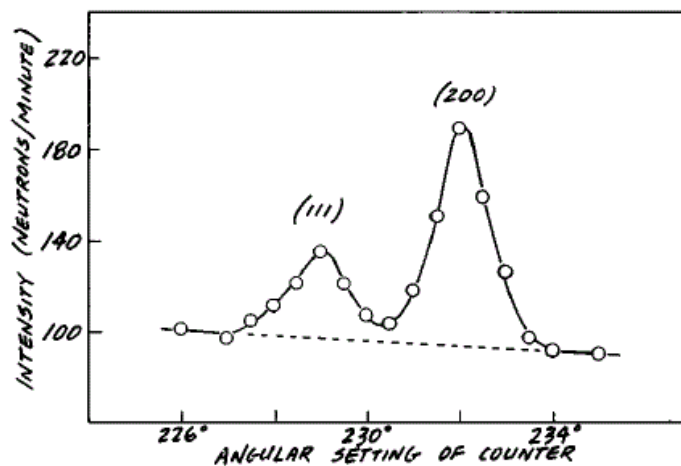


Figure 2.3: Portion of the first powder-diffraction pattern of NaCl taken at the Clinton Pile in Oak Ridge during the early months of 1946. The experiment was an effort led by Ernest O. Wollan and Clifford Shull. This graph is taken from Ref. [20](#).

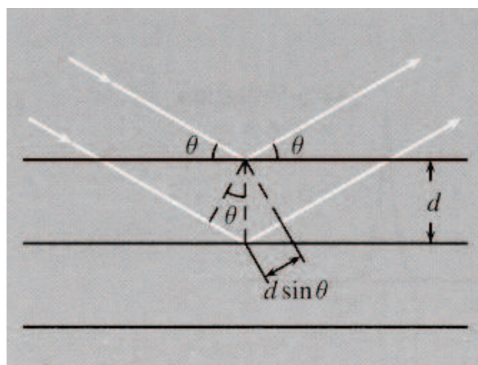


Figure 2.4: Shown here is a simple geometric diagram illustrating Bragg's law. The angle between the incident and scattered beam is 2θ . (Diagram taken from Ref. [1](#))

orthorhombic, tetragonal and cubic structures, i.e. $\alpha = \beta = \gamma = 90^\circ$, d_{hkl} can be calculated by the following expression.

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (2.4)$$

Here, h,k,l are the Miller indices for the d_{hkl} of interest, and a,b,c, are the lattice constants, i.e. the width, length, and height of the unit cell. Besides the peak position, the relative intensity of the peak also contains crucial information about the crystal structure and perhaps more importantly, the chemical content of each specific plane. The integrated intensity of a nuclear Bragg peak is given by (21):

$$\mathcal{I}_N = A \frac{m_{hkl} |f(hkl)|^2}{v_0^2 \sin\theta \sin 2\theta} \quad (2.5)$$

Here, m_{hkl} is the multiplicity of the reflection associated with each scattering plane, which is the number of equivalent permutations of the Miller indices hkl of the plane. A is an overall scale factor and v_0 is the velocity of the incoming neutron, both are constant for all peaks within the same dataset, and therefore can be neglected when only the relative intensity of the peaks are concerned. $F(hkl)$ is the form factor. Depending on whether the Bragg peak scattered from planes formed by layers of nuclei, i.e. a nuclear Bragg peak, or layers of ordered magnetic moment, i.e. a magnetic Bragg peak, the relevant $F(hkl)$ is needed for a refinement. Details concerning the elastic scattering of nuclear and magnetic Bragg peaks will be covered in next section.

Neutron Powder Diffraction (NPD), which includes both nuclear and magnetic diffraction, is perhaps the most common elastic neutron scattering technique. Fig.2.5 shows the schematic of the POWDER instrument of HFIR, ORNL, a neutron instrument specialized in NPD. It is also commonly referred to as the HB2A beamline by local users. As indicated in the schematic, the incoming neutron beam comes out directly of the instrument shutter towards the sample table. The scattered neutrons are then collected by the array of 44 ^3He detectors or stopped by the shielding around

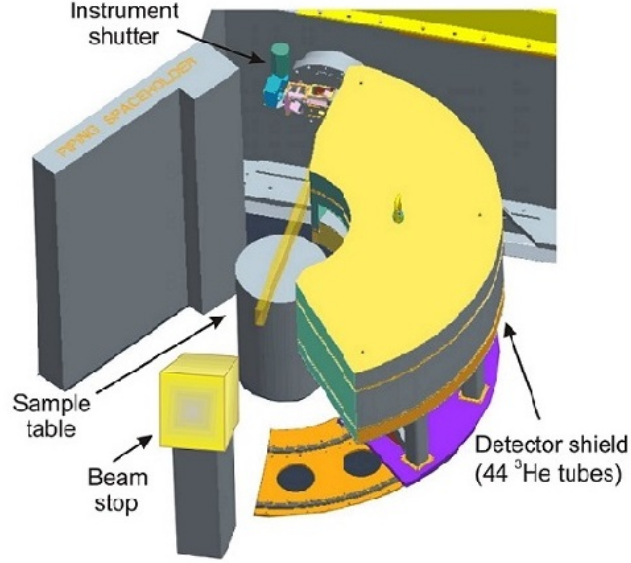


Figure 2.5: Schematics for the neutron powder diffractometer POWDER of HFIR, ORNL. (Courtesy of <http://neutrons.ornl.gov/powder/>.)

the instrument. The detectors have some mobility along the elastic scattering line to cover the desirable q -range. Unscattered neutrons from the incident beam are absorbed by the beam stop.

Nuclear Bragg peaks

Fig.2.6 shows a refined NPD pattern taken for $\text{PrFe}_{0.9}\text{Ru}_{0.1}\text{AsO}$ at POWGEN. The series of green indicators mark the calculated Bragg peaks' positions for a chosen crystal structure. There is no magnetic peak present in this dataset.

For a nuclear Bragg peak, $f(hkl)$ refers to the structural form factor f_N , which is defined as follow.

$$f_N(hkl)(\vec{Q}) = \sum_d \bar{b}_d e^{i\vec{Q} \cdot \vec{d}} e^{-W_s(\vec{Q})} \quad (2.6)$$

b_d is the coherent scattering length of the element in the plane, which is an experimental quantity that can be looked up from databases such as the Neutron Data Booklet published by Institut Laue-Langevin (22). $\vec{Q}$ is the wavelength of the

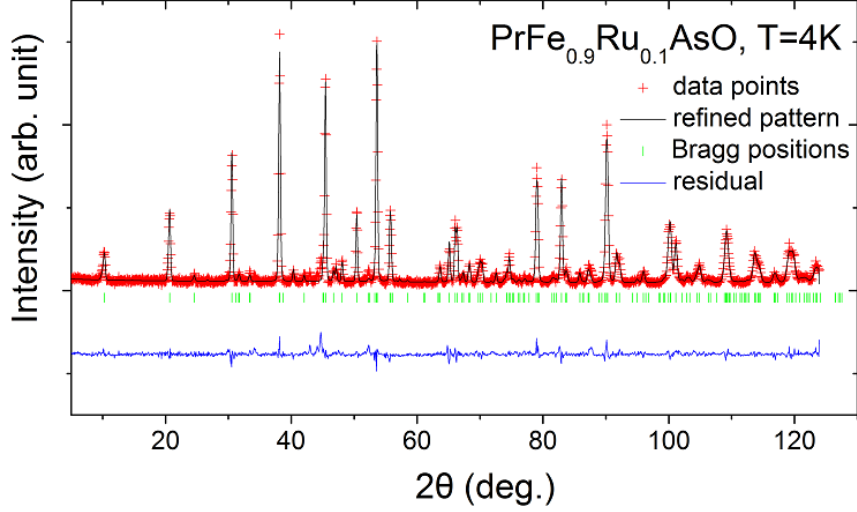


Figure 2.6: Neutron Powder Diffraction pattern taken for $\text{PrFe}_{0.9}\text{Ru}_{0.1}\text{AsO}$ at 12K.

scattered neutron. $\vec{d}$ defines the location of the atom within the unit cell. $W_s(\vec{Q})$ represents the Debye-Waller factor. $f_N(hkl)$ is also related to the differential cross section $d\sigma/d\Omega$, i.e. the flux of neutrons scattered into solid angle $d\Omega$ (23).

$$\frac{d\sigma}{d\Omega} = |f_N(hkl)(\vec{Q})|^2 \quad (2.7)$$

With an intelligent guess of the crystal structure and lattice parameters, one can use a crystallographic softwares such as FullProf (24) to automatically generate, scale, and fit a series of line profiles for the measured Bragg peaks. Such software generally performs these fits using a technique called Rietveld refinement, which, in short, is a fitting algorithm that uses the least square approach to match the experimental data to the theoretical line profile which is calculated using information of the measured crystal provided by the user.

Magnetic Bragg peaks

One of the main advantage of neutron scattering is the ability to detect magnetic moment inside a material. Magnetic neutron diffraction referred to the neutrons that are elastically scattered by an ordered magnetic structure, analogous to those scattered by the lattice structure. The main difference between the two is that for magnetic neutron diffraction, the neutrons are scattered through interactions with unpaired electrons from the ordered magnetic structure instead of the nuclei from the crystal structure.

Similar to the calculation for the intensity of a nuclear Bragg peak, the intensity for a magnetic peak can be calculated using Eq.2.5. One simply need to substitute the magnetic structure factor $f_M(hkl)$ in place of $f_N(h_M k_M l_M)$ (21), and also $h_M k_M l_M$ of the magnetic structure instead of the hkl of the crystal structure (21). Also unlike the structural form factor for nuclear Bragg peaks, the magnetic structural factor is Q-dependent, as seen by the following expression (25).

$$f_M(h_M k_M l_M)(\vec{Q}) = \frac{\gamma e^2}{2m_e c^2} \sum_s m_{\perp s} f_s(\vec{Q}) e^{-i\vec{Q} \cdot \vec{r}_s} e^{-W_s(\vec{Q})} \quad (2.8)$$

$\gamma e^2/1m_e c^2 \approx 2.696 \times 10^{-15} m$ is the average magnetic scattering length for a spin-1/2 particle. $m_{\perp}$ represents the thermal average of the magnetic moment at the s th site in position r_s . $W_s(\vec{Q})$ again represents the Debye-Waller factor. $f_s(\vec{Q})$ is the magnetic form factor of the ion, which is the Fourier transform of the magnetization density of the ion. The function is element- and Q-dependent and can be approximated by equations. Such equations are listed in databases such as the Neutron Data Booklet (22).

Fig.2.7 shows the schematics for FIE-TAX, also commonly referred to as the HB1A beamline of HFIR. It is the instrument used during our measurement of magnetic Bragg peaks for $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$. Since FIE-TAX is a trip-axis spectrometer, its detecting range is not limited to the elastic line and is also capable to detect inelastic neutrons. However we only used this instrument for our measurement of magnetic

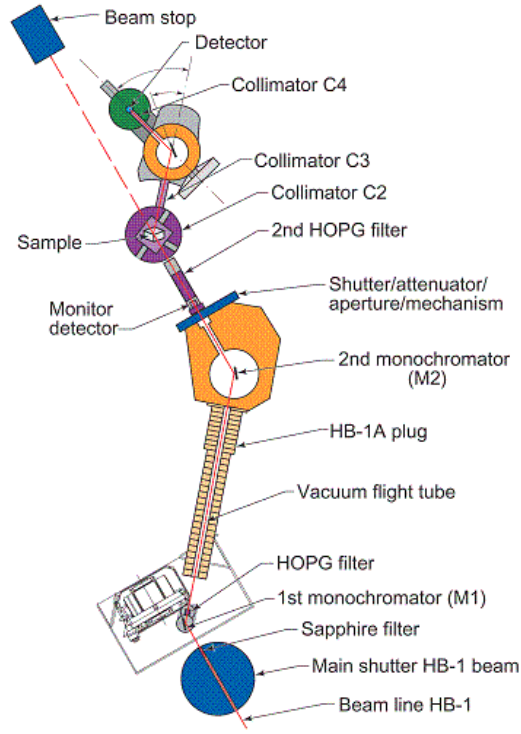


Figure 2.7: A detail schematic for FIE-TAX, the Fixed-Incident-Energy Triple-Axis Spectrometer, also known as HB1A, of HFIR, ORNL. (Courtesy of <http://neutrons.ornl.gov/fietax/>)

Bragg peaks in $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ along the elastic line, to measure the temperature and doping dependence of individual magnetic Bragg peaks. A triple-axis instrument, hopefully apparent from the schematics in Fig. 2.7, enables the user to focus on specific areas in Q -space.

Small angle neutron scattering (SANS)

Small-angle neutron scattering (SANS) is a specialized elastic neutron scattering technique that focuses on small scattering angles, typically with a range of $0.001 \leq q \leq 1 \text{ \AA}^{-1}$, which corresponds to about 10 to 1000 $\text{\AA}$ in real space. Due to the technique's ability to study structure and interaction in this size range, SANS is ideal for our investigations of the helimagnetic ordering in $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ which ranges from 400 to 700 $\text{\AA}$.

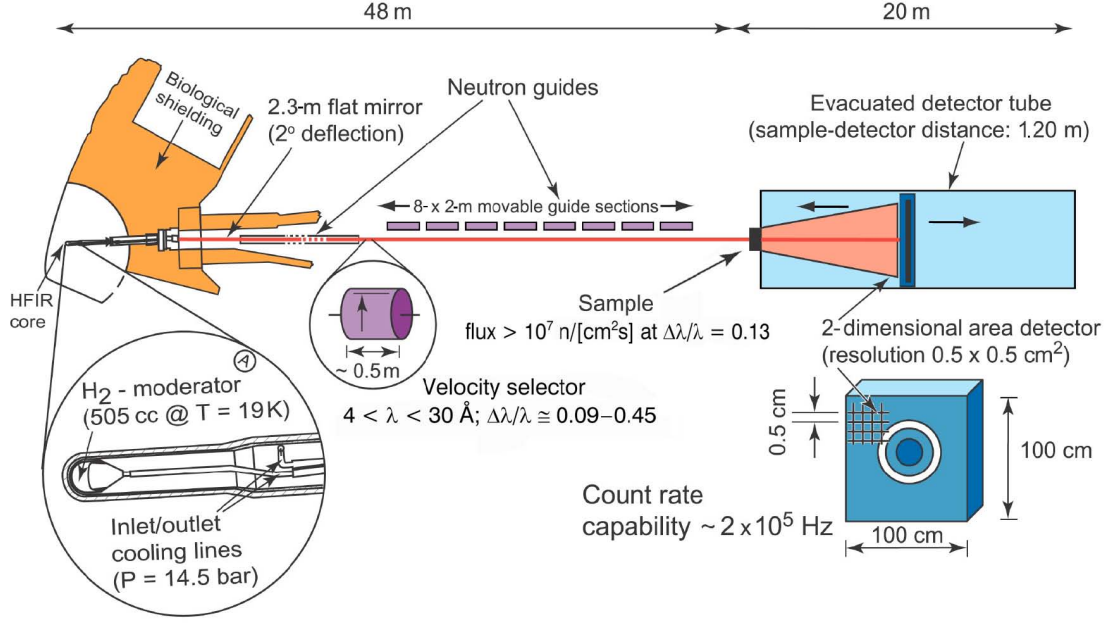


Figure 2.8: A detailed schematic for GP-SANS, the General-Purpose Small-Angle Neutron Scattering Diffractometer of HFIR, ORNL. (Courtesy of <http://neutrons.ornl.gov/gpsans/>)

Fig.2.8 shows the schematic for the General-Purpose Small-Angle Neutron Scattering Diffractometer (GP-SANS) of HFIR, ORNL. As shown in the figure, the incoming neutron beam is directed at the sample, then elastically scattered via nuclear or magnetic interaction. One of the main different for a SANS instrument from that of a typical diffractometer is the location of its detector. For a SANS instrument the detector is placed much further from the sample, so that for the same density of detector pixels, the resolution can be maximized by minimizing the range of covered 2θ . In other words SANS instruments are geometrically set up to be in favor of collecting scattered neutron with small 2θ . For GP-SANS of HFIR, the detector is placed on a movable stage along a 20 m rail inside an evacuated chamber. The user can move the detector to the desirable position to focus on a certain 2θ —, and therefore Q-range.

2.3.2 Inelastic neutron scattering

Inelastic neutron scattering (INS) as stated by its name is the measurement and study of inelastically scattered neutrons. Inelastically scattered neutrons carries one extra criteria of information than the elastically scattered ones, namely the change in speed $\rightarrow$ momentum $\rightarrow$ energy of the scattered neutrons (23). By measuring the energy transfered between the measured system and the incoming neutrons, one can study the dynamics of a physical system such as spin and phonon excitations. The velocity, consequently the momentum and energy of the scattered neutron can be interrelated by the following equation.

$$\hbar\omega = E_i - E_f = \frac{\hbar^2}{2m}(\vec{k}_i^2 - \vec{k}_f^2) \quad (2.9)$$

Here ω and $\vec{Q} = \vec{k}_i - \vec{k}_f$ are quantities that can be experimentally measured in an INS experiment. The partial differential cross section, which is the flux of neutrons scattered into a solid angle of size $d\Omega$, and with final energy between E_f and $E_f + dE_f$, is related to the dynamic structural factor $S(Q, \omega)$ by the following equation (23).

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{k_i} S(Q, \omega) \quad (2.10)$$

$S(Q, \omega)$ is characteristic to the material, not unlike the nuclear structural factor, which depends on the material's crystal structure and composition, the dynamic structure factor $S(Q, \omega)$ depends on the material's lattice dynamic, including phonon and spin excitations. Similarly a good theoretical understanding of the dynamics of a material should be able to predict an INS dataset, just like a correct crystal structure describes an NPD dataset.

A number of neutron instruments have been designed to accommodate INS experiments, including the aforementioned triple axis spectrometers, and the relatively newer time-of-flight spectrometers with detectors that covers a large solid angle. For INS experiments performed for the research in this thesis, we used a pair of time of

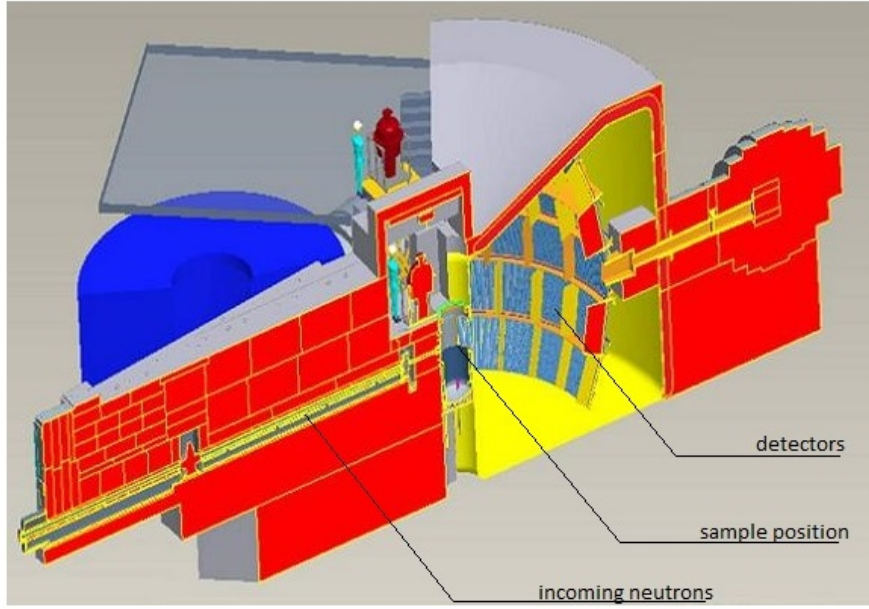


Figure 2.9: A detail schematic for SEQUOIA, the Fine-Resolution Fermi Chopper Spectrometer at SNS of ORNL. (Courtesy of <http://neutrons.ornl.gov/sequoia/>)

flight spectrometers at SNS, ORNL, namely SEQUOIA and ARCS. Shown in Fig. 2.9 is a schematic for SEQUOIA at SNS of ORNL, note the large detector coverage.

Time-of-flight (TOF) is an experimental method to calculate and select the velocity for incoming neutrons. As self described by its name, the velocity and thus the kinetic energy of a neutron is known by measuring the time it spent to move over a fixed distance. The selection process is then done via a series of rotating slitted discs called choppers, by blocking out neutrons that don't possess the selected speed. Using the de Broglie's relationship: $\lambda = h/mv$, where λ , m , and v are the wavelength, mass, and velocity of the neutron, and h is the Planck constant, one can then calculate the wavelength and energy by knowing the selected speed of the incoming neutrons.

The Wide Angular-Range Chopper Spectrometer (ARCS) and the Fine-Resolution Fermi Chopper Spectrometer (SEQUOIA) are a pair of complementary TOF chopper spectrometers at SNS of ORNL. Both provide a large solid angle of detector coverage (for SEQUOIA it's -30° to 60° in the horizontal and -18° to 18° in the vertical).

2.4 X-Ray diffraction

The basic principle of X-Ray diffraction (XRD) is very similar to that of neutron diffraction. For instance, the location of a nuclear peak in XRD also follows Bragg's law. One of the major difference between X-ray and neutron diffraction techniques is that XRD is not sensitive to the magnetic structure of the studied material due to the non-magnetic nature of photons. X-ray scatters from the electron clouds of an atom instead of the nucleus as for neutrons, as a result the scattered intensities for a XRD peak is different from that of an NPD pattern for the same element. The atomic form factor for a Bragg reflection of X-ray is proportional to the Fourier transform of the electronic charge distribution of the element/ion of interest, and is given by the following equation (2).

$$f_i(\mathbf{Q}) = -\frac{1}{e} \int d\mathbf{r} e^{i\mathbf{K}\cdot\mathbf{r}} \rho_j(\mathbf{r}) \quad (2.11)$$

Consequentially one technique is preferred over the other depending on the material of interest. For example in the case of $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$, the neutron scattering cross sections for Fe and Cr are 11.62b and 3.49b, but the atomic number for Fe and Cr are 26 and 24. As a result NPD provides a better contrast between the two site-sharing elements, and is the preferred probe to find out each of the concentration level for Fe and Cr.

For the X-ray diffractometer used to characterize samples from the $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ series, the Bruker D2-Phaser, a Cu target is used, which corresponds to a $K\alpha$ wavelength of 1.5418Å. Fig.2.10 shows an example of refined XRD pattern, collected for $\text{Fe}_{0.97}\text{Cr}_{0.03}\text{Ge}$. The pattern is refined using the software FullProf, the same shown for an NPD pattern. The principle of the refinement process is also similar, both using the Rietveld method, except in the X-ray option has to be chosen in place of neutrons in the software, so that the correct scattering cross section for each element is used.

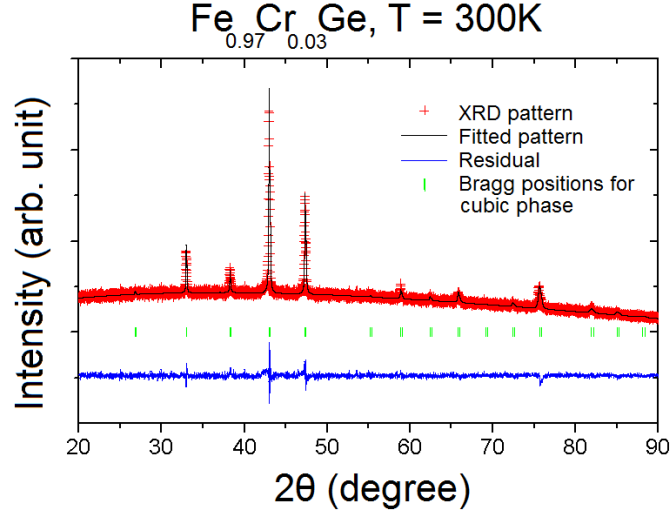


Figure 2.10: Refined XRD pattern for $\text{Fe}_{0.97}\text{Cr}_{0.03}\text{Ge}$.

2.5 Muon spin spectroscopy

Muon Spin Spectroscopy, common known as μSR , is the general term for muon spin rotation, resonance, and relaxation. For our purposes, it is a technique that uses spin-polarized muons as probes for local magnetic environment of a sample. In short, spin polarized muons are projected and embedded into the sample. The muons then spend short periods of time (in orders of $10\ \mu\text{S}$) interacting with the local environment inside the sample before being ejected out. The outgoing muons are then collected and analyzed for the change in spin polarization, revealing magnetic information about the system.

One of the key concept in μSR is Larmor precession. Muons, along with other leptons with magnetic moments precesses when an external field is present. This precessing movement is called Larmor precession and the angular frequency of the precession is called the Larmor frequency. This frequency for the incoming muons can be controlled by an applied magnetic field on the incoming muons. After the muons have interacted and ejected from the sample, changes in the Larmor frequency of the muons reveal information about the sample's local magnetic environment.

In our investigation of magnetic ordering in $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$, a series of zero field and longitudinal field muon spin rotation and resonance experiments were performed by a collaboration group. The series of experiments were necessary to complete the investigation of the material even after investigations by neutron scattering. This is because unlike neutrons, μSR probes local magnetic fields instead of magnetic ordering, and thus is able to detect magnetic moments that is undetectable by neutrons due to a slow fluctuation (correlation time of $< 1\mu\text{s}$), or a short coherence length (less than 10 lattice spacing). Since this method is only used during the investigation of $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$, readers may refer to the corresponding chapter for a more detailed discussion on the technique and related data.

Chapter 3

Structural and Magnetic phase transitions of $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$

Since the discovery of high temperature superconductivity in cuprates during late 1980's, experimentalists and theorists alike have been in need of more high T_C superconductors to extend the study of the phenomenon. A breakthrough came in the form of a number of Fe-pnictide compounds discovered in 2008 (5; 6) that are similar to cuprates in many ways. Studies of substitutionally altered or doped Fe-pnictides have proved particularly valuable and have led to the discovery of several superconducting materials, for which the main families are often referred to as 1111s such as LaFeAsO , 122s such as BaFe_2As_2 , 111s such as LiFeAs , and 11s such as FeSe . We here report our study on one of the members from the 1111 family, the Ru/Fe substituted $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ (26).

3.1 Superconductivity in iron-pnictides

In general, the undoped parent compounds of the 1111 family iron-pnictide superconductors are tetragonal paramagnets at high temperatures. As the temperature is lowered the undoped parent material does not reach a superconducting ground

state. Instead, it undergoes a structural transition, followed or accompanied by a spin density wave (SDW) ordering of the Fe moments, and sometimes antiferromagnetic (AFM) ordering of the rare earth moments (6; 27). The undoped parent compound PrFeAsO undergoes a tetragonal-orthorhombic structural transition at $T \sim 150$ K, followed by a SDW transition at $T \sim 140$ K associated with the AFM ordering of Fe, and then finally AFM ordering of the Pr moments at 14 K (18).

For superconductivity to emerge in these materials, all of the transitions must be eliminated or suppressed down to a sufficiently low temperature (28; 29). This can be done by doping with the appropriate element, e.g. F on the O-site in CeFeAsO (30), Co on the Fe-site in LaFeAsO (31; 32), etc. In certain members of the Fe oxypnictides, superconductivity can also be induced by simply applying pressure externally, e.g. LaFeAsO under 120 kbar for a T_C of 21 K (33) and BaFe₂As₂ under 40 kbar for a T_C of 29 K (34). This however does not work in some other members. For instance CeFeAsO achieved no superconductivity up to 500kbar (35). The structural and magnetic transitions in these materials exhibit complicated relationships with each other and strongly affects the presence of superconductivity. Therefore it is important for us to carefully explore the correlations between these transitions (36; 26; 37).

It is however worth mentioning that there are instances where AFM ordering and superconductivity can coexist. For example, in 122 materials such as in BaFe_{2-x}Co_xAs₂ (27). This is less often the case in 1111 materials such as LaFeAsO, where long range AFM ordering were usually completely destroyed before superconductivity can emerge; there have been exceptions, such as in SmFeAsO_xF_{1-x}, but the occurrence is much rarer when compared to that from the 122 family, where the coexistence of superconductivity and magnetism has been an recurring theme (38). There have also been examples where suppression of the structural and magnetic transitions leads to new non-superconducting ground states, for example ferromagnetism (39). It has been concluded that suppressing the structural and magnetic transitions is necessary for superconductivity, but not necessarily sufficient (28).

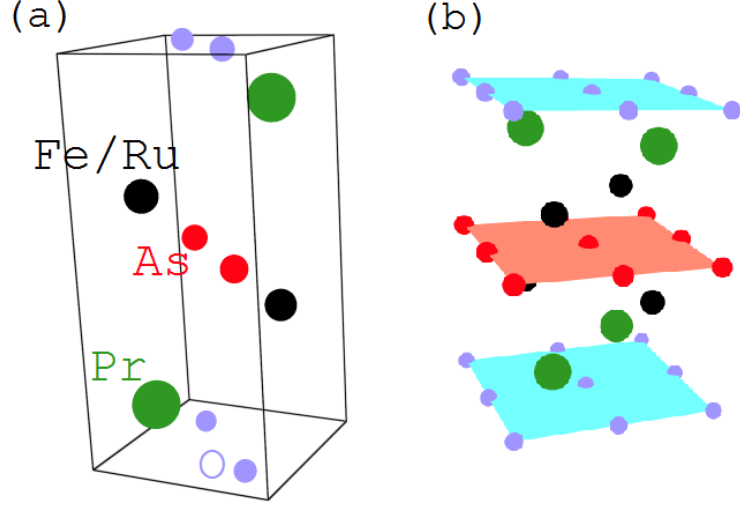


Figure 3.1: (a): The unit cell of the $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ in its room temperature tetragonal structure; (b): An alternative illustration of the same structure, with emphasis on the rare earth-oxygen and Fe-As layers.

Fig.3.1 shows the crystal structure for $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ shared with other 1111 compounds, in the room temperature tetragonal structure. Most of the 1111 materials with the highest reported superconducting T_C 's are doped in the rare earth oxygen layer, either at the oxygen site or the rare earth site (6; 40). The T_C 's are generally lower for materials doped on the Fe-As layer, possibly due to undesirable lattice distortions and disorder in the conducting Fe-As layer (27; 41).

The use of isoelectronic substitutes, for example the substitution of Ru for Fe, allows for investigations of the physics without the complications induced by changing the electron count. Moreover, Ru/Fe substitution can lead to superconductivity in certain Fe-oxypnictides, although this has only been confirmed in some 122 materials, i.e. $\text{BaFe}_{2-x}\text{Ru}_x\text{As}_2$ (27; 42) and $\text{SrFe}_{2-x}\text{Ru}_x\text{As}_2$ (43), but at a much larger Ru content than has been observed with non-isoelectronic substitutes (44; 45). On the contrary, Ru/Fe substitution on 1111s has yet to succeed in yielding any superconducting samples, even after the complete suppression of the structural and magnetic transitions, as has been confirmed in LaFeAsO (29), PrFeAsO (46), SmFeAsO and GdFeAsO (47).

As mentioned in the last paragraph, Ru/Fe substitution in PrFeAsO does not induce superconductivity, even after the complete suppression of the structural and magnetic transitions, down to at least $T = 2$ K (46). Indeed, no indication of any new ground state has been observed (46). Transport property data and results of electronic density of state calculations for $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ have been reported in ref (46), and have shown indications for the complete suppression of sharp magnetic transitions for $x \geq 0.1$ and structural transitions for $x \geq 0.33$ (46). Doping at 33% is a rather high level when compared with carrier doped Fe-pnictides, where the transitions are suppressed with less than 10% doping in most cases. Thus, Ru/Fe substitution provides a wider stoichiometric range, aiding one to have a better look at the progression of the suppression of the structural and magnetic transitions. Besides the parent compounds, Ru/Fe substitution has also been done in already superconducting samples, such as $\text{LaFe}_{1-x}\text{Ru}_x\text{AsO}_{0.89}\text{F}_{0.11}$ (48) and $\text{SmFe}_{1-x}\text{Ru}_x\text{AsO}_{0.85}\text{F}_{0.15}$ (49). Similarly, results showed that a much higher level of isoelectronic substitution (than carrier doping) was needed to suppress superconductivity in those samples.

Arguably, when Ru is substituted for Fe in the 1111 compounds, the main effect on the magnetism can be understood by considering the substitution as simply equivalent to spin dilution. This is consistent with density functional theory with the local density approximation calculations for $\text{LaFe}_{1-x}\text{Ru}_x\text{AsO}$ (49), which illustrates that Ru atoms do not show any tendency to sustain a magnetic moment regardless of their concentration. This is also compatible with previous experimental data on $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ (46). Here, we report our findings from neutron diffraction measurements, complemented by new muon spin relaxation measurements. Our neutron work (50) showed no evidence for the structural transition in $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ above $x = 0.4$ as determined by Rietveld refinements. Remarkably, it is observed that all signatures of magnetic order disappear at the percolation concentration of the $J_1 - J_2$ square-lattice model (51).

Another phenomenon of interest in the parent compound PrFeAsO is the observation of negative thermal expansion (NTE) along the c-axis, where the sample

gradually expands along the c direction as it is cooled below 60 K (52). Interestingly such NTE is absent in superconducting F-doped PrFeAsO (52). A different behavior has been observed in the superconducting samples of Co doped BaFe_2As_2 where a sudden onset of NTE along the c axis appears at T_C . This feature is absent in the non-superconducting parent BaFe_2As_2 (53). It seems worthwhile to explore whether or not there is a systematic correlation between the NTE and the presence or absence of superconductivity. Despite voluminous reports of the dependence of lattice constants on stoichiometry in Fe As based materials there has been surprisingly little published data showing the temperature dependence of the lattice constants, especially the c -axis.

We report results on Ru/Fe substituted $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$, related to the 1111 Fe-based superconductors, including detailed studies of the temperature dependence of lattice parameters in Ru/Fe substituted PrFeAsO . As mentioned above, undoped PrFeAsO shows NTE. As discussed below, we observe that Ru/Fe substitution in PrFeAsO suppresses the structural and magnetic phase transitions without leading to superconductivity, however NTE along the c axis persists for all substitution levels up to at least 75% Ru on the Fe site.

This research project have resulted in 2 publications, titled “Neutron diffraction study and anomalous negative thermal expansion in nonsuperconducting $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ ” (50) and “Tuning the magnetic and structural phase transitions of PrFeAsO via Fe/Ru spin dilution” (54).

3.2 Sample synthesis and bulk properties characterizations

Methods reported earlier (46; 55) were used to synthesize the samples. $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ samples were made from powders of PrAs , Fe_2O_3 , RuO_2 , Fe and Ru. The starting materials were crushed and mixed inside a He glovebox, then pressed into a $1/2''$



Figure 3.2: Shown here is a photo of the one of the $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ powder samples. This vial contains about 2g of $\text{PrFe}_{0.9}\text{Ru}_{0.1}\text{AsO}$.

diameter pellets ($\sim 2\text{g}$ each) and placed in covered alumina crucibles inside silica tubes. The tube was evacuated, backfilled with ultra-high-purity Ar and flame sealed. Each individual sample was heated at 1200°C for 12 – 36h several times, and was thoroughly ground and pressed into pellets between the heating cycles. Fig.3.2 shows a photo for one of the powder samples used in this study.

3.2.1 Specific heat

We now report and discuss the specific heat measurements measured using the PPMS system by Quantum Design. As seen in Fig.3.3(a), the sharp feature around 12 K associated with the magnetic ordering of the Pr moment is visible only for $x = 0$, suggesting that at least the long range ordering of the Pr moment is greatly suppressed by $x = 0.1$.

It is instructive to plot $c_p T^3$ vs $\ln T$ (56). Typically the low temperature limit of the plot is a constant that instantly yields the Debye temperature and optical modes that are more Einstein like contribute to a bell shaped curve at higher temperatures (1). Fig.3.3(b) shows such a plot for a range of PrRuAsO , with the large bell shaped

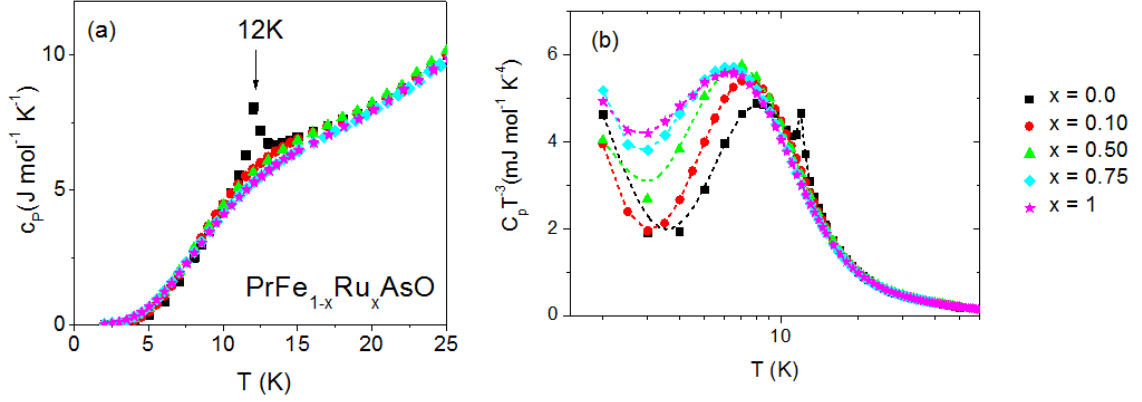


Figure 3.3: (a): Specific heat vs. temperature for $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$. The peak at 12 K indicates the AFM ordering of Pr. For samples with $x \neq 0$, the said 12 K is suppressed but a broad hump remains, possibly indicating short range magnetic ordering of the Pr sublattice; (b): $c_p T^3$ vs. $\ln T$ plot for the series, note the large bell shaped Einstein peak around 8K as mentioned in the text.

Einstein peak centering around 6-8 K. Interestingly, the expected Debye region is not very apparent. In addition, the optic mode peak occurs at relatively low temperatures. It is notable that this characteristic is ubiquitous among the famous family of AB_2O_8 NTE material, such as HfW_2O_8 , HfMo_2O_8 , ZrMo_2O_8 and ZrW_2O_8 (57; 58; 59; 60).

Since the Pr sublattice in PrFeAsO is a magnetically ordered system, we can also analyzed the entropy of the interacting spins at low temperature. The general formula for entropy S as a function of the specific heat c_p takes the following form.

$$S(T_p) = \int_0^{T_p} \frac{c_p}{T} dT \quad (3.1)$$

However, in order to isolate the magnetic contribution from the overall specific heat, we need to first subtract off the non-magnetic components of the specific heat. For this we obtained temperature dependent specific heat data for LaFeAsO , a closely related member to PrFeAsO of the 1111 iron pnictide family. LaFeAsO and PrFeAsO share an identical structure, and possess similar lattice dynamics according to phonons density of states and dispersion measurements (18; 61; 62), however unlike PrFeAsO , the La sublattice does not order magnetically at low temperature. This allows us to

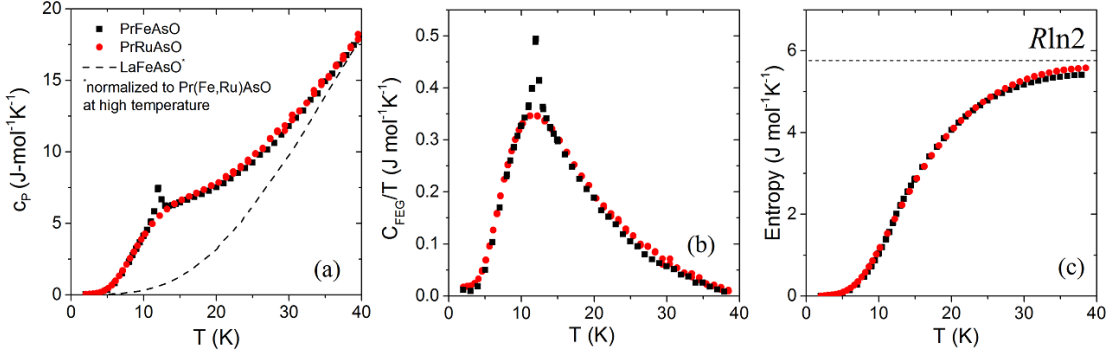


Figure 3.4: (a): Temperature dependence of the specific heat for PrFeAsO, PrRuAsO, and LaFeAsO. The LaFeAsO data has been scaled to be used as a pseudo model for the lattice contribution of specific heat at low temperature, due to the non-magnetic nature of the La sublattice; (b): c_{FEG} , which stands for the specific heat as contributed by Free Electron Gas (FEG); (c): Temperature dependence of the entropy of the free electron gas of PrFeAsO and PrRuAsO, both approaching the asymptote of $R \ln 2$.

use the LaFeAsO heat capacity data as a psuedo-model for the non-magnetic part of the specific heat. The LaFeAsO data was scaled to fit the $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ data at high temperature, as shown in Fig.3.4(a). We decided to use this method instead of the more straightforward Debye model ($c_p \approx T^3$), since the latter method demands more data points at higher temperatures, which we regrettably do not possess.

Fig.3.4 shows the analysis process as described above. Fig.3.4(a) shows the scaling of LaFeAsO data to that of PrFeAsO. Fig.3.4(b) shows the subtracted specific heat data, which represents the magnetic contribution of the specific heat. Fig.3.4(c) shows the temperature dependence of the entropy, which is the temperature integrated c_{FEG}/T . The entropy for both PrFeAsO and PrRuAsO reaches the asymptote of $R \ln(2)$ at high temperature, the expected value of spin entropy for a spin-1/2 system. (R is the molar gas constant $\approx 8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$.)

3.2.2 Magnetic susceptibility

We report dc magnetic susceptibility measurements measured using the MPMS SQUID by Quantum Design. As seen in Fig.3.5(a) and Fig.3.4(a) from the last

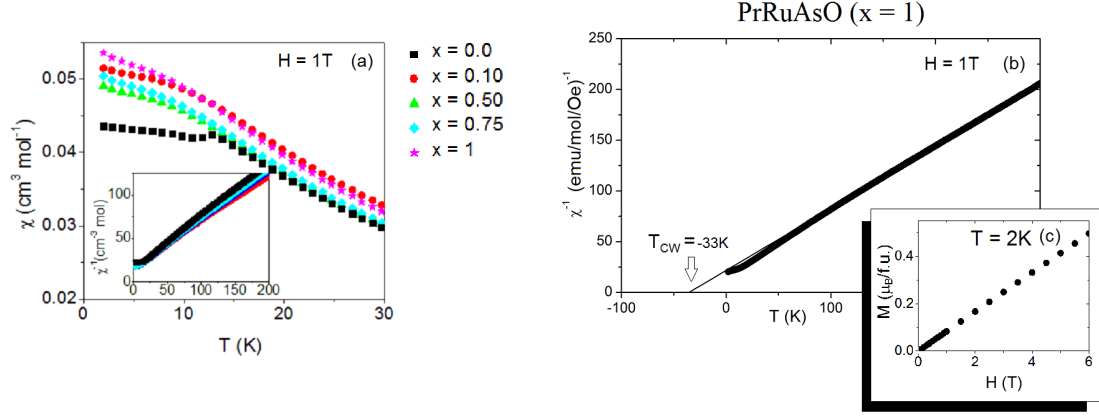


Figure 3.5: (a): χ vs. T , the inset shows a closer look at the lower temperature range for χ^{-1} vs. T . A kink is observed in all concentrations of $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ around 12 K, related to the Pr ordering. The feature is much less prominent in the $x \geq 0.1$ samples; (b): χ^{-1} vs. T for PrRuAsO . The Curie-Weiss temperature is labeled in the plot as T_{CW} ; (c): M vs. H for PrRuAsO , showing no saturation of moment up to 6 T.

section, the AFM ordering of Pr can be detected by both methods, indicated by an anomaly around 12 K in both cases, which disappears for $x \geq 0.1$. Furthermore, we fitted the magnetic susceptibility data using the Curie-Weiss law for all values of x 's. The Curie-Weiss law states the following.

$$\chi = \frac{C}{T - T_C} \quad (3.2)$$

Fig.3.5(b) shows the fit for the end point PrRuAsO ($x = 1$). The Curie-Weiss law describes the data well down to around 50 K. Data points for $T > 50\text{K}$ were fitted to the Curie-Weiss law, with the resultant fit intersecting the temperature axis at $T_{CW} = -33(5)$ K with a Curie constant of 1.4(1), close to the expected value of 1.6 for Pr^{3+} . Fig.3.5(b) shows the field dependence of the magnetization at $T = 2\text{K}$, with no sign of saturation up to 6 T. Fig.3.3(a) shows the temperature dependence of the specific heat. The data for $x = 1$ is very similar to the data for all concentrations $x > 0$, with a broad hump observed around 12 K, coinciding with the Néel temperature for Pr

Table 3.1: Curie-Weiss temperatures and Curie constants extracted from the magnetic susceptibility data shown in Fig.3.5

Ru%	T_{CW} (K)	C
0	38(1)	1.764(3)
10	41(1)	2.997(4)
33	36(1)	1.742(6)
50	34(1)	1.843(5)
75	33(1)	1.796(3)
100	33(1)	1.398(3)

ordering in PrFeAsO. This is presumably related to short range order involving the Pr spins. Table 3.1 shows the list of Curie-Weiss temperatures and Curie constants for the measured materials obtained with the method discussed above.

3.3 Neutron powder diffraction

We performed neutron powder diffraction (NPD) on $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ using the neutron powder diffractometer HB-2A (for $x = 0.1, 0.33$, and 0.75) and the fixed incident-energy triple-axis HB-1A (for $x = 0.05$ and 0.1) of HFIR at ORNL to study the structural and magnetic transitions, respectively. Additional measurements were performed at the high-resolution powder diffractometer POWGEN of SNS at ORNL to study the effect of Ru/Fe substitution on the anomalous NTE and also to have a closer look at the suppression of the structural transition (for $x = 0.33, 0.4, 0.5, 0.6, 0.75$, and 1). The neutron powder diffraction data collected at HB2A and POWGEN will be presented together below, however, the captions of tables and graphs will contain information indicating the source of the data, i.e. whether the data was collected at HB2A, or POWGEN.

3.3.1 Structural phase transition

Undoped PrFeAsO goes through a tetragonal-orthorhombic structural transition (46). Structural transitions can be observed by NPD since the position of every

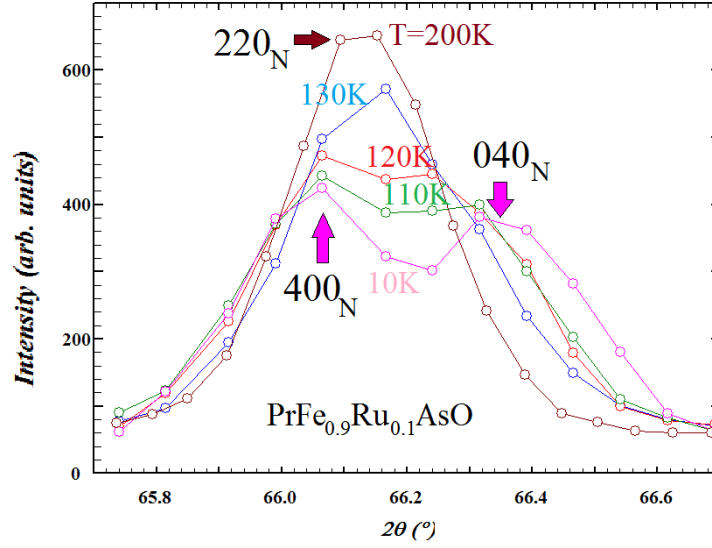


Figure 3.6: Shown is NPD data collected of $\text{PrFe}_{0.9}\text{Ru}_{0.1}\text{AsO}$. The peak centering around $2\theta = 66.2^\circ$ broadens and eventually splits as the system is cooled past $T \approx 125$ K

nuclear Bragg peak responds to changes in the crystal structure. Fig.3.6 shows the temperature evolution of the 220 peak in the tetragonal structure, the “N” subscripts clarifies that the listed Bragg peaks are nuclear Bragg peaks. One can see the gradual broadening and eventual splitting of the peak, into two separate peaks, 400 and 040, in the orthorhombic structure. The reason of the split is as follow. In the tetragonal structure $a = b \neq c$, in the orthorhombic structure $a \neq b \neq c$, therefore for Bragg peaks of which the intensity is enhanced as a result of degeneracy from symmetry in a tetragonal system, i.e. $a = b$, separate into two separate peaks once the symmetry is broken and become orthorhombic, i.e. $a \neq b$. As evident in the data shown in Fig.3.6, the tetragonal-orthorhombic structural transition in $\text{PrFe}_{0.9}\text{Ru}_{0.1}\text{AsO}$ occurs around $T = 125$ K.

Fig.3.7(a) presents the refined NPD data collected at HB-2A for the $x = 0.1$ sample at 4 K. The detailed structures were fitted via Rietveld refinement using the FULLPROF program (24). Fig.3.7(lower) shows a closer look on the evolution of the 220 nuclear peak for $x = 0.1, 0.33$ and 0.75 . The structural transition is evident in

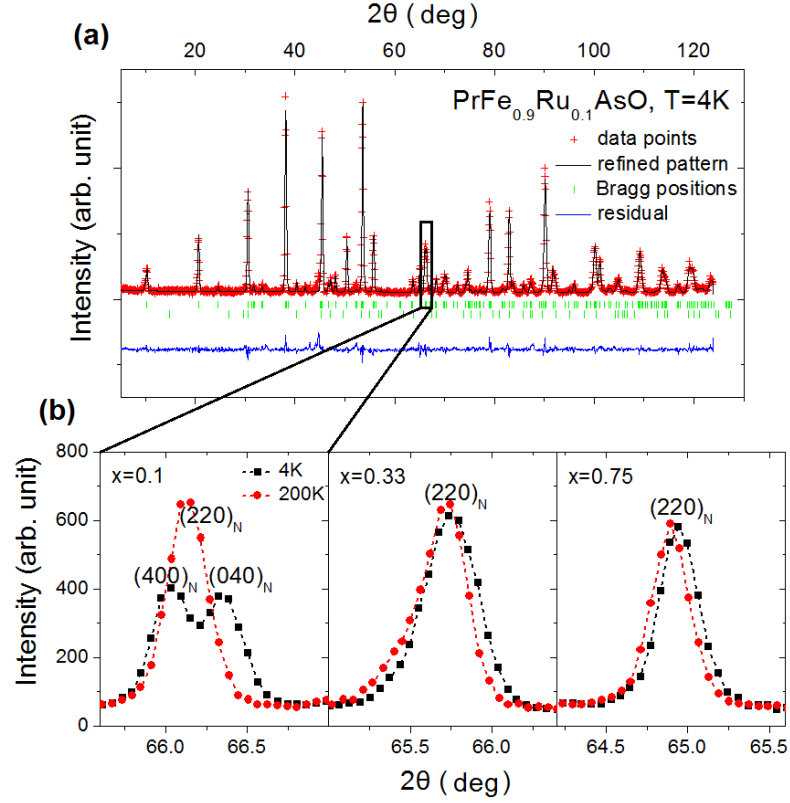


Figure 3.7: (Upper): Fully refined NPD pattern collected at HB2A of HFIR for $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ at 4 K; (Lower): 220_N peak for $x = 0.1, 0.33$ and 0.75 at $T = 200$ K (red circles) and 4 K (black squares). Peak splitting is clearly visible for $x = 0.1$, and disappears at $x = 0.33$.

Table 3.2: Structural parameters and χ^2 values from Rietveld refinement of NPD data from HB2A (for Ru% = 10 only) and POWGEN, at T = 12 K. (Space group: C m m a for 10% and 33%, P 4/n m m otherwise.)

Ru%	a/b (Å)	c (Å)	z_{As}	z_{Pr}	χ^2
10	3.9687(8)/3.9851(8)	8.5623(2)	0.6551(7)	0.1398(9)	3.336
33	4.0006(3)/4.0073(3)	8.5154(1)	0.6576(3)	0.1380(5)	3.639
40	4.0085(3)/4.0149(4)	8.4911(2)	0.6579(5)	0.1375(6)	3.505
50	4.0249(6)	8.4613(2)	0.6616(4)	0.1350(5)	2.822
60	4.0335(7)	8.4364(3)	0.6600(6)	0.1340(9)	4.042
75	4.0508(4)	8.3980(1)	0.6579(4)	0.1369(6)	3.263

the $x = 0.1$ sample as the peak splitting in 220_N is easily discernible; this is much less obvious for samples with $x \geq 0.33$. However, a more comprehensive method of analysis of the POWGEN data, shown later in this section, will reveal that the structural phase transition in $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ persists to Ru level x higher than 0.1.

Fig.3.8 shows 6 refined NPD patterns, collected at both HB2A and POWGEN, for $x = 0.1, 0.33, 0.4, 0.5, 0.6$, and 0.75 , all at 10K. For all samples, both models, i.e. the tetragonal, and the orthorhombic structures, are used to fit NPD patterns. It is expected that even if the sample is orthorhombic, the tetragonal structure would still be able to “fit” the data, but the values for parameters a and b is expected to differed by less than their respective error bars. This method is a different yet more sensitive method to determine the temperature and Ru concentration for which the orthorhombic-tetragonal structural transition cease to be. Table 3.2 shows a list of parameters extracted from the refinements, including structural parameters a , b , c , atom positions of As and Pr (positions of Fe and O are locked by symmetry), and the goodness of fit χ^2 .

Fig.3.9 shows the temperature dependence of the orthorhombicity, defined as $(a - b)/(a + b)$. At high temperature all of the samples are tetragonal and the orthorhombicity is zero by definition. The orthorhombicity values plotted in Fig.3.9 were determined as follows: lattice parameters a and b were extracted by imposing an orthorhombic structure on the Rietveld refinement over the entire temperature range

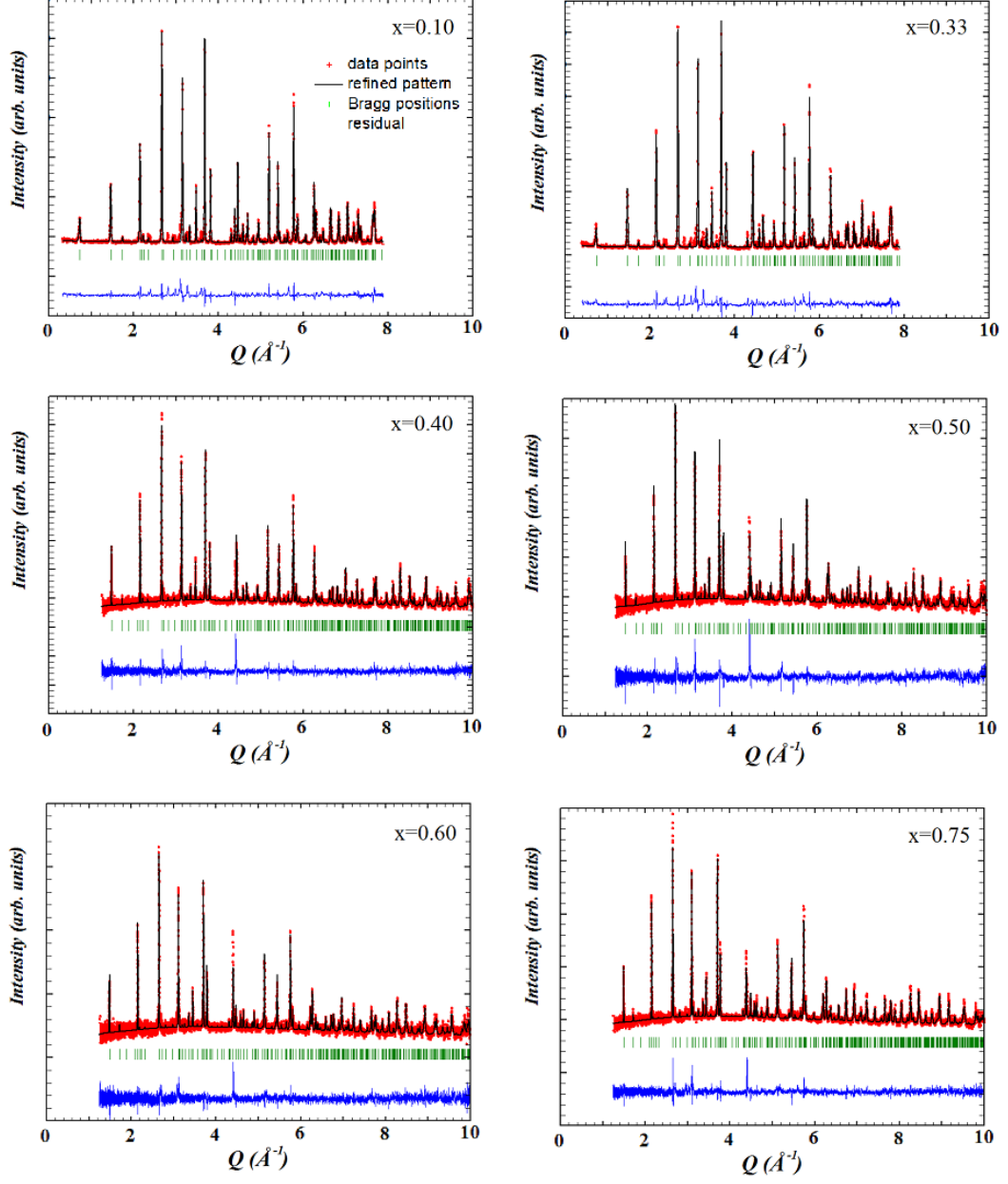


Figure 3.8: Fully refined NPD pattern collected at HB2A of HFIR for $x = 0.1$ and 0.33 , and POWGEN of SNS for $x = 0.4, 0.5, 0.6$, and 0.75 , at $T = 10\text{K}$.

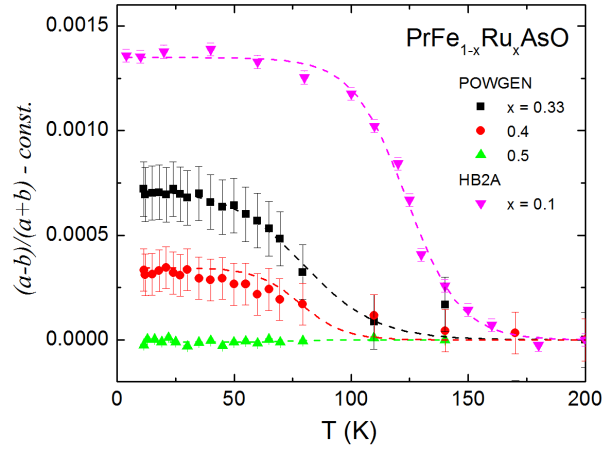


Figure 3.9: Temperature dependence of the orthorhombicity for $\text{PrRu}_{1-x}\text{Ru}_x\text{AsO}$ as discussed in the text. The lines are guides to the eye.

for all samples. For each Ru concentration the fitted value $(a - b)/(a + b)$ determined by the refinement to an orthorhombic structure at $T = 200$ K was subtracted from the corresponding values at other temperatures. This analytical method is useful for detecting structural transitions that are too subtle to be observed via the splitting or broadening of a single nuclear Bragg peak. The data shows clear evidence for the structural transition temperature T_S in samples up to $x = 0.4$. (Here T_S is defined operationally as the temperature at which the orthorhombicity reaches 1/2 of the asymptotic low temperature value.) Rietveld refinement of the data confirmed that samples with $x \geq 0.5$ are isostructural to PrFeAsO at room temperature, and remains in the tetragonal $P4/nmm$ structure down to the base temperature of 10 K, similar to other $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ samples with $x \geq 0.33$ (50). This suggests the existence of structural phase transition in samples with x higher than 0.1, and agrees with the results from previously published resistivity data by McGuire et. al., where it showed anomalies near 130 K for $x = 0.1$ and 80 K for $x = 0.33$ (46).

Interestingly for other isoelectronically substituted 1111 materials the structural phase transition has been observed to persist to concentrations well above the 10% level; for example in $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$ both the transition to an orthorhombic structure

and antiferromagnetic order are present up to $x = 0.4$ (39). In contrast, a much smaller level of carrier doping is needed to affect the transitions. In $\text{RFeAsO}_{1-x}\text{F}_x$ all structural and magnetic transitions were suppressed with less than 10% doping (5; 63; 64; 65; 66). In fact the doping level resulting in the highest observed superconducting transition temperature occurs at $x = 0.1$ for $\text{R} = \text{La}$ (5), 0.11 for Pr (63; 64), 0.11 for Nd (65) and 0.1 for Sm (66), with superconductivity usually disappearing around $x = 0.2$ (64; 65; 66).

3.3.2 Negative thermal expansion along the c-axis

NTE along the c-axis is a prominent feature observed previously in the undoped parent compound: the lattice parameter c reaches a minimum at $T = 50$ K, and then expands as the system is further cooled (52). Kimber *et. al.* ascribed the presence of c-axis NTE in the non-superconducting parent compound to the effects of spin-lattice coupling (52). This was based on their observation that both magnetic order and NTE are absent in the superconducting $\text{PrFeAsO}_{1-x}\text{F}_x$, and the proximity of the temperature dependence of the NTE and that of the dome-like feature observed in the intensity of magnetic peaks associated with the ordering of the Fe moments (52). In this context, the observation of NTE in $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ with $x > 0.1$ is surprising, since magnetic order is absent. Fig.3.10(a), (b), and (c) show the temperature dependence of the fractional change in the refined lattice parameters a and c for several concentrations. As seen clearly in Fig.3.10(c), the anomalous NTE along c-axis is observed in all samples up to at least $x = 0.75$. The dashed red lines in (b) and (c), and later (d), are extrapolations based on a Grüneisen fit to the volume defined by a^3 and c^3 for the data at 40K and above.

The Grüneisen model of thermal expansion in solid materials

The temperature dependence of c^3 and the unit cell volume above a certain temperature (50 K for c^3 and 20 K for the cell volume) were fitted using a model

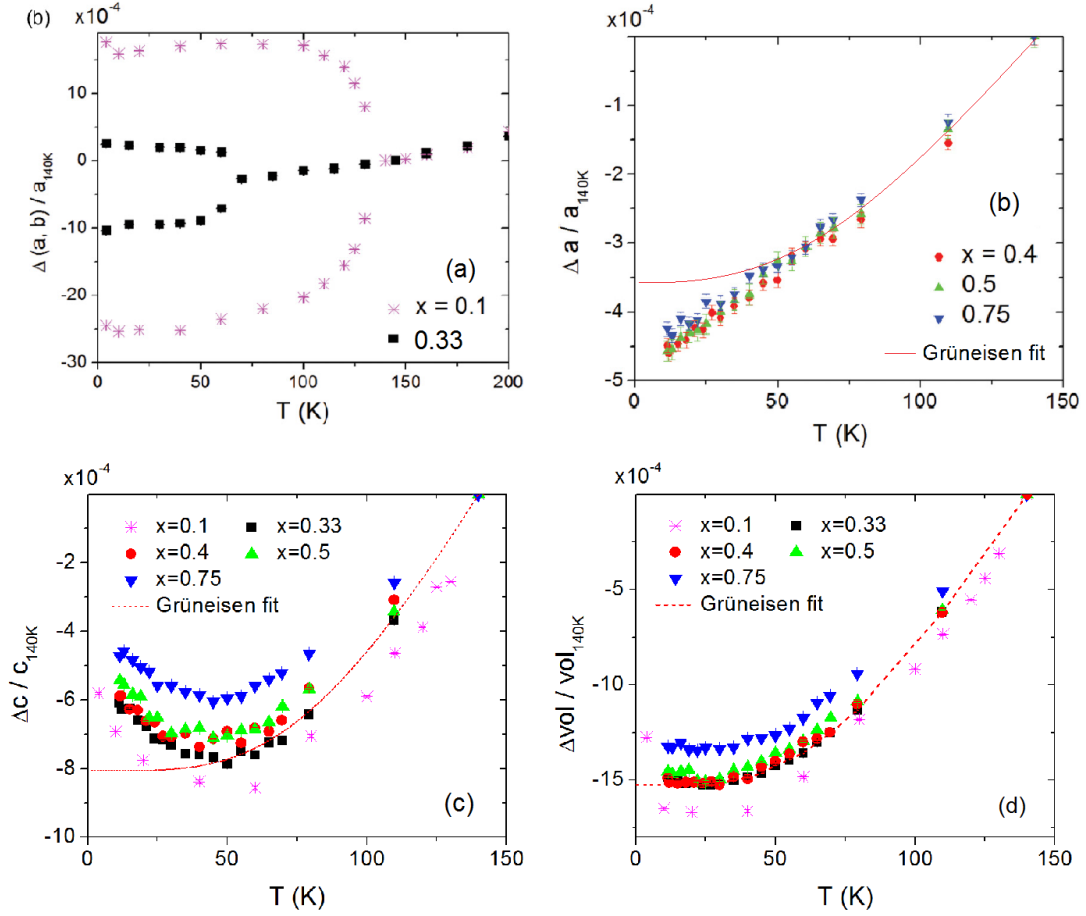


Figure 3.10: Temperature dependence of $\Delta a/a_{140K}$ at 10K for (a): $x = 0.1$ and 0.33 , and (b): $x = 0.4, 0.5$ and 0.75 . The quantity $\Delta a/a_{140K}$ is defined as $(a(T) - a(T = 140 \text{ K}))/a(T = 140 \text{ K})$; (c): Temperature dependence of $\Delta C/c_{140K}$ at 10 K for $x = 0.1, 0.33, 0.4, 0.5$, and 0.75 . $\Delta C/c_{140K}$ is defined in fashion similar to that of a . Negative thermal expansion is clearly visible in all samples for $T \leq 50 \text{ K}$; (d): The unit cell volume of the samples as a function of temperature. The red lines in (b), (c), and (d) are the Grüneisen model predictions for thermal expansion along the axes and cell volume based on fits to data for $T \geq 40 \text{ K}$.

described by Vočadlo *et al.* (67). The model describes the temperature dependence of the volume of a solid as the following.

$$V(T) = V_{T_r} \int_{T_r}^T \alpha(T) dT \quad (3.3)$$

Here, V_{T_r} is the volume at a chosen reference temperature T_r , and $\alpha(T)$ is the thermal expansion coefficient. In our case it is assumed that α is independent of temperature, i.e. $\alpha(T) = \alpha_0$. In order to use the Grüneisen approximations for the zero pressure equation of state, in which the effects of thermal expansion are considered to be equivalent to elastic strain, $V(T)$ takes the following form, to second order.

$$V(T) = \frac{V_0 U}{Q - bU} + V_0 \quad (3.4)$$

Here, $Q = V_0 K_0 / \gamma'$ and $b = (K'_0 - 1)/2$, γ' is the Grüneisen parameter, K_0 and K'_0 are the incompressibility and its first derivative relative to pressure at $T = 0$ K, and V_0 is the volume at $T = 0$ K. U is the internal energy which can be calculated using the Debye approximation as shown here.

$$U(T) = 9Nk_b T \left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^3 dx}{e^x - 1} \quad (3.5)$$

N is the number of atoms per unit cell, θ_D is the Debye temperature.

We allow Q , b , V_0 , and θ_0 to float independently for the fit using Eq.3.4, with an array of experimental $V(T)$ values as input. In the cases for a and c, the cubed values are used as the input value.

In comparison to the Grüneisen prediction, the magnitude of NTE along c-axis is about 0.02% at 10 K. Conversely, lattice parameter a deviates from the Grüneisen in the opposite fashion, and compensates somewhat for the NTE along c-axis, resulting in a smaller NTE as determined by the unit cell volume shown in Fig.3.10(d). This behavior is not uncommon among materials that are anisotropic, where expansion

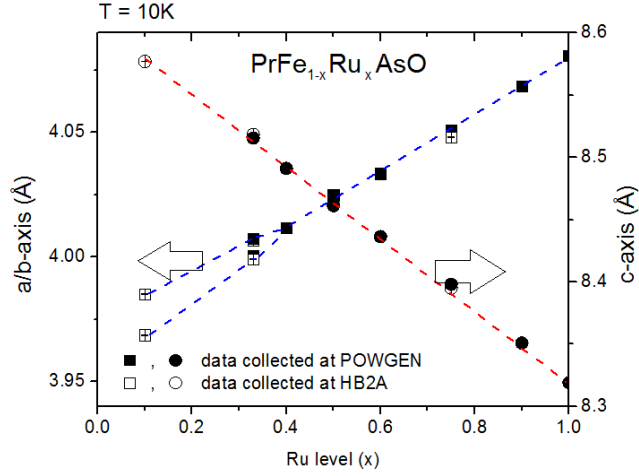


Figure 3.11: Doping dependence of the lattice parameter a and c at 10 K, extracted through Rietveld refinement of NPD data. Plotted in a double y-axis setup.

along one direction is often accompanied by contraction along another in order to preserve the overall volume; graphite is one well known example (68). Despite this compensation, a modest NTE of the unit cell volume is still visible in all samples for $T \leq 20$ K.

The opposing behavior between a and c can be explained by considering that an expansion in the a - b plane forces the unit cell to shorten along c in order to satisfy Fe/Ru-As bonding requirements (46). The in-plane expansion as a function of x has been attributed to the substitution of larger Ru atoms for Fe atoms, which stretches along the a - b plane (46). This behavior can also be observed in the Ru concentration dependence of the two lattice parameters. Fig.3.11 shows the Ru concentration dependence of lattice parameters a , b and c . It is interesting to compare the Ru concentration dependence of a and c to the low temperature thermal variation of the two. In both cases the parameters vary in the opposite direction. The reason for the opposite temperature dependence of a and c remains an open question.

Speculatively speaking the combination of NTE along the c -axis and near conservation of volume may lead to subtle but important changes in the effective magnetic and electronic interactions of the Fe-As layer, both internally and with the

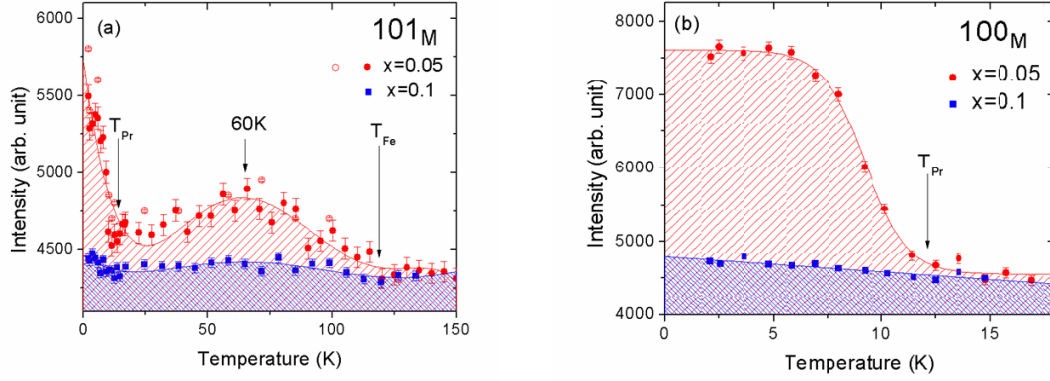


Figure 3.12: (a): The intensity of the 101_M peak as a function of temperature. The AFM ordering of both Pr and Fe are visible in $x = 0.05$ but not $x = 0.1$. The intensity of the 101_M peak reaches a domelike maximum around 60 K for $x = 0.05$. Solid dots represent single data points collected from counting at the center peak position; hollow dots represent normalized data from fits of entire magnetic peaks. The lines and shadings are merely guides to the eye; (b): Intensity of the 100_M peak as a function of temperature, showing the size difference of the Pr moment between $x = 0.05$ and 0.1.

rest of the sample. The existence of c-axis NTE in concentrations without magnetic order suggests that the origin of this behavior might involve more than simply spin-lattice coupling. Even though there are only an inconclusive amount of published data on c-axis' temperature dependence of 1111 materials, the NTE is absent among those which data is accessible, including the superconducting $\text{PrFeAsO}_{0.85}\text{F}_{0.15}$ (52), both the doped and undoped samples of $\text{LaFeAsO}_{1-x}\text{F}_x$ (69; 70), and some other 1111- related compounds such as SrFeAsF (71) and CaFeAsF (72).

3.3.3 Magnetic ordering of Fe and Pr

We now turn to a detailed examination of the magnetic transition that is observed in $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ with 5% Ru substitution. In Fig.3.12 we present temperature dependent measurements of the intensities of the 101_M and 100_M magnetic peaks measured using HB-1A for Ru levels $x = 0.05$ and 0.1. The 101_M peak shows contributions from both Pr and Fe moments while the 100_M peak is only sensitive

to the Pr moments. It is apparent in Fig.3.12(a) and (b) that magnetic ordering of both Pr and Fe exist at $x = 0.05$ but are suppressed at $x = 0.1$. Fe orders antiferromagnetically in the $x = 0.05$ sample at 120K which may be compared to 137 K (18) observed in the undoped PrFeAsO; no AFM order is visible in $x = 0.1$. Evidently in $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$, the magnetic transition is more sensitive to Ru substitution than is the structural transition. In any case, both transitions are not observed for $x \geq 0.33$.

The temperature dependence of the magnetic intensity of the 101_M peak is particularly interesting. As seen in Fig.3.12(a), in the $x = 0.05$ sample the intensity of the 101_M peak reaches a dome-like maximum at $T \sim 60$ K, followed by a modest decrease as the temperature is lowered, increasing again below $T \sim 14$ K, the AFM ordering temperature for Pr. This feature has also been observed in undoped PrFeAsO at $T \sim 60$ K (52). Critical fluctuations in the Pr magnetic subsystem may have contributed to this phenomenon (52).

3.4 μSR results

Zero field (ZF) and longitudinal field (LF) μSR experiments were performed on the GPS spectrometer at the Laboratory for Muon Spin Spectroscopy of Paul Sherrer Institut. Here the findings are presented in two parts, one for the SDW ordering involving FeAs layers, and the other for the magnetic ordering of the Pr moment.

3.4.1 Suppression of spin density wave ordering

The following methods were used to interpret the data. For the ZF-data, the time dependence of the spin-polarization function for a positive, 100% spin-polarized muon in a magnetic sample can be described as:

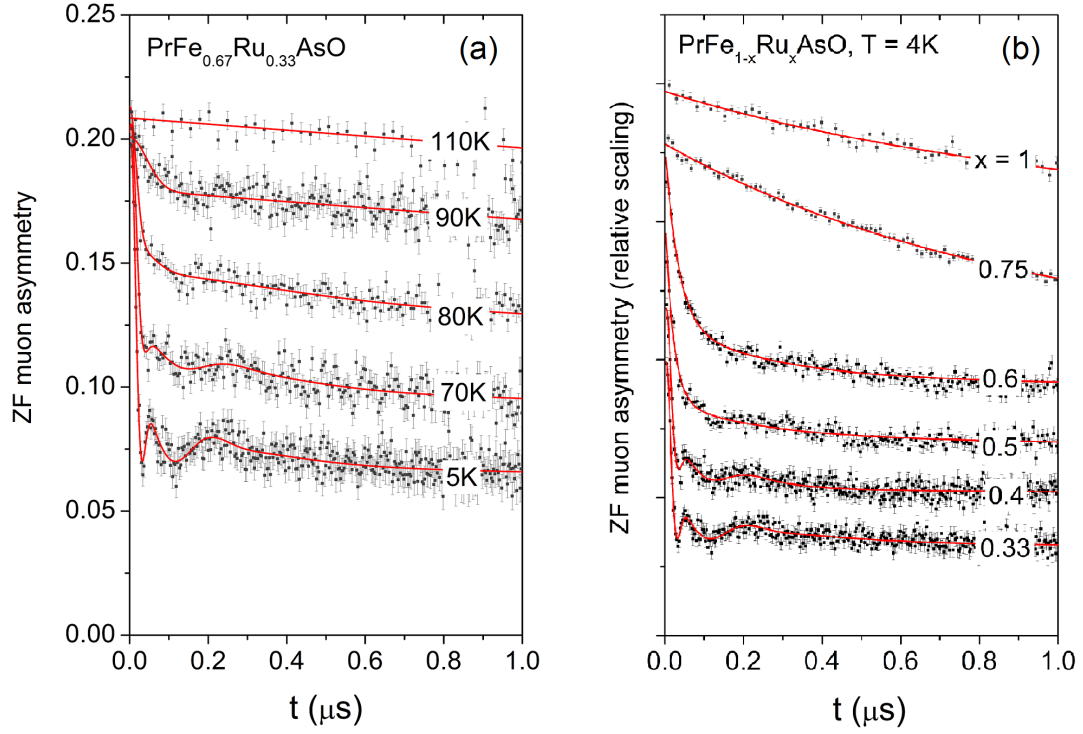


Figure 3.13: Time dependence of ZF- μ SR asymmetry for $x = 0.33$ between 110 K and 5 K, the lines represent the best fit using Eq.3.6. Time dependence of ZF- μ SR asymmetry for $x = 0.33, 0.4, 0.5, 0.6, 0.75$ and 1 at $T = 4$ K. For graphing purposes, each composition is shifted along the vertical axes by an arbitrary constant.

$$\begin{aligned} \frac{A_{ZF}(t)}{A_0} &= (1 - V_m) e^{-\frac{\sigma_N^2 t^2}{2}} \\ &+ \sum_{i=1}^N f_i \left[w_i^\perp F_i(t) e^{-\frac{\sigma_i^2 t^2}{2}} + w_i^\parallel e^{-\lambda_i t} \right] \end{aligned} \quad (3.6)$$

A_{ZF} is the asymmetry of the muon decay and A_0 is the initial muon asymmetry (i.e. $t = 0$). V_m represents the fraction of muons probing a static local field $\mathbf{B}_i$, i.e. the sample's magnetic volume fraction. The index i represents each of N crystallographically-inequivalent muon stopping sites and each stopping site is characterized by a stopping probability f_i , with $\sum_{i=1}^N f_i = V_m$. The two terms in the square brackets reflect the orientation of the internal field with respect to the initial muon spin S_μ direction: transverse for $\mathbf{B}_i \perp \mathbf{S}_\mu$ and longitudinal for $\mathbf{B}_i \parallel \mathbf{S}_\mu$. For powder samples, the ratio of the two terms is related and normalized by $w_i^\perp = 2/3$ and $w_i^\parallel = 1/3$.

The longitudinal component ($\parallel$) can be described by a Lorentzian decay function with relaxation rate λ . For the transverse component ($\perp$), $F_i(t)$ represents the time dependence, and σ_i is the depolarization rate which reflects the second moment of the field distribution $\Delta B_i \equiv (\overline{B_i^2} - \overline{B_i}^2)^{1/2} = \sigma_i / \gamma_\mu$, where $\gamma_\mu / 2\pi = 136$ MHz/T is the muon gyromagnetic ratio. When the muon goes through a local field B_i , for example inside a long range ordered sample, the muon asymmetry displays Larmor oscillations described with $F_i = \cos(\gamma_\mu B_i t)$, with B_i proportional to the mean magnetic order parameter $\langle S(T) \rangle$. In case of a short range ordered sample, the width of the field distribution at the muon site broadens and as a result, the transverse muon fraction yields to a fast decay rate ($\sigma_i \gtrsim 1/\gamma_\mu B_i$), with overdamped oscillations and $F_i = 1$.

For the undoped parent PrFeAsO the ZF- μ SR time spectra are well fitted with $N = 2$ and occupancy $f_1 \approx 75\%$ and $f_2 \approx 25\%$, which reflects the presence of two inequivalent muon sites (73; 74; 75). In the $x = 0.33$ and 0.4 samples, the two frequencies are still detectable, but with f_2 reduced in half. The complementary

missed amplitude gives rise to overdamped oscillations and can be easily fitted as a third additional non-oscillating component $i = 3$, with $f_3 \approx f_2$, $F_3 = 1$ and $\sigma_3 \sim 5\mu s^{-1}$. This change might be simply due to the increase of disorder by Ru.

These three components provide a good fit of the time evolution of the ZF muon asymmetry, as seen in Fig.3.13(a), which shows data for $x = 0.33$ at different temperatures, fitted with Eq.3.6. At higher temperatures the oscillations become overdamped and the transverse amplitude ($\propto V_m$) reduces and vanishes at $T \geq 100K$. Fig.3.13(b) displays the low temperature ZF- μ SR time spectra for all our samples. For $x = 0.5$ and 0.6 the coherent oscillations are absent and the fit uses only 2 components but with $F_1 = F_2 = 1$, suggesting that the increase of Ru/Fe substitution induces field inhomogeneity. Accordingly, the presence of the magnetic phase is reflected by the sizeable decay rate detected corresponding to $\Delta B_1 \approx 40mT$ and $\Delta B_2 \approx 5mT$. The same behavior has also been reported in Ru/Fe substituted LaFeAsO (76) at a similar concentration.

Fig.3.13 shows the components with fast decay rates in samples from $x = 0$ up to 0.6 which are also characterized by the longitudinal fraction $\sum_i w_i^{\parallel} = 1/3$, typical of fully magnetic samples. The lack of a fast decay component in the $x = 0.75$ and 1 samples indicates that Fe moments do not order in those samples. However, for T below $\approx 14K$, the fit of the LF muon asymmetry requires two non-oscillating amplitudes with distinct relaxation rates, as shown in Fig.3.14(a) and (b). This behavior can be attributed to activities in the Pr sublattice around $T_{Pr} \approx 14K$, where there is noticeable features in both the susceptibility and specific heat measurements (50).

To summarize, the temperature dependence of the magnetic volume fraction for all samples is shown in Fig.3.15. We are able to detect ordering in the FeAs layer up to $x = 0.6$. For the construction of a phase diagram later in this chapter, we define T_{SDW} as the temperature at which the magnetic volume fraction is 80%. For $x \leq 0.40$, the magnetic transition temperatures, T_{SDW} , can be directly determined from the evolution of the mean magnetic order parameter $\langle S(T) \rangle \propto B_i(T)$ as

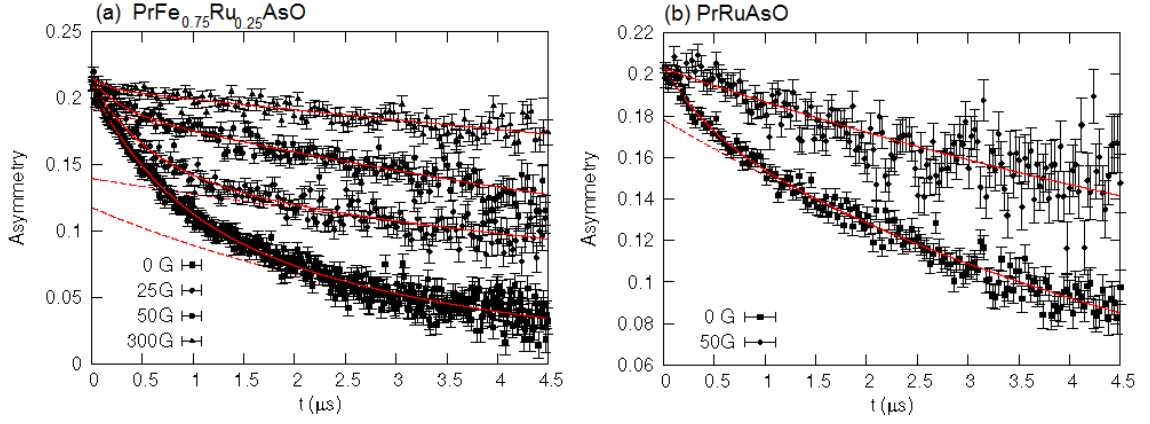


Figure 3.14: LF- μ SR time spectra for (a): $\text{PrFe}_{0.25}\text{Ru}_{0.75}\text{AsO}$ and (b): PrRuAsO , for different external fields $H \parallel \mathbf{S}_\mu$. The lines are fits to the two non-oscillating amplitudes with distinct relaxation rates.

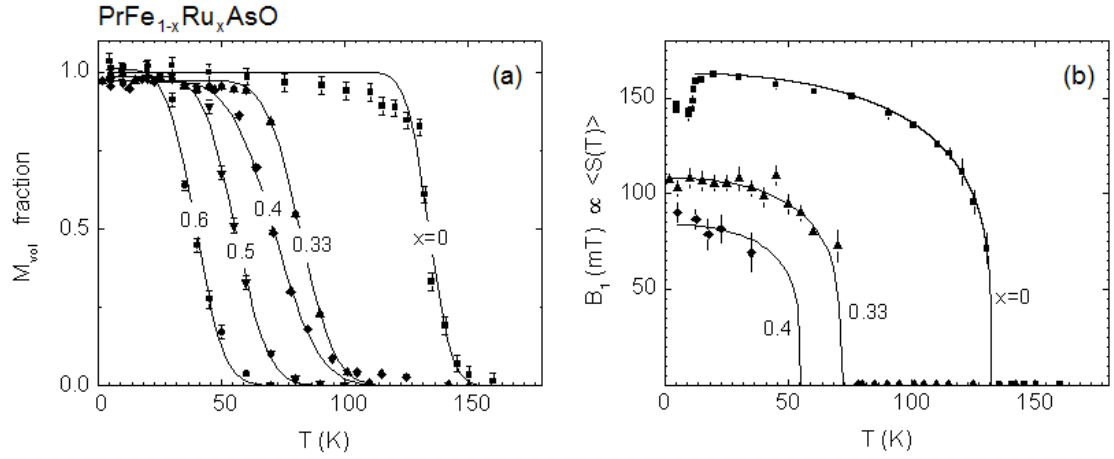


Figure 3.15: (a): Magnetic volume fraction as a function of temperature for $x = 0.33, 0.4, 0.5$ and 0.6 , with the main contribution from SDW ordering. The lines are guides for the eye fits; (b): Temperature evolution of the internal field at the muon site, B_1 , proportional to the mean magnetic order parameter $\langle S \rangle$. The lines are the best fit to a phenomenological mean field-like function as described in the text.

a function of temperature, shown in Fig.3.15(b). The magnetic order parameter $\langle S(T) \rangle$ has been successfully fit to the phenomenological function $\langle S(T) \rangle = S(0)[1 - (T/T_{SDW})^{2.4}]^{0.24}$, which is found to hold generally for 1111 compounds (73). The values of T_{SDW} determined using the two criteria are consistent to within about 2 K.

3.4.2 Persistence of static Pr moments

Previous neutron diffraction measurements did not detect long range ordering (LRO) of Pr in samples with $x \geq 0.1$ (50). However, the μSR data shows that the muon relaxation rate increases below $T \sim 14$ K in $\text{PrFe}_{0.25}\text{Ru}_{0.75}\text{AsO}$, hinting at a possible short range ordered (SRO) state involving the Pr sublattice. Fig.3.14 shows the LF- μSR spectra for $\text{PrFe}_{0.25}\text{Ru}_{0.75}\text{AsO}$ and PrRuAsO . For $x = 0.75$, the muon relaxation function (A_{ZF}) in zero magnetic field consists of two separate components: $A_f e^{-\lambda_f t} + A_s e^{-\lambda_s t}$, where $\lambda_f = 1.4 \mu s^{-1}$ represents the fast decay rate and $\lambda_s = 0.25 \mu s^{-1}$ represents the slower one.

This empirical fitting function mimics the trend expected for a quasi-static Kubo-Toyabe relaxation (77) with a Lorentzian distribution of internal fields having HWHM $\Delta B = \lambda_f / \gamma_\mu \sim 2$ mT and characterized by a slow dynamics with correlation time $\tau \sim 1/\lambda_s$. Notably, the HWHM of the $x = 0.75$ sample is nearly 20 times lower than for the $x = 0.6$ sample. In the static case ($\tau \rightarrow \infty$) $A_f = 2A_s$, but A_s is expected to grow as dynamics sets in.

The onset of longitudinal fields decreases the fast decay rate and increases the slow decay rate in both samples. For $x = 0.75$, a field of $H = 300$ G completely suppresses the faster (static) component of the muon relaxation and only leaves the slower dynamical component. This suggests that the ordering is quasi static. The observed values of ΔB are consistent with the dipolar field from Pr moments ($\sim 3.6 \mu_B$). Fig.3.14(b) shows the same for $x = 1$. In this case a longitudinal field $H = 50$ G completely suppresses the faster (static) component of the zero field relaxation and

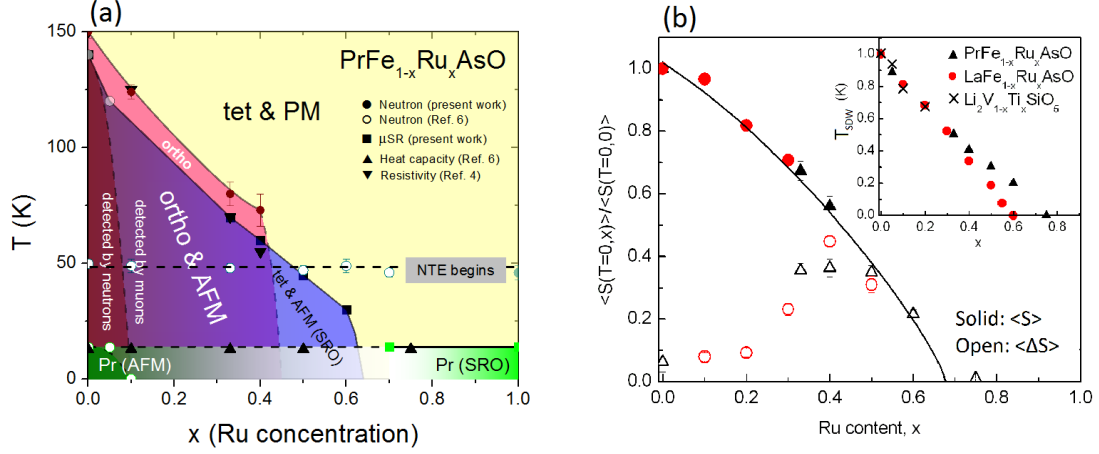


Figure 3.16: (a): A phase diagram for $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ constructed using data presented in this paper and also data from Ref. 50. (tet: Tetragonal; ortho: Orthorhombic; AFM: Antiferromagnetic; PM: Paramagnetic; SRO: Short range order; NTE: Negative thermal expansion) The location of the structural transition is defined by the orthorhombicity analysis discussed in the text; (b) The Ru concentration dependence of the staggered magnetization at zero temperature $S(0, x)$ (solid symbols) and of its distribution width $\Delta S(0, x)$ (open symbols) in $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ (triangles) and $\text{LaFe}_{1-x}\text{Ru}_x\text{AsO}$ (circles, from Ref. 76). The data are normalized to the value of the undoped member $S(0, 0)$; (b,inset): Doping dependence of magnetic transition temperatures, T_{SDW} , normalized to the undoped value for $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$, $\text{LaFe}_{1-x}\text{Ru}_x\text{AsO}$ and $\text{Li}_2\text{V}_{1-x}\text{Ti}_x\text{SiO}_5$.

the residual dynamics is a little bit faster. The difference between the $x = 0.75$ and 1 amplitude weights, field dependences and decay rates of the faster component might arise from the fact that in the $x = 0.75$ material an extra contribution from Fe fluctuations, indirectly driven by the Pr fluctuations, is possible. It should be noticed that such fluctuations are absent in the $\text{LaFe}_{1-x}\text{Ru}_x\text{AsO}$ for $x > 0.6$ where no Pr is present (76).

3.5 Phase diagram

Fig.4.20(a) displays the T versus x phase diagram for $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ as determined by neutron diffraction and μSR , with some additional points determined from

anomalies detected in specific heat and resistivity measurements. Using the orthorhombicity criterion described above, the tetragonal to orthorhombic structural transition is detected by neutron scattering for x up to 0.4. Long range magnetic order as detected by neutron diffraction is observed only for $x \leq 0.1$. Conversely, from the μ SR data one detects signs of static moments in the FeAs layers to approximately $x = 0.6$, and evidence for Pr moments up to $x = 1$. To reconcile these observations it must be noted that the neutron measurements of magnetic Bragg peaks are sensitive to spatially dependent long range order. Conversely, muons provide a sensitive probe of local magnetic fields, and therefore may detect local fields associated with static short range order, i.e. with magnetic moments that fluctuate slowly (correlation times less than $1 \mu s$) and with a short magnetic coherence length (even less than 10 lattice spacings) (78). Such SRO does not contribute to the magnetic Bragg peaks detected via neutron diffraction.

The muon data for samples with $0.4 \leq x \leq 0.6$ exhibits overdamped oscillations and the μ SR asymmetry displays a component with a fast decay rate ($\sigma_1 \sim 50 \mu s^{-1}$), indicating that the system is still magnetically ordered but the muons' spin precessions have become incoherent. Conventionally, this implies that the correlation length of the Fe ordered domains has become shorter than about 10 unit cells (78). This suggests a transition from LRO to SRO as detected by muons. This is indicated by a dashed vertical line in Fig.4.20(a) around $x = 0.4$, which interestingly coincides with the suppression of the structural transition as detected by neutrons. The fact that the progressive reduction of T_{SDW} is closely accompanied by the reduction of T_S hints at significant magneto-elastic coupling in the FeAs layers.

Our data agrees with that previously published on $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ including Ref.(46) and (50). The μ SR data provide new clues for the lack of superconductivity after the suppression of structural and magnetic ordering in the material. For instance the μ SR observed persistence of static moments despite the absence of LRO implied by the neutron measurements.

Fig.4.20(b) shows the evolution of the magnetic order parameter $\langle S(T \rightarrow 0) \rangle$ vs x as determined by μ SR. The spin dilution caused by Ru/Fe substitution reduces both the ordering temperature T_{SDW} and the moment size gradually. The complete suppression of the SDW ordering is determined to be around $x = 0.6$ which is similar to the concentration inferred from previous resistivity measurements (46). Perhaps coincidentally, this is very close to the disruption of superconductivity by Ru/Fe substitution in F-optimally doped 1111 (79; 80; 81; 82). This value may be very significant as discussed below within the framework of a $J_1 - J_2$ model.

3.5.1 $J_1 - J_2$ picture

A proper description of the magnetism in the Fe-pnictides must account for the fact that the systems are itinerant, however despite this many of the main features can be understood in terms of Hamiltonian models related to local spins. The two dimensional $J_1 - J_2$ model with Heisenberg nearest neighbor (J_1) and next nearest neighbor (J_2) interactions on a square lattice (83) exhibits a striped phase for $J_2/J_1 \geq 1/2$. Moreover, any non-zero coupling to the lattice results in an Ising-nematic transition associated with a rectangular lattice. It can be argued on the basis of symmetry that spin driven Ising nematic order must be accompanied by both a structural phase transition and orbital order (84), and that nematic order may arise from a correlation driven electronic instability. In any case, the close association of the orthorhombic structural transition and striped antiferromagnetic order in the iron pnictides inspired many applications of the $J_1 - J_2$ model to explain the underlying physics (85; 86; 87; 88; 89; 90). Caution must be exercised in applying the $J_1 - J_2$ model to iron pnictide systems. Inelastic neutron scattering experiments (91; 92; 93; 94) and first-principles calculations (95) found that fitting observed magnetic excitations using the $J_1 - J_2$ Hamiltonian led to parameters that were physically incompatible with the known ordering scenarios and incapable of giving an acceptable explanation of the response functions. Since then there has been much

work (96; 97; 91; 98) showing that a minimal effective model must also include a biquadratic exchange term $K(S_1 \cdot S_2)^2$ and a small interplane coupling J_c .

The biquadratic exchange term must exist in the system and also accounts at least partially for the expected effects of itinerancy. With this Hamiltonian the observed magnetic excitations can be explained with physically reasonable fitted parameters. Within the context of this expanded model, the scenario for magnetic and structural order remain the same as that expected for the $J_1 - J_2$, with some minor renormalizations of the parameters (96).

As the moment size is reduced the significance of the biquadratic term is also diminished and one expects that the $J_1 - J_2$ model can provide an even better description of the system. In this context, it is very interesting to consider the vanishing of detectable magnetic order near $x = 0.6$. In the simplest scenario for magnetic dilution, magnetic order is expected if the concentration of magnetic ions (here $1 - x$) is greater than or equal to the percolation concentration of the lattice. When the interactions are of the same magnitude, the percolation concentration of the $J_1 - J_2$ model should be essentially the same as the square lattice with nearest neighbor and next nearest neighbor connectivity. This model leads to a percolation concentration for magnetic ions almost exactly at the value $1 - x = 0.4$ (51). The fact that this coincides with the disappearance of static magnetism in $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ is a strong indicator that the core physics of the $J_1 - J_2$ model is at play. We note that the J_1 only model exhibits percolation at $1 - x = 0.59$ (51). The inset of Fig.4.20(b) compares the Ru dependence of T_{SDW} in $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ to two other systems that also cited the $J_1 - J_2$ model for magneto-elastic coupling, namely $\text{LaFe}_{1-x}\text{Ru}_x\text{AsO}$ (76) and $\text{Li}_2\text{V}_{1-x}\text{Ti}_x\text{SiO}_5$ (99), the latter being an archetype of the $S = 1/2$ $J_1 - J_2$ square lattice model. The close association of the structural transition with the magnetic order is also explained naturally by the Ising-nematic scenario predicted for localized spins in the $J_1 - J_2$ model. If one takes into account the presence of a magneto-elastic coupling in the system, the structural transition is closely linked to the occurrence of

a spin nematic phase at T_S which anticipates the breaking of the rotational symmetry that is associated with the magnetic transition at T_{SDW} .

As discussed earlier, μ SR shows that SRO of the Pr moments in $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ persists up to $x = 1$. This is consistent with the anomalies observed in the susceptibility and specific heat measurements around $T_{Pr} \sim 14\text{K}$. The ZF- μ SR results indicates a moderately fast depolarization rate in the muon asymmetry around the same temperature. This implies the presence of a broad field distribution generated by a non-collinear arrangement of the Pr moments. LF- μ SR spectra shown in Fig.3.14 suggests that the magnetic phase is mainly quasi static. Notably, the NTE seen in the c-axis also persists over the entire range of Ru concentrations. Although T_N^{Pr} and T_{NTE} are markedly different, the continuous presence of both throughout the entire range leads one to speculate that there is a relation between the ordering of the Pr sublattice and the NTE, and if the latter is driven by magneto-elastic coupling as suggested by Ref. (52), the Pr moments are relevant. Indeed, as shown in Fig.4.20(b), the Ru dependence of the quantities T_{SDW} and $\langle S(0) \rangle$ in $\text{LaFe}_{1-x}\text{Ru}_x\text{AsO}$ is similar to that seen in $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$, yet the NTE effect has not been observed in $\text{LaFe}_{1-x}\text{Ru}_x\text{AsO}$ (100).

3.5.2 Lack of superconductivity

The lack of superconductivity in $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ is not common among iron pnictides where both the structural and magnetic transitions have been suppressed. For this we need to first try to understand what are the general necessary conditions for superconductivity to emerge. Although superconductivity almost always emerges in these materials when both the structural and magnetic transitions are suppressed, there are theories suggesting that an additional necessary condition is the persistence of magnetic fluctuations (101). One can speculate that mutually uncorrelated but effectively frozen Fe spin clusters might exist in randomly diluted $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ at low temperatures. As a consequence a static moment might be detected by a local

probe such as μ SR, and the absence of significant magnetic fluctuations could impede the emergence of a superconducting ground state. On the other hand, there have been reports on superconductivity being observed in the collapsed tetragonal phase of $\text{Ca}_{1-x}\text{R}_x\text{Fe}_2\text{As}_2$ ($\text{R} = \text{Sr}, \text{Pr}, \text{or Nd}$ (102; 101; 103)), which is surprising since magnetic fluctuations are absent in the collapsed tetragonal phase of the undoped CaFe_2As_2 (101). Another subject of interest is the coexistence of superconductivity and slow glass-like spin fluctuations in $\text{NdFeAsO}_{1-x}\text{F}_x$ (104). These new discoveries provoke further investigations of multiple phases as the source of superconductivity are necessary.

Even though the current understanding of spin fluctuations and superconductivity may not be sufficient to fully explain the lack of superconductivity in $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$, some empirical conclusions can be reached by comparing the experimental observations to other doped iron pnictides. For instance, superconductivity in iron pnictides has been successfully induced by using many different methods of doping, at almost every single element site. Consider 122 materials such as BaFe_2As_2 , where superconductivity can be induced by hole doping (K/ or Na/Ba substitution), electron doping (Co/ or Ni/Fe substitution), or isoelectronic substitution (Ru/Fe or P/As substitution) (26; 41; 105). For 1111 compounds the results are very similar for electron and hole doping (26), except for some materials where isoelectronic substitution is used. These materials include $\text{CeFeAs}_{1-x}\text{P}_x\text{O}$ (41), $\text{LaFe}_{1-x}\text{Ru}_x\text{AsO}$ (76), and $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ of this investigation (50). In all three cases, isoelectronic substitution lead to the suppression of the structural and magnetic transitions without the onset of superconductivity. It should be noted that although both P/As and Ru/Fe substitution are considered isoelectronic substitution, there exist fundamental differences between the two. Both methods introduce chemical pressure into the system, however P/As substitution also changes the Fe/As bond covalency (106) but Ru/Fe substitution does not. On the other hand Ru/Fe substitution delocalizes the 3d electrons in Fe (42), but P/As substitution does not. All in all, both methods of isoelectronic substitution suppress the ordering of Fe moments, but only in some cases

lead to the onset of superconductivity, which includes the 122 examples given earlier, and also P/As substituted $\text{LaFeAs}_{1-x}\text{P}_x\text{O}$, where superconductivity is observed at $x = 0.25$ (106). Since the behavior of superconductivity among iron pnictides have been demonstrated to be rather material specific, a general conclusion among different methods of doping is difficult.

There are two pieces of empirical facts that can help narrate the absence of superconductivity in these materials. First, despite the fact that P/As and Ru/Fe substitutions act on the system in different ways, coincidentally all isoelectronic substitutions have been found to be less effective than their carrier doping counterparts, i.e. a relatively higher % of isoelectronic substitute is needed in order to suppress the structural and magnetic transitions in the same material. Generally only 10-20% of hole or electron doping is needed to suppress the magnetic ordering (26), compared 30-40% for isoelectronic substitution (76; 50; 41). Second, atomic substitutions in the FeAs layer can lead to less than optimal conditions for superconductivity, i.e. the resulting maximum T_C is lower in materials doped in the FeAs layer than those doped in the rare earth layer. For example, the T_C in the optimally Co-Fe doped PrFeAsO is 11 K (107), whereas in the optimally F-O doped T_C is 52 K (26), or in the optimally Ni-Fe doped SmFeAsO T_C is 9 K (108), compared to the optimally F-O doped where T_C is 43K (26). It is believed that atomic substitutions in the conducting FeAs layer introduces lattice distortions and disorders which can be detrimental to superconductivity (41; 50; 109).

Therefore, it is reasonable to assume that the lack of superconductivity in these materials can be attributed to a combination of these two reasons. In plainer words, it is possible the lack of superconductivity in $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ is due to isoelectronic substitution failing to effectively suppresses the magnetic ordering before introducing a critical level of disorder that prohibits superconductivity from ever emerging in the FeAs layer.

Chapter 4

Helimagnetism in $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$

The emerging popularity in solid-state devices of spintronics during the last decade have sparked interests in materials with novel magnetic properties. This market generated interest conveniently coincides with the relatively recent discovery of the skyrmion, a 2D topological magnetic object that forms in specific materials under certain conditions (110; 111; 112; 113; 114). Many of these materials are able to form such incommensurate magnetic objects due to the presence of Dzyaloshinskii-Moriya (DM) interactions, which stems from the lack of inverse symmetry in the crystal structure (115; 116; 117). One of such structures is the $P2_13$ space group. One of the families of interest within this space group is the B20 cubic family, which includes FeGe (118; 119), FeSi, MnGe, and MnSi (120; 121). Fig.4.1 shows the standard B20-structure labeled for $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$.

4.1 B20 cubic helimagnets

Due to the presence of Dzyaloshinskii-Moriya (DM) interactions which arose from the lack of inversion symmetry in the B20 crystal structure (115; 116; 117), these materials also form a long-wavelength incommensurate helimagnetic order below the Néel temperature, often in lengths many times the unit cell (116; 119; 121). Helimagnetism is a form of incommensurate magnetic ordering where the magnetic

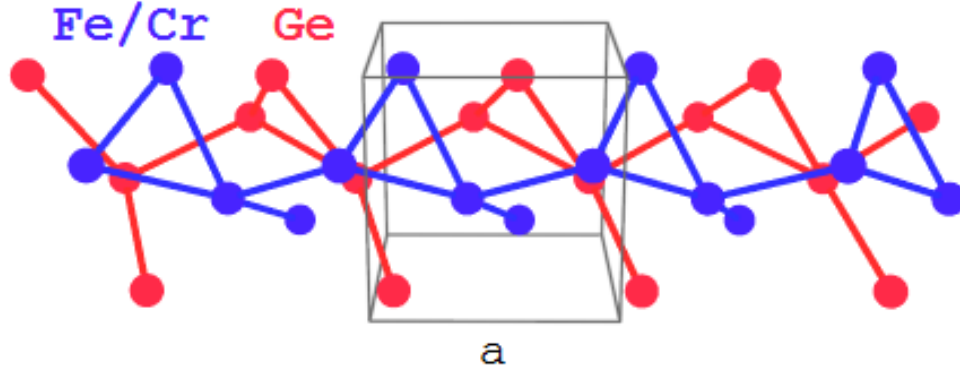


Figure 4.1: Crystal structure of $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ ($P2_13$, #129).

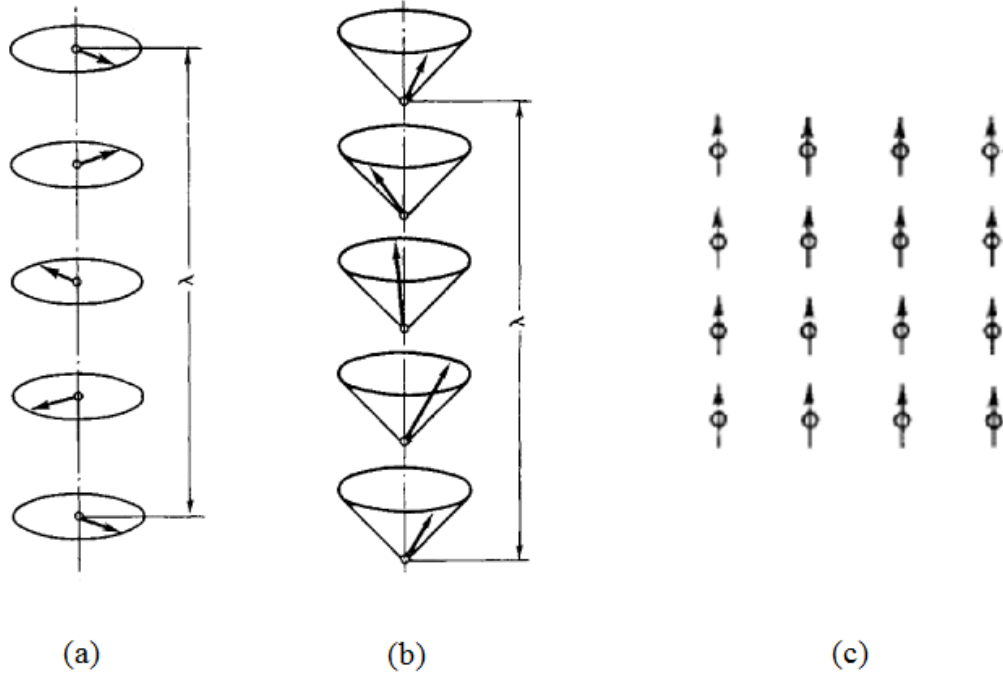


Figure 4.2: An illustration of the 3 possible magnetic structure for FeGe, (a): helical, for $H < H_{C1}$; (b): conical, for $H_{C1} < H < H_{C2}$; and (c): ferromagnetic, in external fields larger than $H_{C2} < H$. λ is the length of the helix and is 700 Å for FeGe. Illustration taken from Ref.(122).

moments slowly rotate around the propagating direction of the series. Fig.4.2(a) provides a graphic illustration of the helical magnetic structure, with each arrow representing a single magnetic moment. The length of the helix (λ) is often much larger than the unit cell, as in FeGe λ is around 700 Å (119).

The understanding of helimagnetism in B20 materials has been an ongoing effort spanning the past few decades (118; 119; 120; 121). Among the materials, much focus has been dedicated to two of the archetypes, MnSi and FeGe. Though sharing the identical crystal structure, the helimagnetic ordering in FeGe and MnSi behave differently from each other in many subtle ways. For example the helimagnetic ordering in FeGe has a much longer wavelength of 700 Å compared to MnSi's 180 Å, and orders at a much warmer 278 K compared to MnSi's 30 K (119; 121). In both cases, the propagating direction of the helix is fixed by a weak anisotropy in the crystal, and a small field H_{C1} is able to overcome the anisotropy, and fix the helix direction to the direction of the field. Between H_{C1} and another critical field H_{C2} the system is in a conical phase (123). The pitch of the cone (θ) is determined by $\sin\theta = H_{\parallel}/H_{C2}$, where $H_{\parallel}$ is the applied field's component along the helix direction (124). The magnetic structure becomes ferromagnetic when the applied field exceeds H_{C2} . Fig.4.2 provides an illustration for all of the 3 possible magnetic structures.

The extent of investigation for FeGe has been somewhat limited due to an experimental obstacle: the synthesis of the material. B20 cubic FeGe is difficult to synthesize due to the presence of multiple metastable structures (125; 126). There are at least 3 known stable structures for FeGe, including the hexagonal CoSn type which orders antiferromagnetically at 410 K, the monoclinic CoGe type which orders antiferromagnetically at 340 K, and finally the B20 cubic type (125). Both the monoclinic and the hexagonal structures have been cited as more stable than the B20 cubic structure, making the synthesis of B20-FeGe a difficult process (125; 126).

Indeed only small single crystals of B20-FeGe with sizes no larger than 1mm^3 have been reported, most synthesized using different variations of the vapor transfer method (127; 128). Fig.4.3 shows one of the published SANS data on FeGe from

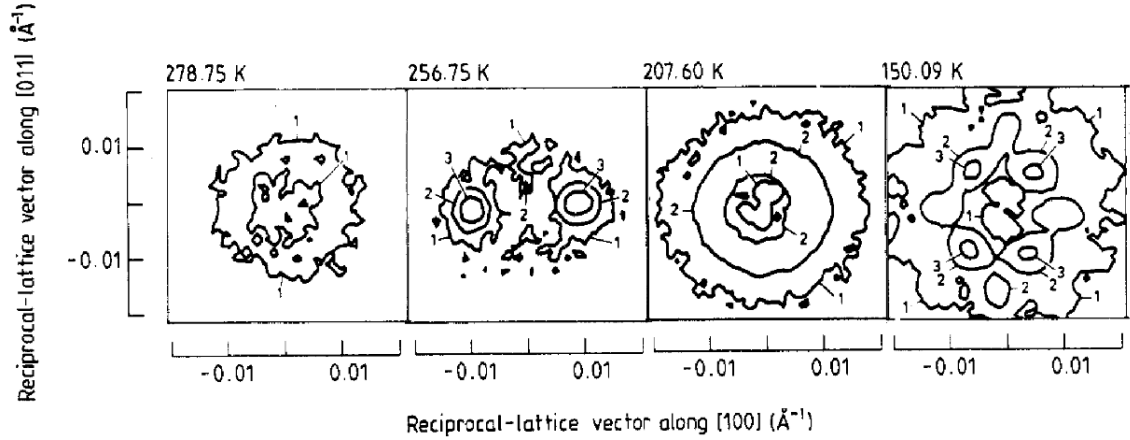


Figure 4.3: Shown here is an excerpt from Ref. (119): the temperature dependent SANS data for single crystal FeGe.

1989. However there is still no known way to reliably synthesize larger quantity of FeGe for neither single crystals or polycrystals. Nevertheless there have been a number of highly cited papers on FeGe that have chosen the different approach to study FeGe as thin films (129; 97; 130; 131). Nonetheless certain information can still only be obtained effectively with a single crystal sample that is both voluminous and phase pure, such as for an inelastic neutron scattering measurement. Therefore, the stabilization of the B20 structure of FeGe remains an important riddle to be solved.

For this reason we are motivated to search for other B20-type materials that can potentially be used as a structural template for the synthesis of B20-FeGe. CrGe is a known B20-type paramagnet with no magnetic ordering down to at least 2K (132), and has been described as a near-ferromagnet (132). Unlike FeGe, CrGe does not have other metastable structure and is relatively easy to synthesize. Moreover, $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ is also a known compound with some properties already published such as the magnetic susceptibility (133). $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ was originally reported as ferromagnetic for $x \leq 0.3$ and paramagnetic for $x \geq 0.3$ (133). There was no mention of helimagnetism in the series. We decide to systematically reinvestigate the series with magnetic susceptibility measurements accompanied small angle neutron scattering experiments (SANS).

4.2 Existing theoretical model

There have been studies on the doping dependence of helical ordering in B20 compounds, including $Mn_{1-x}Fe_xGe$ (134), $Fe_{1-x}Co_xSi$ (124), $Mn_{1-x}Fe_xSi$ (135), $FeSi_{1-x}Ge_x$ (136; 137), and possibly others. A detailed theoretical model that interprets the principal interactions of B20 magnets have been developed by Maleyev (123; 138) based on previous work in Ref.(139) and (140). The helix vector is determined by the competition between the DM interaction (D) and the exchange interaction, or sometimes referred to as the spin-wave stiffness (A), i.e. $k = SD/A$, where S is the unit cell spin and can be calculated by $M = g\mu_B S/v_0$, where M is the magnetization, g is the Landé g-factor ≈ 2 , and v_0 is the unit cell volume (123; 138; 124; 135). For FeGe magnetic moment per spin is $\approx 0.8 \mu_B$ (141), and with 4 magnetic ions per unit cell, $S = 0.8 \times 4/2 = 1.6$.

The Maleyev model also provides a description for the spin configuration of the materials, based on the consideration of 6 principal interactions: (i) conventional exchange interaction (EX), (ii) the DM interaction (DM), (iii) the anisotropic exchange interaction (AE), (iv) the magnetic dipolar interaction (D), (v) the Zeeman energy (Z), and (vi) the cubic anisotropy (123). The model's interpretation of the spin configuration of B20 materials in magnetic field and the spin-wave spectrum is based on the first 5 interactions. The cubic anisotropy is associated with the origin of the spin-wave gap and is beyond the scope of this study. The Hamiltonian of the overall system, and individual energy of each interaction in q-space as described by the model are listed as follow (123). Here $\mathbf{S}_q$ is the total spin of the unit cell in q-space.

$$H = H_{EX} + H_{DM} + H_{AE} + H_D + H_Z \quad (4.1)$$

$$H_{EX} = \frac{1}{2} \sum J_q \mathbf{S}_q \cdot \mathbf{S}_{-q} \quad (4.2)$$

$$H_{DM} = \sum iD_q \mathbf{q} \cdot [\mathbf{S}_q \times \mathbf{S}_{-q}] \quad (4.3)$$

$$H_{AE} = \frac{1}{2} \sum_{\nu=x,y,z} F_q q_\nu^2 S_q^\nu S_{-q}^\nu \quad (4.4)$$

$$H_D = \frac{\lambda_0}{2} \sum [(\mathbf{S}_q \cdot \hat{q})(\mathbf{S}_{-q} \cdot \hat{q}) - \frac{1}{2}(\mathbf{S}_q \cdot \mathbf{S}_{-q})] \quad (4.5)$$

$$H_Z = \sqrt{N} \mathbf{H} \cdot \mathbf{S}_{q=0} \quad (4.6)$$

From this framework the model is able to relate some of the principal interactions including A and F to the aforementioned critical fields H_{C1} and H_{C2} , by the following equations.

$$g\mu_B H_{C1} \approx \frac{Fk^2}{2} \quad (4.7)$$

$$g\mu_B H_{C2} = Ak^2 \quad (4.8)$$

Furthermore please note that D and A can be related by $k = SD/A$ as stated earlier. This provides us with 3 quantities that can be experimentally measured, namely k , H_{C1} , and H_{C2} , and use this remarkably simple model is able to calculate for A , D , and F , as is the case for Ref. (124), (135), and (134). From here on we report the effect of Cr doping on the synthesis and helimagnetism of FeGe. We present our data and findings on $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ from magnetic susceptibility measurements, X-ray scattering (XRD), neutron powder diffraction (NPD) and small angle neutron scattering (SANS).

For this research effort, one publication with tentative title “Structural stabilization and suppression of helical order in FeGe by Cr doping” has been planned for submission in 2015.

4.3 Sample synthesis

In order to synthesize $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$, polycrystals of cubic CrGe is needed. Ref. (132) and (142) describe the method to prepare cubic CrGe powder. In short, pieces of



Figure 4.4: Shown here is a photo of the one of the $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ powder samples. This vial contains about 4 g of $\text{Fe}_{0.97}\text{Cr}_{0.03}\text{Ge}$.

metallic Cr and Ge are arc-melted in an 1:1 ratio, then crushed and grounded into fine powder, and finally pressed into a pellet. The pressed powder pellet is then annealed for 100 h at 600 C. Once the powder is verified by X-Ray diffraction (XRD) to be entirely in the B20 cubic phase, it is mixed with arc-melted and crushed stoichiometric Fe-Ge powder to match the desired ratio for each member of $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$. The powder mixture is then pressed and annealed for a final time in the according temperature depending on x , as reported in Ref. (133):

For $x < 0.1$: 600 C for 100 h;

For $0.1 < x < 0.3$: 800 C for 50 h, then 600 C for 50 h;

For $0.4 < x$: 800 C for 100 h.

Fig.4.4 shows a photo of $\text{Fe}_{0.91}\text{Cr}_{0.09}\text{Ge}$ powder sample used in this study.

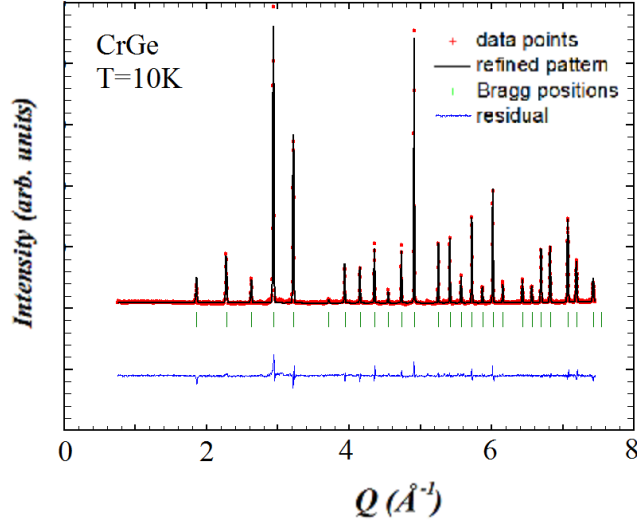


Figure 4.5: Refined neutron powder diffraction data of CrGe collected at 10 K.

4.3.1 Properties of CrGe

Before the final annealing process of $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ samples, it is essential to confirm the quality of the CrGe polycrystals. Neutron powder diffraction experiments were performed on the samples, producing the refined pattern shown in Fig.4.5.

There have been interests in the near-ferromagnetic paramagnetic behaviors of CrGe. Ref.(132) observed a maximum at $T = 50$ K in their magnetic susceptibility measurement, and cited the paramagnon theory for near-ferromagnetic materials proposed by Beal-Monod to explain the feature. Fig.4.6(c) shows one of the examples used in Ref. (143), $\text{CeIn}_{1.5}\text{Sn}_{1.5}$. Fig.4.6(a) shows the original data published in Ref. (132) compared to our data in (b). In comparison, our data does not show the same relatively sharp peak around 50 K, but the wide downturn that centers around the same temperature range $T = 50$ K remains. The original sharper feature around $T = 50$ K is likely to be related to the para-antiferromagnetic transition of molecular oxygen that was present in the system (144). Moreover we also observed additional upturn for $T < 10\text{K}$, which further resembles the magnetic susceptibility data of $\text{CeIn}_{1.5}\text{Sn}_{1.5}$. We should also mention that in the NPD data for CrGe shown in

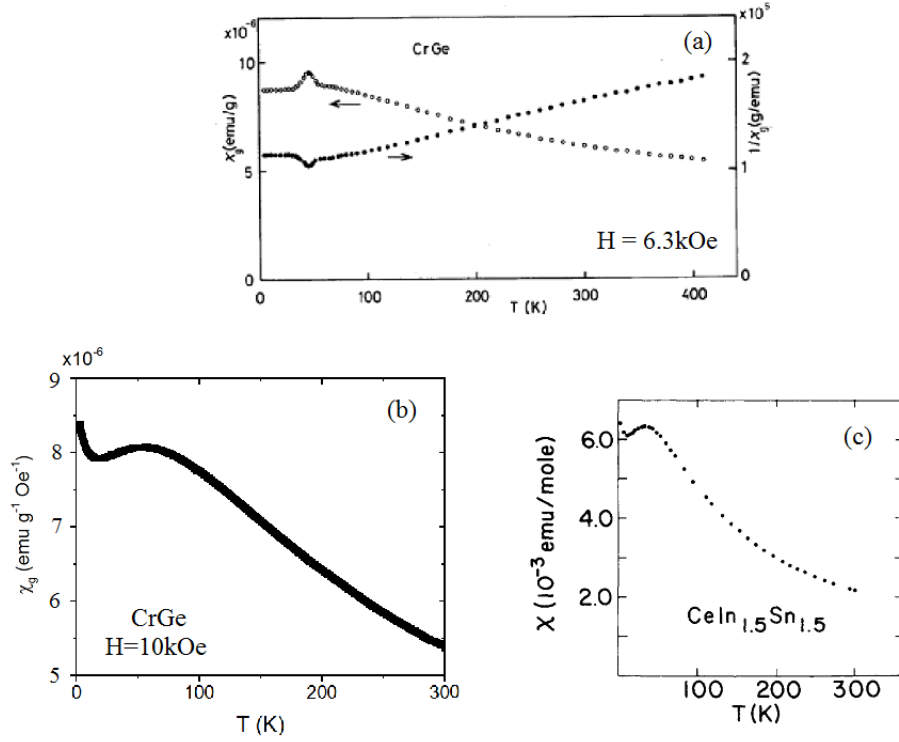


Figure 4.6: Shown here is the temperature dependence magnetic susceptibility of CrGe in (a): published by Sato et al. in Ref. (132), and (b): from the current work; (c): temperature dependence magnetic susceptibility of CeIn $_{1.5}$ Sn $_{1.5}$, a near-ferromagnetic paramagnetic material included by Ref. (143).

Fig.4.5, no magnetic diffraction peaks were observed, likely due to the weakness of the magnetic moment, and the relatively large nuclear peaks that mask the same Q where the ferromagnetic peaks might be, if any. Though this is not the focus of this study, a future investigation into the magnetic behavior of CrGe is recommended.

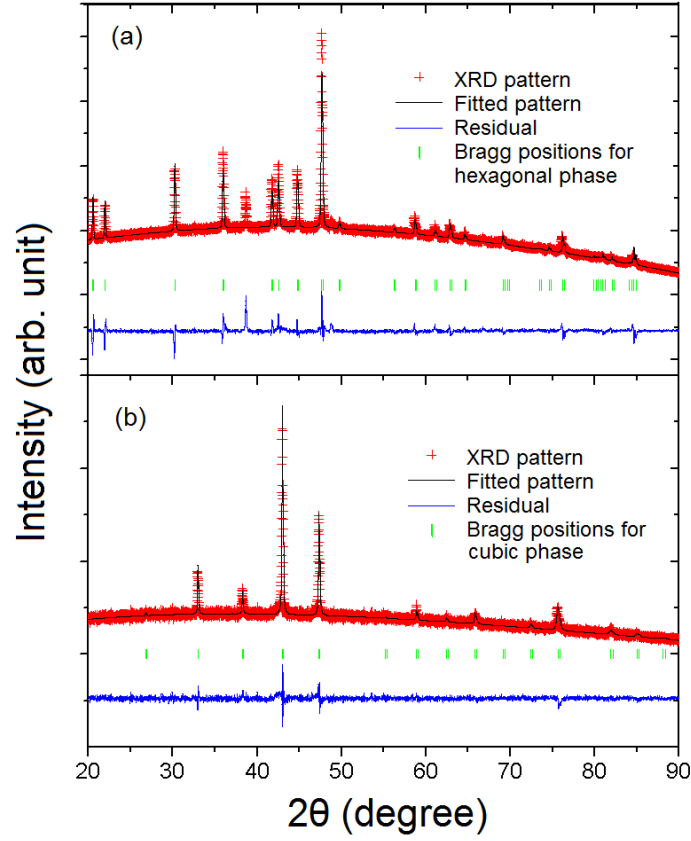


Figure 4.7: The room temperature XRD pattern for (a): stoichiometric mixture of Fe-Ge annealed at 600 C for 100 h without the presence of cubic-CrGe; (b) stoichiometric mixture of Fe-Ge and cubic CrGe ($Fe_{0.97}Cr_{0.03}Ge$) annealed together at 600 C for 100 h using the method stated in the text, notice that the material is now almost entirely cubic, as opposed to mostly hexagonal in (a).

4.4 Temperature and doping dependence of lattice parameters

Fig.4.7(a) shows the room temperature X-Ray pattern for a stoichiometric Fe-Ge that was annealed without any cubic CrGe added. The resulting pattern contains multiple phases of Fe-Ge for which the hexagonal phase is the most dominant. In contrast, Fig.4.7(b) shows the XRD pattern for $Fe_{0.97}Cr_{0.03}Ge$, which is almost entirely in the B20-phase. This confirms that Cr doping plays a crucial role in stabilizing the cubic structure and converting the non-cubic polymorphs of FeGe into the B20-phase.

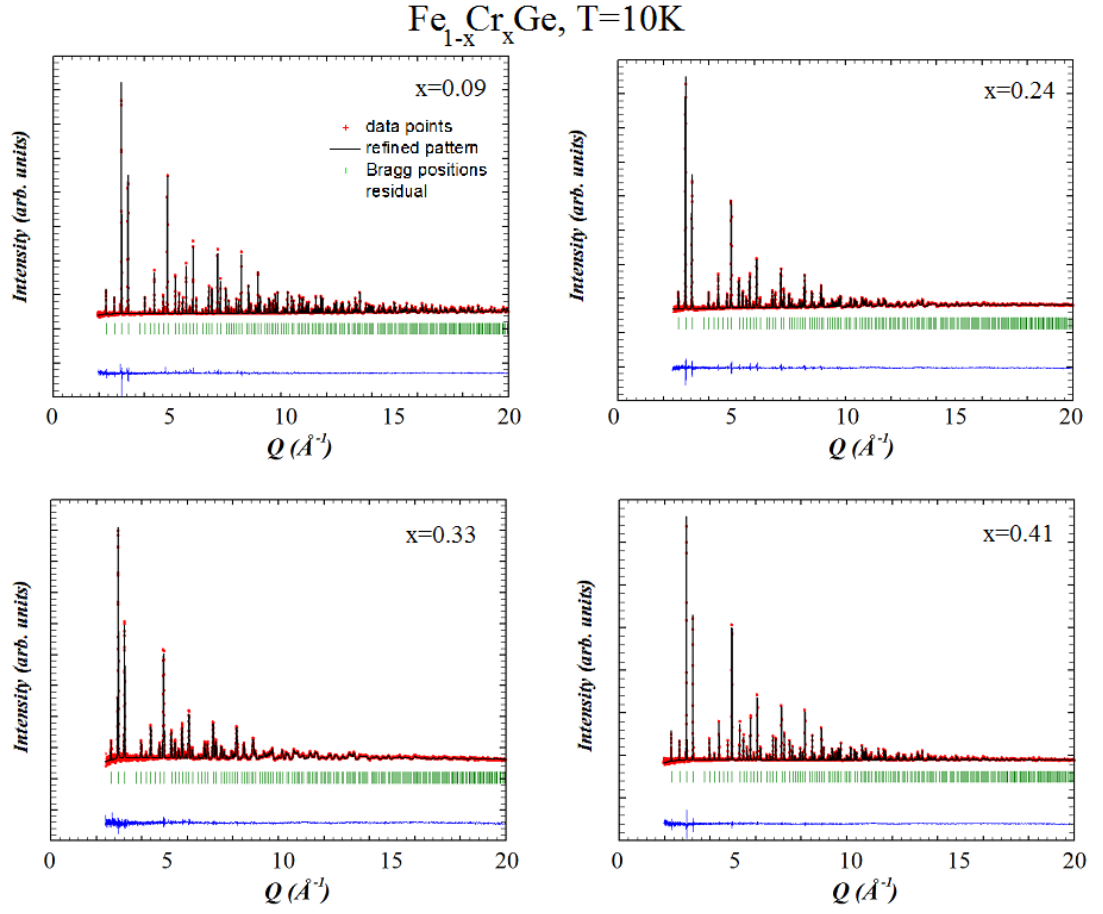


Figure 4.8: Neutron Powder Diffraction data of $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ collected at POWGEN at 10K, for $x = 0.09, 0.24, 0.33$, and 0.41 .

The Cr levels in the samples are confirmed by Neutron Powder Diffraction (NPD) at the POWGEN instrument of the Spallation Neutron Source (SNS) in Oak Ridge National Laboratory (ORNL) in addition to the XRD data. All of the measured samples remain in the B20 structure down to the base temperature of 10 K. Fig.4.8 shows the refined NPD patterns, collected for the $x = 0.09, 0.15, 0.24,$ and 0.41 samples, all taken at $T = 10$ K. The Cr doping level for each measured sample is determined by Rietveld refinement of the NPD data using FullProf. However, for samples with $x_{nominal} = 0.03, 0.15,$ and values ≥ 0.5 , NPD data is not available. The “nominal” x values here is defined as the stoichiometric percentage of the dopant during the weighing process of sample preparation. Room temperature XRD are available for those samples, but a direct extraction of Cr doping level based on XRD data is difficult due to similar XRD scattering intensities shared by Fe and Cr. The scattering intensity for XRD is differed by the atomic mass number of the target (Fe’s 26 to Cr’s 24). In comparison, the scattering intensity for NPD is determined by the target’s scattering cross section (Fe’s 9.45 to Cr’s 3.64). As a result NPD provides a much better contrast for the measurement of Cr/Fe level in this particular experiment. Therefore, we have to estimate the Cr concentrations for those two samples using Vegard’s law. The Cr concentration values for $x(nominal) = 0.03, 0.15,$ and values higher than 0.4 , are calculated by extrapolating the lattice constant (a) values measured by XRD, to a Vegard’s law fit using both previously published data and our NPD data.

Fig.4.9 shows the Cr doping dependence of the lattice constant in the series, including previously published values for the lattice constants of FeGe (119) and CrGe (132). The data points obtained from Rietveld refinement of the NPD data were used to create a Vegard’s law fit, as shown in Fig.4.9. The line was later used to estimate the Cr level for the rest of the series measured by XRD, nominally $0.5, 0.7, 0.8, 0.9$ and 1 . Table 1 shows a list of nominal Cr concentration levels versus its corresponding values determined by methods described earlier.

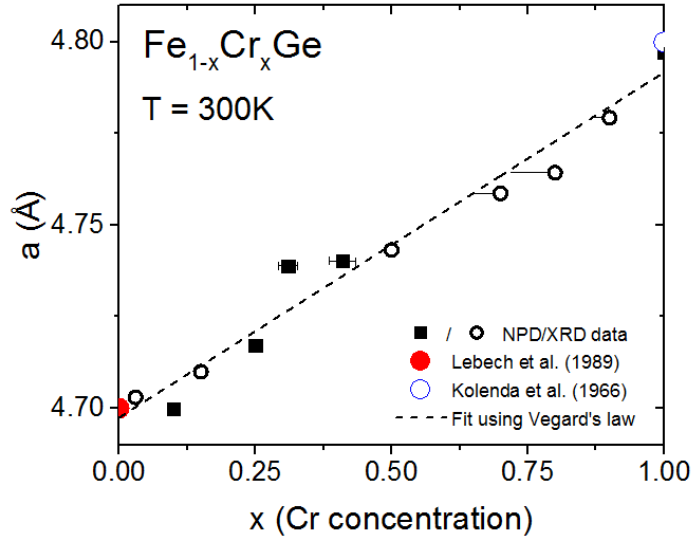


Figure 4.9: Lattice constant a as a function of Cr level x . The dotted line is a linear fit according to Vegard's law based on the NPD data. Corresponding x values for samples measured by XRD were calculated by extrapolating each of the sample's measured lattice constant to the dotted line.

Table 4.1: The nominal and experimental Cr level for the series extracted from both NPD and XRD measurements as described in text.

Nominal	NPD	XRD*
0.03	-	0.04(2)
0.10	0.09(2)	-
0.15	-	0.15(2)
0.20	0.24(1)	-
0.30	0.33(2)	-
0.40	0.41(1)	0.38(2)
0.60	-	0.59(5)
0.80	-	0.78(5)
1.00	-	-

* estimates using Vegard's law as describe in text.

Table 4.2: List of H_{C1} , H_{C2} for $x = 0.09, 0.15, 0.24$ and 0.33 at $T = 10$ K. $x = 0$ data were taken from Ref. (113; 145; 146; 119; 126).

x	$H_{C1}(T)$	$H_{C2}(T)$
0	≈ 0.1	≈ 0.36
0.09	0.076	0.199
0.15	-	0.194
0.24	-	0.120
0.33	-	0.089

4.5 Field dependent magnetization

Here we present the field dependence of the magnetic susceptibility in $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ within the framework of the aforementioned Maleyev model. Both of the critical fields H_{C1} and H_{C2} can be determined by a simple field dependence magnetization measurement, as H_{C1} is often indicated by a change in slope before the saturation field H_{C2} . Fig.4.10(a) shows the field dependence of the magnetic susceptibility for $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ at $T = 10$ K. The saturated moment is systematically suppressed by Cr doping. Fig.4.10(b) plots d^2M/dH^2 to help pinpointing the two critical fields H_{C1} and H_{C2} , indicated by a maximum and a minimum, respectively. Note that H_{C1} disappears for $x \geq 0.15$, with H_{C2} gradually decreases for higher x 's. However future measurements at lower temperatures might be able to detect H_{C2} for $x \geq 0.1$ samples, as in $\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ the onset of H_{C2} was suppressed down to $T = 7$ K at $x = 0.1$. Table 4.2 shows a list of H_{C1} and H_{C2} for the measured samples.

4.6 Temperature dependent magnetic susceptibility

Fig.4.11(a) shows the temperature dependence of the magnetic susceptibility for $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ with $H = 0.1$ kOe. Both Fig.4.10 and 4.11 show clear signs of the suppression of the moment and the ordering temperature by Cr doping, and eventually led the system into a disordered state for $x > 0.4$.

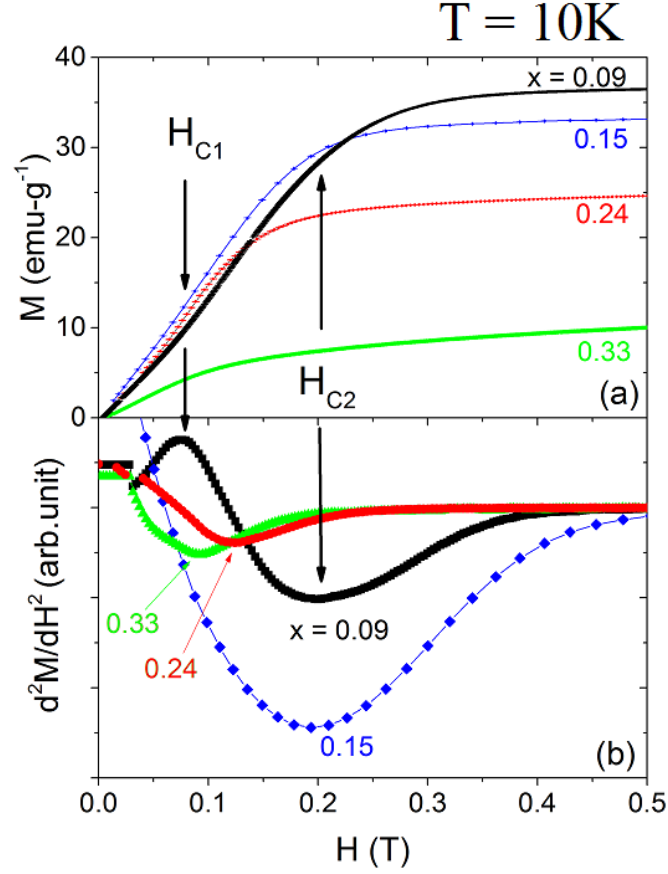


Figure 4.10: Field dependence of (a): magnetization at $T = 10\text{ K}$, and (b): d^2M/dH^2 , for $x = 0.09, 0.15, 0.24$, and 0.33 . The arrows mark the values for H_{C1} and H_{C2} for $x = 0.09$. Both critical fields H_{C1} and H_{C2} are suppressed by doping. H_{C1} is absent in samples with $x \geq 0.15$.

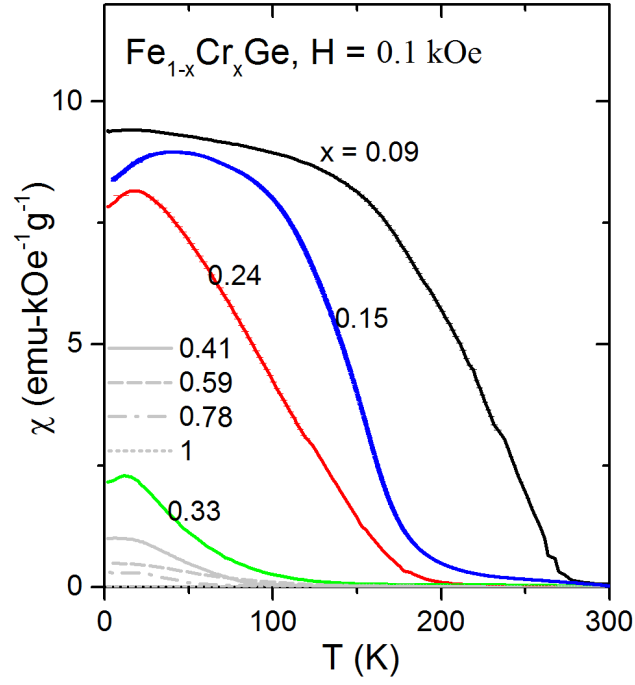


Figure 4.11: Temperature dependence of magnetic susceptibility for $x = 0.09, 0.15, 0.24, 0.33, 0.41, 0.65,$ and 0.87 . Note the broad maximum present in samples with $x \geq 0.15$ around 20 K.

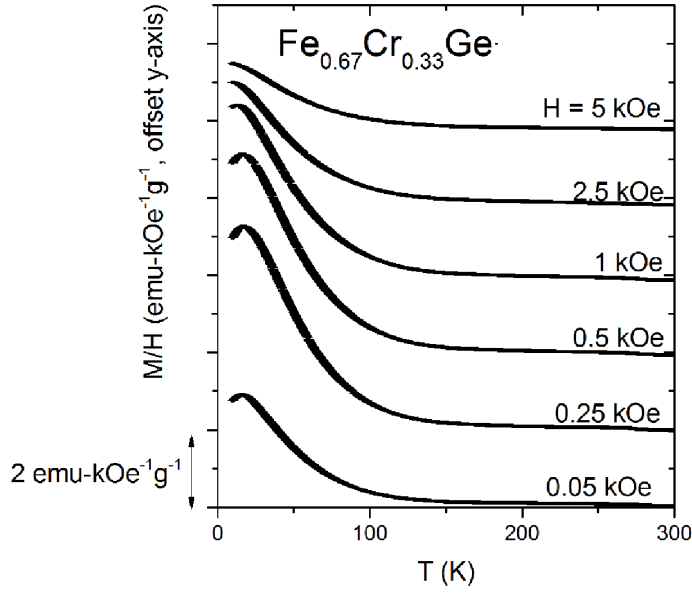


Figure 4.12: Temperature dependence of magnetic susceptibility for the $x = 0.33$ with external field from 0.05 to 5 kOe. The curve for each individual field is offset by $\approx 2 \text{ emu} \cdot \text{kOe}^{-1} \text{g}^{-1}$. Note the maximum around 20 K is suppressed for $H \geq 2.5 \text{ kOe}$.

Fig.4.11 also shows a broad maximum at low temperature ($\approx 20 \text{ K}$) in all samples except $x = 0.09$. Ref. (132) reported the same feature for CrGe and suggested that the broad maximum as a signature for near-ferromagnetic metal based on the paramagnon theory proposed by Beal-Monod (132; 143). It is worth mentioning that in the previously published magnetic susceptibility data on $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ by Ref. (133), for which the measurements were performed at $H = 6.3 \text{ kOe}$, the broad maximum is not observed for $x \leq 0.9$. In contrast, our data as shown in Fig.4.11 is measured at a lower field $H = 0.1 \text{ kOe}$ and the broad maximum is present in all but the $x = 0.09$ sample. Fig.4.12 shows the field dependent evolution of this broad maximum down in $x = 0.33$, the feature is not observed for $H \geq 2.5 \text{ kOe}$ down to 10 K. Based on the previously proposed association of this feature as a sign for a near-ferromagnetic paramagnetic material, a systematic investigation of the paramagnon behavior of this series can be the focus of a future study.

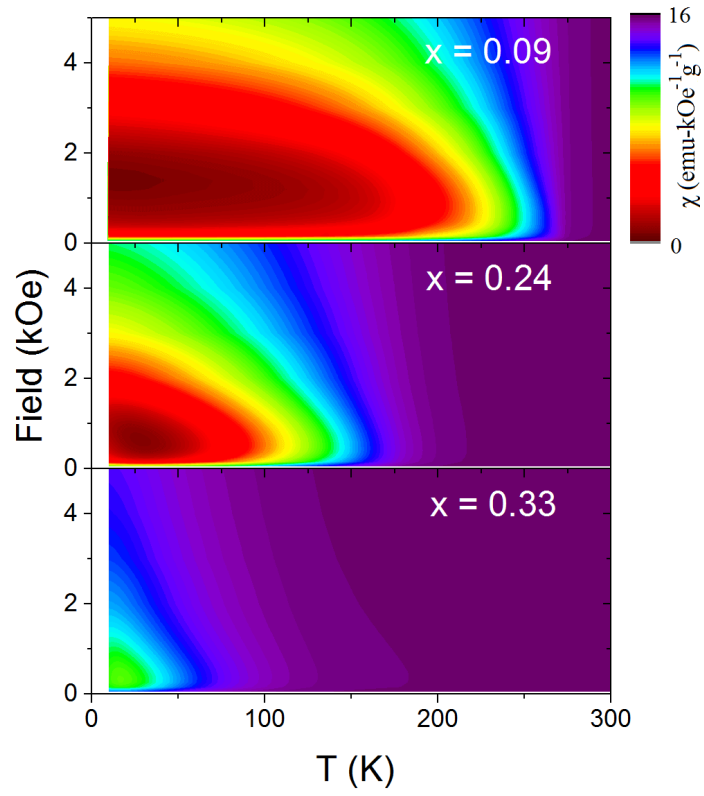


Figure 4.13: Contour plot showing the temperature and field dependence of M/H for $x = 0.09$, 0.24 , and 0.33 .

Fig.4.13 provides a series of contour plots for M/H as a function of both external field and temperature, for $x = 0.09, 0.24$, and 0.33 . The plot sums up the observations presented in both Fig.4.11 and Fig.4.10, showing the decreasing of both ordering temperature T_C and critical field H_{C2} as a function of doping. The broad maximum said to be a sign for a near-ferromagnetic paramagnetic material can also be observed in the form of a dome in the contour, suppressed above $H = 1.2$ kOe for $x = 0.24$ and $H = 0.8$ kOe for $x = 0.33$.

4.7 Small angle neutron scattering results

In order to investigate the helimagnetic order in $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$, we performed temperature dependent zero field small angle neutron scattering (SANS) on samples with $x = 0.09, 0.15, 0.24$ and 0.33 . The experiment was performed on the GP-SANS instrument at HFIR, ORNL. The samples were placed in a cryostat that allowed temperature range from 2 K to 300 K. A neutron wavelength of $10 \text{ \AA}$ with a standard deviation of $\Delta\lambda/\lambda = 15\%$ and a collimation distance of 17.6 m were used. The diffraction patterns were collected on a position sensitive detector with a pixel resolution of about 5 mm that was 19.7 m away from the sample position. To estimate the instrument resolution, we consider the region of data collected around $q = 0.01 \text{ \AA}^{-1}$. Using equation (4) of Ref. (147), $\Delta q/q$ is calculated to be around $0.0011 \text{ \AA}^{-1}$, which means the FWHM for the narrowest resolvable peak is around $0.0025 \text{ \AA}^{-1}$, more than sufficient for this experiment, for which the range of interest is around $Q = 0.01 \text{ \AA}^{-1}$.

SANS data were collected at about 15 different temperatures for each of the samples, including temperatures above and below the transition. Fig.4.14 shows some of the raw SANS data. Since the emphasis of the experiment is the temperature dependence of the helical ordering, data collected at temperatures well above the magnetic ordering were subtracted from the rest of the data. The dataset collected at the highest temperature for each sample are shown at the bottom row of Fig.4.14. A simple illustration of this process can be seen on the top of Fig.4.15, followed by the

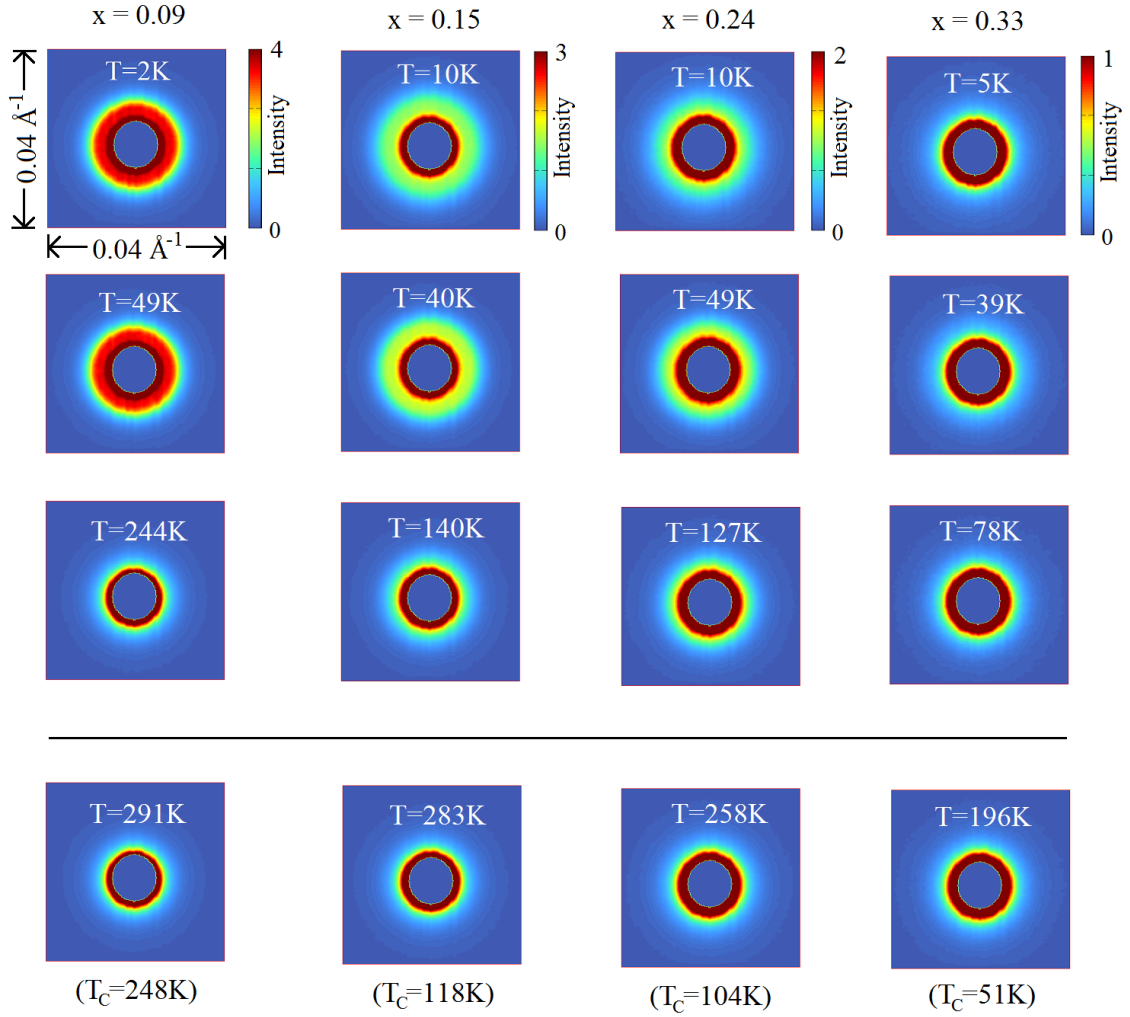


Figure 4.14: Raw SANS data collected for $x = 0.09$, 0.24 and 0.33 at various temperatures. The graphs displayed below the horizontal line are data collect above the helical ordering temperature for each concentration, with the measured T_C listed underneath.

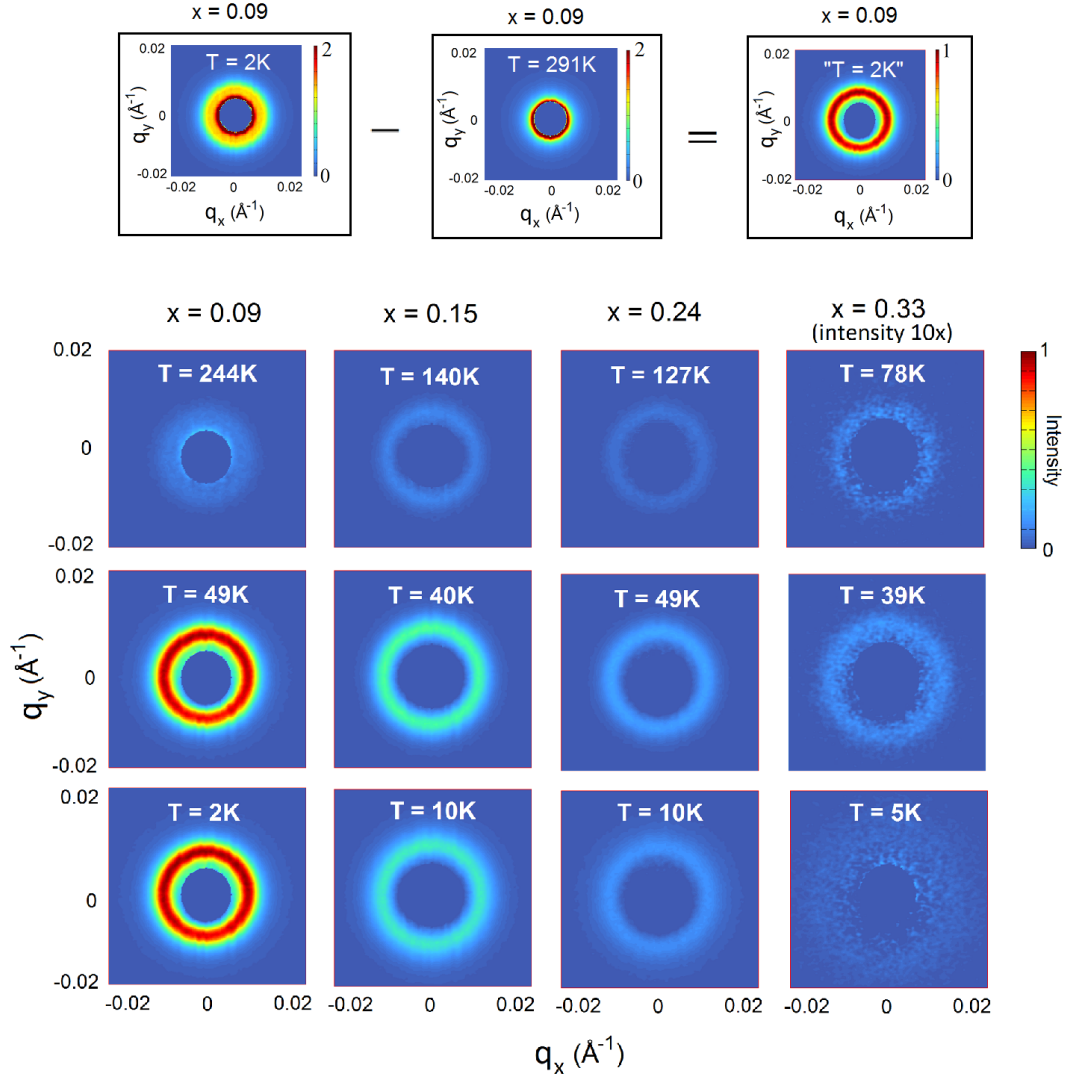


Figure 4.15: (top):A diagram illustrating the data processing method used for data with $T < T_c$ as described in the text; (bottom): SANS data of the helical magnetic peak for $x = 0.09, 0.24$ and 0.33 at various temperatures. The intensities of the rings are representative of the sizes of the ordered helimagnetic moments.

resulting plots. For $x = 0.09$, the ring is clearly visible from the ordering temperature down to the base temperature, with little change in intensity. For $x = 0.15$, the ring appears below its T_C , but softens slightly at 10 K compared to 40 K. For $x = 0.24$ and 0.33, the softening is even more pronounced, with the ring appearing much weaker and more diffuse at low temperature. Moreover, the wavelength of the helical order in FeGe is known to be nearly independent of temperature and therefore independent of its two propagating directions (i.e. $\langle 100 \rangle$ and $\langle 111 \rangle$) (119), we are not able to determine the propagating direction of the helical ordering detected in the powder samples. The temperature dependence of the rings' intensities seem to complement the broad maximum observed in the χ vs T data shown earlier in Fig.4.11.

Fig.4.16 shows the q -dependence of the SANS signal by azimuthally averaging centering around $q_x = q_y = 0 \text{ \AA}^{-1}$ and plots $Q = \sqrt{q_x^2 + q_y^2}$. The averaging process is carried out with the ‘‘Averaging: Radial and Azimuthal’’ function in the software *GRAS_{ans}P*. The algorithm is designed specifically for this intended purpose, the reader can refer to Ref.(148) for more details about the process. Furthermore, a similar data subtraction technique described earlier for Fig.4.15 is also used here, i.e. data collected at a temperature much higher than the ordering temperature T_C is used as a pseudo-background to be subtracted from data with $T < T_C$. This process is illustrated in Fig.4.16(a), where an example for $x = 0.09$ is shown. The normalized data at $T = 291$ K is subtracted from all other data collected at $T < T_C$, in this case the 4 K data. Fig.4.16(b) shows the averaged intensity versus Q data for $x = 0.09, 0.15, 0.24$ and 0.33 for a selection of temperatures. In the $x = 0.09$ data, the peak centering at $Q = 0.09 \text{ \AA}^{-1}$ gradually intensifies towards the base temperature. In the $x = 0.15, 0.24$ and 0.33 samples, the amplitudes of the helimagnetic peak first reach a maximum at some intermediate temperature $T \approx 50 \text{ K}$, then decreases at lower temperatures. This temperature dependence of the helical peak's amplitude is similar to the the magnetic susceptibility data shown earlier in Fig.4.11.

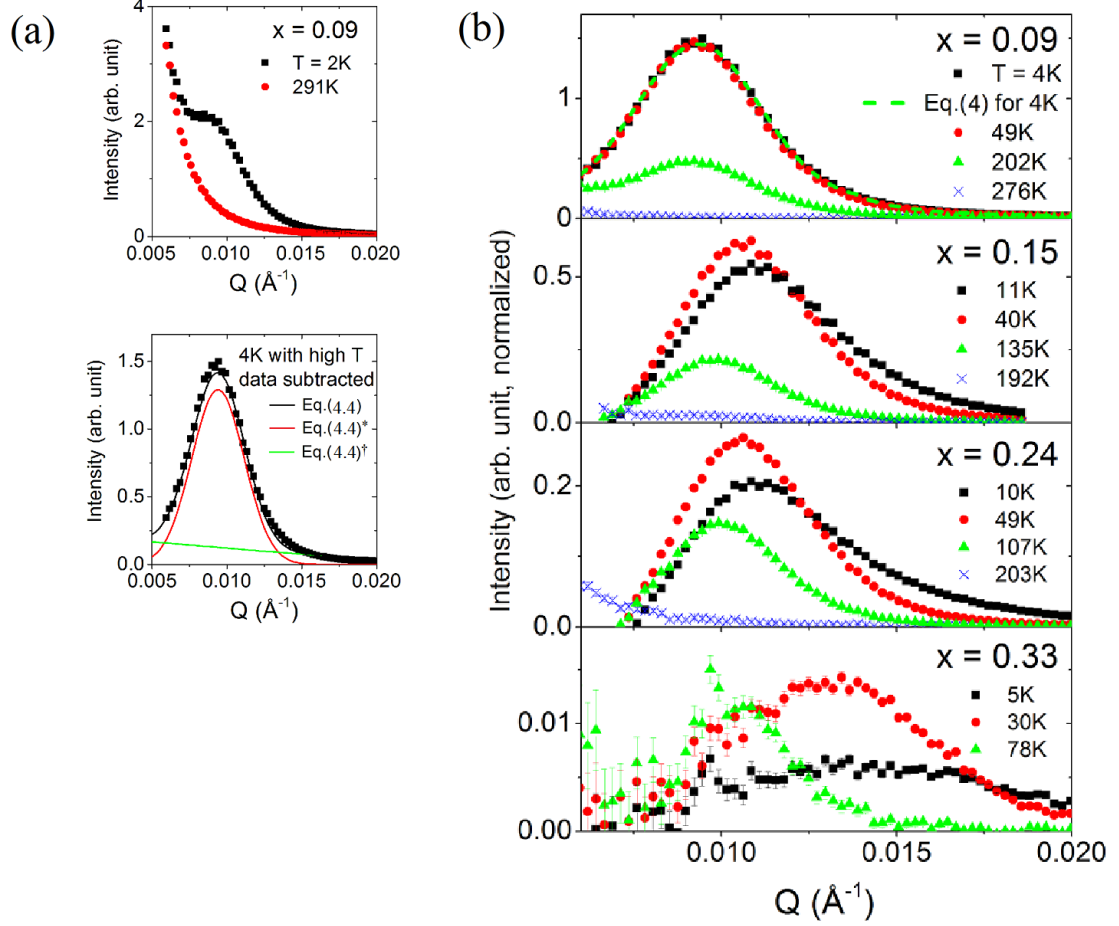


Figure 4.16: (a, left): Azimuthally averaged intensity of the SANS ring versus Q for $x = 0.09$ at 4 K and 291 K of the raw data; (a, right): The difference between the 4 K and 291 K data. The principle of this process is similar to that shown in Fig.4.15(top). The solid lines are the fitted curve and each of the individual components from Eq.4.4. The individual terms are as listed in Eq.4.4, i.e. the first term: a Gaussian centering around the peak position $Q = 0.009 \text{ \AA}^{-1}$ (labeled as Eq.(4.4)*), and the second term: a modified Lorentzian centering around $Q = 0 \text{ \AA}^{-1}$ (labeled as Eq.(4.4) †); (b) Azimuthally averaged intensity versus Q plots. Notice the increasing temperature dependence for the peaks' amplitude, width and position for $x = 0.15, 0.24$ and 0.33 .

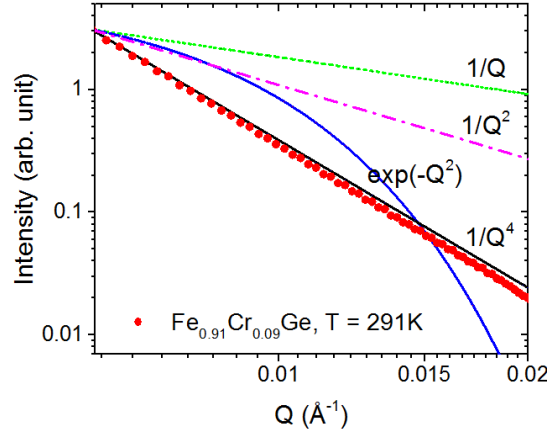


Figure 4.17: A log-log plot of azimuthally averaged SANS data for $\text{Fe}_{0.91}\text{Cr}_{0.09}\text{Ge}$ at 291 K. Graphs also shows curves of $1/Q$, $1/Q^2$, $\exp(-Q^2)$, and $1/Q^4$, of which $1/Q^4$ gives the best fit to the data, indicating the data is in the Porod regime.

4.7.1 Doping and temperature dependence

For the extraction of meaningful parameters from all of the intensity versus Q data, the following equation was used to fit the data in Fig.4.16(b) and all other calculated intensity versus Q . An example of this fit is shown in the 4 K data of the $x = 0.09$ panel in Fig.4.16(b).

$$I(Q) = I_0 e^{-\frac{(k-Q)^2}{2\sigma^2}} + \frac{B}{(b^2 + Q^2)^2} \quad (4.9)$$

The first term of Eq.4.4 is a simple Gaussian function, with I_0 , k , and σ correspond to the amplitude, position, and the standard deviation of the helical peak. For the fitting of a single Bragg peak, a combination of Gaussian and Lorentzian is often used (149), however sometimes just the Gaussian function alone is sufficient, especially if the spread of the peak is limited by the instrumental resolution (150). In our case an additional Lorentzian component did not significantly improve the quality of the fit, therefore we choose to use only the Gaussian for the sake of simplicity. The second term is a slight modified Debye-Porod q^{-4} term (151), that accounts for the diffuse scattering at $q_x = q_y = 0$. Fig.4.17 compares several functions, including $1/Q$, $1/Q^2$,

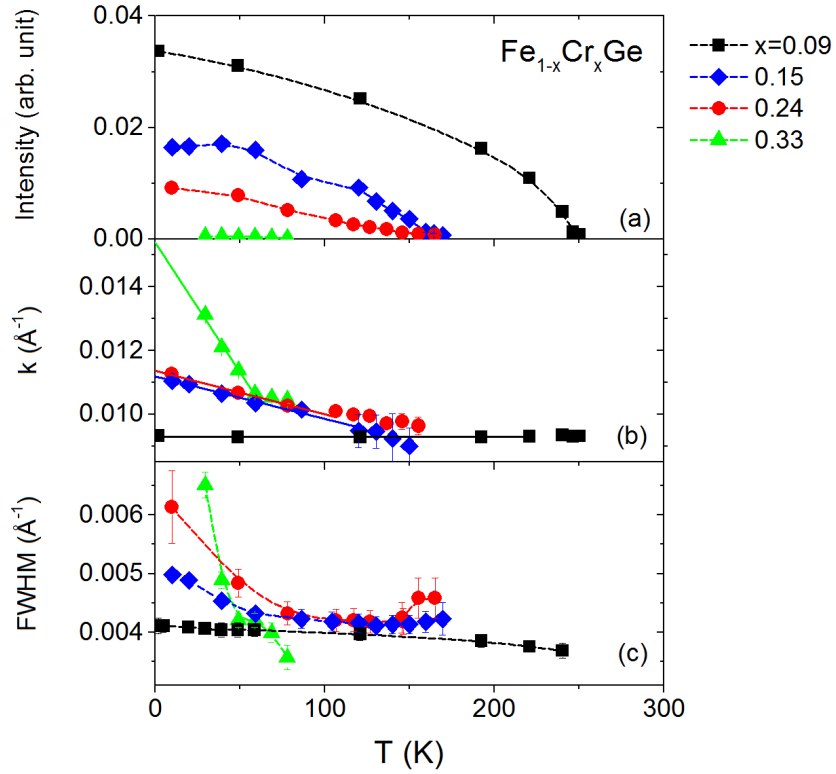


Figure 4.18: The temperature dependences of the three extracted parameters from the helical ordering peaks are shown for $x = 0.09, 0.15, 0.24$ and 0.33 ; (a): the integrated areas of the peaks ($I_0\sigma$), a representation of the relative moment sizes; (b): k , the wavelength of the helical ordering, of which $2\pi/k$ should represent the lengths of the actual helical ordering in real space. Solid lines are fits using Eq.4.5; (c): FWHMs of the fitted peaks, of which the inversed values should represent the correlation length of the ordering.

$\exp(Q^2)$, and $1/Q^4$, and shows that the $1/Q^4$ function provides the best fit for the non-magnetic portion of the SANS data.

Fig.4.18(a) shows the temperature dependence of $I_0\sigma$, k and $\text{FWHM}(= 2.35\sigma)$ of the fitted peaks. $I_0\sigma$, the integrated intensity of the fitted Gaussian peak, represents the relative size of the ordered moment. It is no surprise that the temperature dependence of $I_0\sigma$ resembles that of the magnetic susceptibility as seen in Fig.4.11(a). Fig.4.18(b) shows the temperature dependence for the helical wavelength k . As seen in Fig.4.18(b), k shows little temperature dependence for $x = 0.09$, similar to that

Table 4.3: List of T_C , H_{C1} , H_{C2} , k_0 , helix length λ , and a for $x = 0.09, 0.15, 0.24$ and 0.33 . $x = 0$ data were taken from Ref. (113; 145; 146; 119; 126).

x	$T_C(K)$	$k_0(\text{\AA}^{-1})$	$\lambda(\text{\AA})$	$a_0(\text{\AA})$
0	278.2(3)	0.0090	698	4.700
0.09	248(4)	0.0093	676	4.700
0.15	118(6)	0.0110	571	4.717
0.24	104(7)	0.0114	592	4.723
0.33	51(9)	0.0154	408	4.739

of FeGe (the first-order peaks in Fig.6 of Ref. (119)). However, for all samples with $x \geq 0.15$, k has an increasingly noticeable temperature dependence, with larger dependence for higher Cr concentrations. Ref. (124) observed a similarly linear temperature dependence of k in $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ and provided an expression to describe the temperature dependence of helix wavelength, and define k_0 , as follow.

$$k(T) = k_0 \left(1 - \frac{T}{T_c} \right) \quad (4.10)$$

Table II shows a summary of the important parameters discussed so far, this includes T_C , H_{C1} , H_{C2} , k_0 , $2\pi/k_0$, and a for $x = 0.09, 0.15, 0.24$ and 0.33 . Previously published parameters for the endpoint FeGe are also included for reference.

Fig.4.18(c) shows temperature dependence of the FWHMs of the fitted peaks, of which the inversed values are representative of the correlation length of the ordering. Though the temperature dependence of the helical peaks' FWHMs reach a minimum around 100 K for $x = 0.15$ and 0.24 , the rest of the data are negatively dependent on temperature similar to k . This similarity suggests an identical origin is possible. It is also worth mentioning that for $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ samples with $x \geq 0.15$, the helix wavelength k is negatively dependent on temperature. The opposite is observed in MnSi under pressure (152; 153).

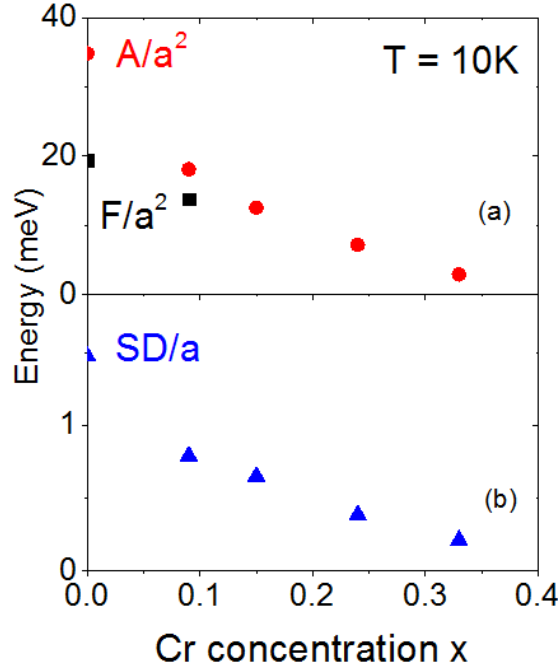


Figure 4.19: The doping dependences of parameters A/a^2 , F/a^2 , and SD/a .

4.8 Evolution of helical order by doping

From the field and temperature dependence of the magnetization and magnetic susceptibility for the series shown earlier in Fig.4.10 and 4.11, one can clearly see that the magnetic ordering temperature and moment size systematically decreases with the presence of Cr. The values of critical fields H_{C1} and H_{C2} were extracted from the measurements, and combined with the helical ordering wavelength k extracted from the SANS data, one can evaluate the principal interactions of the system, the DM interaction D , the “spin-wave stiffness” A , and the anisotropy constant F , using Eq.4.1, 4.2, and 4.3.

Fig. 4.19 plots the doping dependence of the principal interaction energies calculated using Eq.4.7, 4.8, and $k = SD/A$. The figure plots the DM interaction (SD/a), the “spin-wave stiffness” (A/a^2), and the anisotropy constant (F/a^2) at 10 K. Cr doping suppresses all three energies of the system, with A/a^2 and SD/a approaching 0 meV around $x = 0.4$ if linear extrapolation is assumed of the data

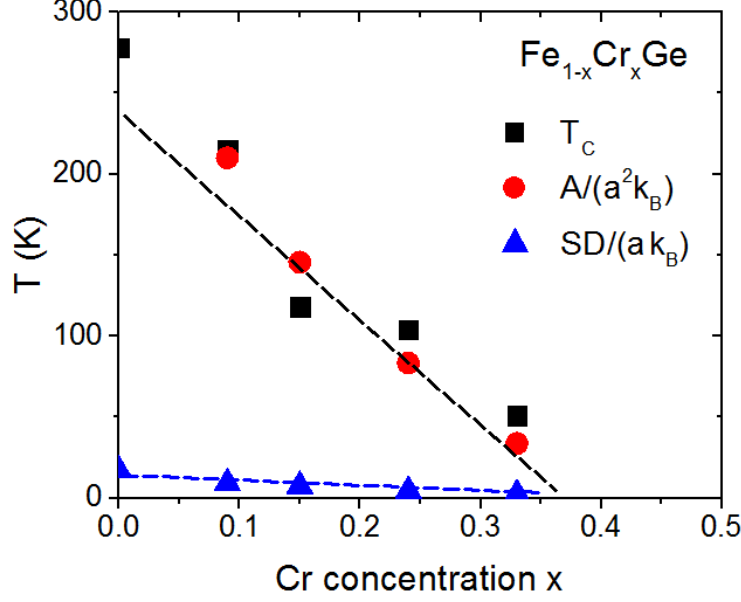


Figure 4.20: The doping dependence of the ordering temperature T_C , and calculated values for $A/(a^2 k_B)$ for comparison. Dotted line is a guide to the eye. The graph also shows $SD/(a k_B)$ which occupies a much lower temperature range.

shown in Fig.4.19. Regrettably H_{C1} is not observed for samples with $x > 0.1$ at 10 K and therefore no values of F is available for those concentrations. However if the temperature dependence of H_{C1} of $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ is similar to that of $\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ (135) and $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ (124), i.e. gets larger when cooled, then H_{C1} might be observable at a lower temperature. As for the suppression of A , it is likely to be a result of frustration enhanced by Cr doping, similar to Fe doping in $\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ (135). This frustration might also be the cause for the decrease in correlation length in samples with larger x 's. The correlation length of the helical ordering is proportional to the inverse FWHM of the helical peak in Fig.4.18. At low temperature, the FWHM of the peaks are much larger for samples with larger x 's.

Fig. 4.20 shows the doping dependence of the ordering temperature T_C , SD/ak_B , A/a^2k_B for comparison. Both A/a^2k_B and T_C decreases almost linearly down to zero around $x = 0.4$, as shown by the dotted line, remarkably sharing a very similar temperature range with each other.

4.8.1 Temperature dependence of the helix

The temperature dependences of helical wavelength k have been observed in $Fe_{1-x}Co_xSi$ (124) and MnSi under pressure (152; 153). Due to the similarity in electronic properties among these compounds, it is likely that the temperature dependence of k in these materials shares a similar physical origin. Similar to our data, the length of the helix in $Fe_{1-x}Co_xSi$ increases with temperature, while in MnSi, the helix length decreases with temperature under pressure. Ref. (153) shows that the helix in MnSi decreases by about 20% at the critical pressure of $p_c = 14.7 \pm 0.1 kbar$, where the magnetic order disappears. For comparison, the difference in helix length is about 40% between the pure FeGe and $Fe_{0.67}Cr_{0.33}Ge$, the highest doped and magnetically ordered member of the series.

In a localized magnetic moment picture, the helical wavelength is governed by balancing of the “spin-wave stiffness” A and the DM interaction D , $k = SD/A$, which is temperature independent if one assumes that A and D do not change with temperature. However, k may vary with temperature if one introduces spin anisotropy, such as easy-axis anisotropy introduced by chemical doping, similar to the microphases in the well studied axial next-nearest-neighbor Ising model (154; 155). As these compounds are weak itinerant magnets, the localized moment model may not be justified, but one still sticks to the localized moment model, it is possible that A and D become temperature dependent due to the spin fluctuations, which results in a temperature dependence of k .

While we are not able to also locate published data for the temperature dependence of σ for FeGe, there is data available for MnSi. In Fig 2(b) of Ref. (156), σ reaches a minimum around 20K, and increases in lower temperatures. The temperature dependence of σ^{-1} , i.e. the correlation length of the order can also be understood by the presence of anisotropy in the system. At low temperature, the amplitude of the ordered moment is relatively large and the moment relatively rigid. In a system with no anisotropy, the ground state energy is at a minimal. However, in the presence of

anisotropy, the system is frustrated and consequently, k fluctuates about its optimal value, resulting in a shorter correlation length. As the temperature increases, the magnetic moments become softer, and the degree of frustration is relieved, resulting in a longer correlation length.

4.9 Possible paramagnon behavior

There is also a broad maximum observed both in the magnetic susceptibility and SANS peak intensity for $T < 50$ K in samples with $x > 0.1$. Since this is only observed in samples with $x > 0.1$, and not in FeGe or even $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ with lower x 's, we conclude that the effect must be due to the presence of CrGe. Ref. (132) have reported a very similar feature around 45 K in the magnetic susceptibility of CrGe. The effect have been explained by the presence of paramagnons, within the paramagnon theory by Béal-Monod (132).

Chapter 5

Quantum Harmonic Oscillations (QHO) in UC and US

The complex electronic structure of uranium leads to a wide variety of unusual and diverse behavior in the uranium salts UX ($X = \text{C, N, P, S, As, Se, Sb, Te, Bi}$), and therefore the materials in this family have been the subject of many past investigations characterizing their magnetic and vibrational properties (157; 158; 159; 160; 161; 162; 163; 164; 165). Although the phonons in the UX systems were first studied decades ago (163), there has been renewed interest in the vibrational properties of these systems accompanied by efforts towards detailed phonon calculations in recent years, as certain members of the UX family such as UN and UC are under active consideration for next generation nuclear fuels (13; 14). Fig.5.1 shows some of the existing work on UC and US, including the optical and acoustic phonon modes for both, measured by inelastic neutron scattering (INS) (163). The published INS data are very helpful as references and we are able to closely reproduce the phonon dispersion measurement data as shown later in this chapter.

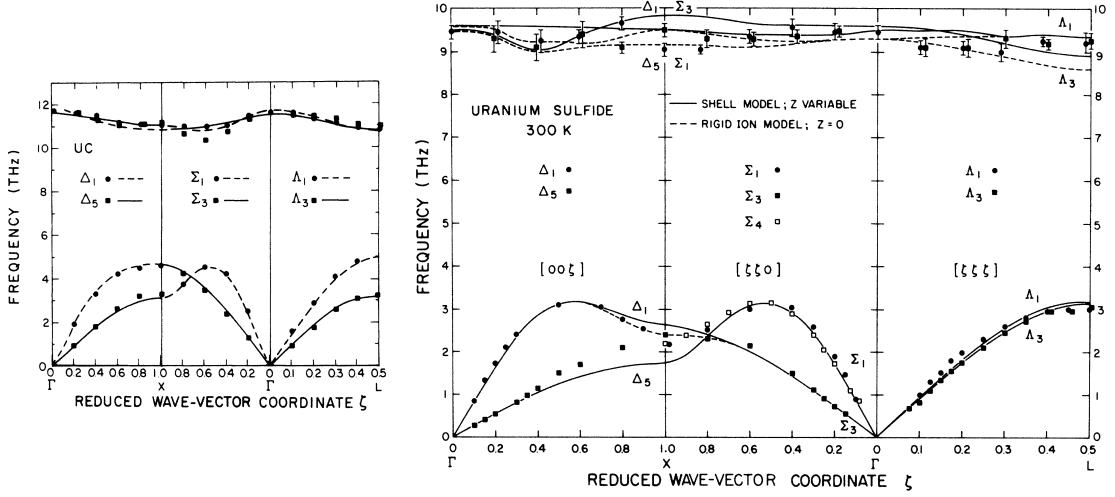


Figure 5.1: Phonon dispersion in UC and US published by Ref.(163).

5.1 QHO observed in UN

In 2012 a series of evenly-spaced, high energy modes were observed in UN by inelastic neutron scattering (15). While the magnetic continuum scattering was observed to persist up to at least 50 meV, the excitation spectrum above the optic phonon modes was dominated by a strong vibrational response. A detailed quantitative analysis showed that these modes could be attributed to the nitrogen atoms behaving as independent, isotropic, 3D quantum harmonic oscillators (QHOs) (15; 166). Significant intrinsic broadening of the QHO modes was observed. The amount of broadening was explained well by the binary solid model (167), which applies to systems with two different types of atoms with disparate masses and explains how the motion of the heavy atoms affects the QHO behavior of the light ones.

The conventional view of vibrational response in crystalline solids above the highest optic phonon modes is usually complicated, weak and non-resolvable (168). Prior to the UN discovery, exceptions to this rule were generally only found in binary metallic hydrides (169; 170; 171). Although the high energy modes in the hydrides usually exhibit significant anisotropic and anharmonic effects, these studies imply that the mass ratio plays an important role in the vibrational properties of binary

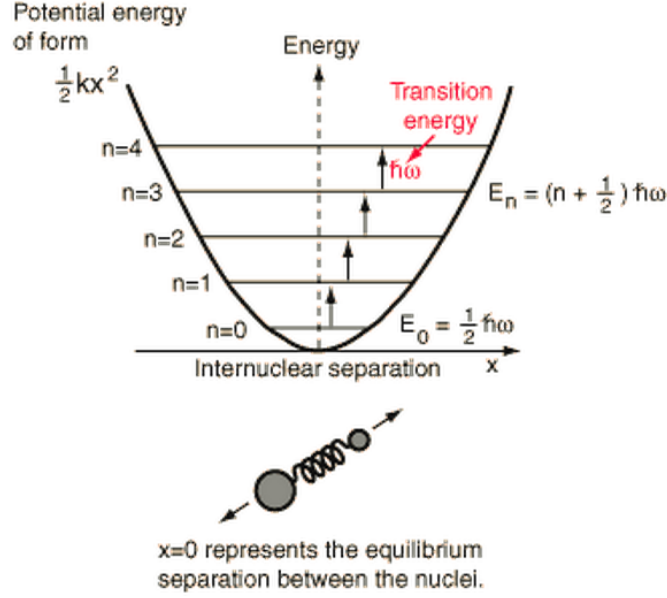


Figure 5.2: A brief explanation of quantum harmonic oscillators(QHO), taken from Ref. (179).

crystals. Our studies performed on the UX family has revealed optic phonon modes that are nearly-dispersionless and well-separated in energy from the acoustic modes, especially when the U:X mass ratio becomes large. In this limit, the intensity of the optic modes is dominated by the light atoms, while the intensity of the acoustic phonon modes is dominated by the heavy U atoms (172; 173).

We recently followed up on the previous UN phonon work by performing time-of-flight neutron spectroscopy measurements using modern instrumentation (15). Data was collected on SEQUOIA (174; 175) and ARCS (176) at the Spallation Neutron Source of Oak Ridge National Laboratory, using the same single crystal measured previously (177; 178; 163).

We have extend the investigation of QHO modes of UN (U:N = 17) by performing time-of-flight neutron spectroscopy measurements for single crystals of UC and US. For UC, we find a series of high energy vibrational modes analogous to those observed for UN. The modes are described well by a QHO model for the carbon atoms, with only a small amount of anharmonicity observed along the different crystalline directions



Figure 5.3: Two separate pieces of US single crystal wrapped in aluminum foil and mounted on aluminum brackets after alignment at the CG1 instrument of HFIR.

that was slightly overestimated by density functional theory (DFT) calculations. While the US data also shows evidence for the high energy vibrational modes, only the lowest few are observed and they are much weaker in intensity compared to the UC and UN cases. While the U:X mass ratio has been confirmed to play a key role in the observation of quantum harmonic oscillator behavior in the UX family, we find that the scattering cross section of the light atoms is also extremely important.

For this research effort, one publication with tentative title “Nature of the light atom vibrations in the uranium rocksalts UC and US” has been planned for submission in 2015.

5.2 Sample history

The depleted uranium single crystals investigated in this work were the same ones measured previously (180; 181). Both samples had similar total volumes on the order of 1 cm^3 . Fig.5.3 shows a photo of the US crystals used for the experiment. Both the US and UC samples were remounted and realigned at the alignment station of HFIR.

5.3 Inelastic neutron scattering experiment

All neutron scattering measurements reported here were collected using the SEQUOIA (174; 175) and ARCS (176) time-of-flight chopper spectrometers at the Spallation Neutron Source of Oak Ridge National Laboratory. For the neutron scattering experiments, the UC and US single crystals were mounted in Al cans and loaded in closed cycle He refrigerators. All the data was collected at $T = 7$ K, with the $[HHL]$ scattering plane horizontal in each case. A Fermi chopper was used to obtain several different incident neutron energies, including $E_i = 80$ meV, 250 meV, 500 meV, 700 meV and 800 meV. The full experimental details for each dataset presented in this work are given in Table 5.1. All datasets were normalized to account for variations of the detector response and solid angle coverage with a vanadium standard. Empty can measurements were performed at room temperature for each incident energy and subtracted from the dataset, however a small amount of Aluminum that made up the sample mount was not perfectly accounted for. This small amount of unaccounted Al background will have a considerable effect on US, but not so much for UC. We will elaborate more on this point later on.

Table 5.1: List of experimental conditions used to collect for (a): UC, and (b): US respectively, on SEQUOIA ($E_i = 80$ meV only) and ARCS ($E_i = 250, 500, 700$ and 800 meV).

(a) UC, T = 7 K				
E_i (meV)	80	500	700	800
d_{FC} (mm)	1.5	0.5	0.5	0.5
R_{FC} (m)	0.58	1.53	1.53	1.53
ν_{FC} (Hz)	480	480	600	600
ν_{T0} (Hz)	90	180	180	180

(b) US, T = 7 K			
E_i (meV)	80	250	500
d_{FC} (mm)	3.6	0.5	0.5
R_{FC} (m)	1.53	1.53	1.53
ν_{FC} (Hz)	240	360	480
ν_{T0} (Hz)	90	180	180

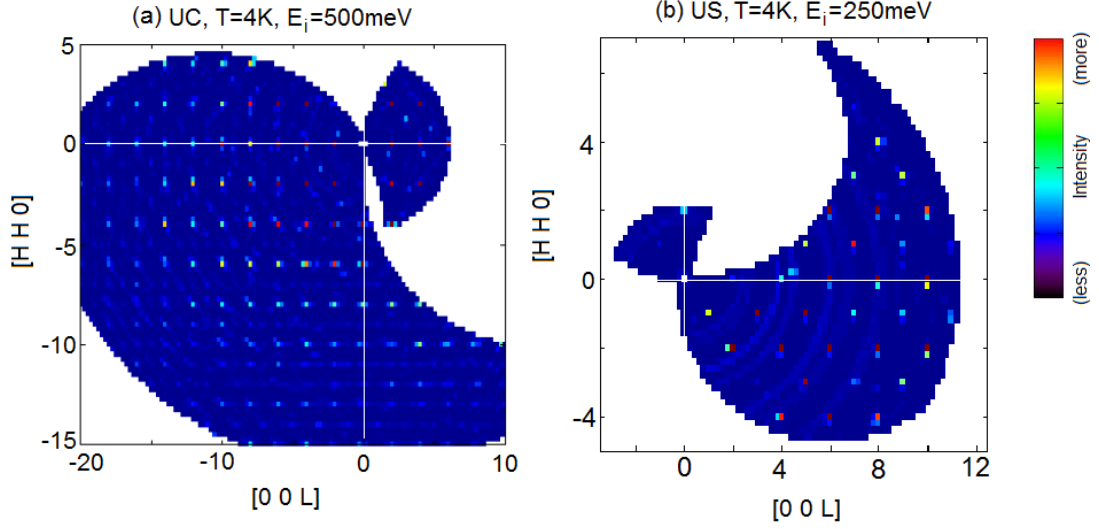


Figure 5.4: A contour plot across the scattering plane of HH0/00L of UC and US at the elastic plane $E(=E_i - E_f) = 0\text{meV}$. Each of the dots indicates a Bragg peak, for example at HH0 = 0 and 00L = 2 is the $[0\ 0\ 2]$ peak. The difference in covered range is due to the difference in E_i 's (UC's 500 meV vs. US's 250 meV) and measured angles (UC's 180° vs. US's 90°).

Since we are also interested in the phonon dispersion of the systems, we first determined the crystal orientation at the alignment station of HFIR, and confirmed again during each of the inelastic neutron scattering experiments. Fig.5.4(a) and (b) shows 2 contour plots of nuclear Bragg peaks for UC and US at 4 K, with $E_i = 500$ meV and 250 meV respectively. Observed at the elastic scattering plane, the Bragg peaks as indicated by dots, line up perfectly with expected position of the peaks. The concentric rings centering at $H = L = 0$ are powder rings from the aluminum cans that contain the samples.

5.3.1 Phonon dispersions of UC and US

Fig. 5.5 shows representative phonon measurements with $E_i = 80$ meV for (a) UC from ARCS and (b) US from SEQUOIA along the $[\bar{2}\bar{2}L]$ direction in reciprocal space. The phonon modes for both systems are characterized by a similar intensity scale.

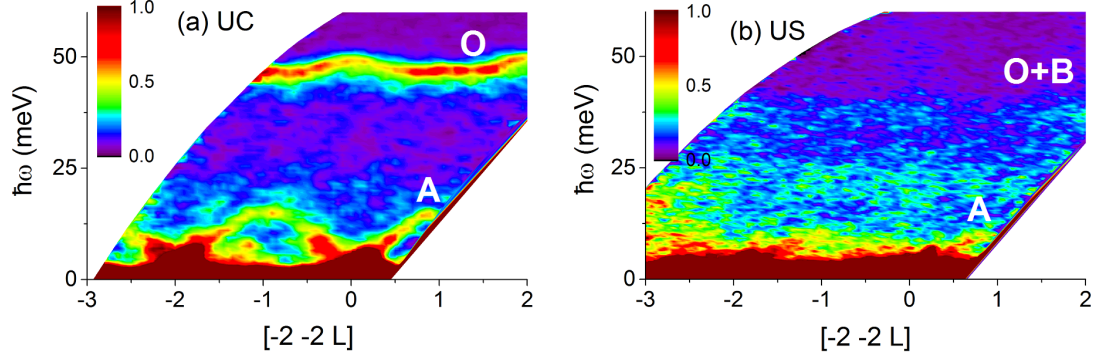


Figure 5.5: The conventional phonons along the $[-2 -2 L]$ direction for (a) UC (ARCS) and (b) US (SEQUOIA) with $E_i = 80$ meV. In both cases, the acoustic and optic phonon modes are well-separated. The optic modes are much more intense for UC as compared to US. The energy of the optic modes for UC and US are known to be 48 meV and 40 meV (163). The white text O and A indicates the general location for the optic and acoustic phonon modes, where B denotes significant background contribution.

As appear in the Fig. , the phonon modes of US are not easily visible in the data. The decreased intensity of these excitations can be understood by considering the one phonon structure factor, g^2 , for the rocksalt structure (182).

$$g^2 = (\mathbf{Q} \cdot \xi)^2 g'^2 \quad (5.1)$$

with

$$g' = \left(\frac{b_U d_U}{\sqrt{M}} \pm \frac{b_X d_X}{\sqrt{m}} \right) \quad (5.2)$$

Here, $\mathbf{Q}$ is the neutron momentum transfer, ξ is the phonon polarization vector, M is the mass of U, m is the mass of the light atom X, d_U and d_X are the relative displacements of the atoms and are normalized to $d_U^2 + d_X^2 = 1$, and b_U and b_X are the neutron scattering lengths. The sign between the two terms in Eq.5.2 depends on the (HKL) indices of the Brillouin zone, where (+) and (-) correspond to all even and all odd indices respectively.

Table 5.2: Relevant parameters for scattering intensities in UC, UN, US, and Al

Atom	m (amu)	$b(10^{-12} \text{ cm})$	$b/m^{3/2}(10^{-16} \text{ cm})$
U	238	0.84	2.29
C	12	0.66	159
N	14	0.94	179
S	32	0.28	15
Al	27	0.34	–

For optical phonons, $d_U M = d_X m$ and therefore g' can be rewritten as:

$$g' = \frac{mM}{\sqrt{m^2 + M^2}} \left(\frac{b_U}{M^{3/2}} \pm \frac{b_X}{m^{3/2}} \right) \quad (5.3)$$

For which in the limit of $M \rightarrow \infty$:

$$\lim_{M \rightarrow \infty} g'^2 = \frac{b_X^2}{m} \quad (5.4)$$

This expression indicates that the light atoms are the primary contributor to the optic modes, and the intensity of the optic modes will start decreasing dramatically as the mass m of the light atoms increases. Table 5.2 further emphasizes this point by comparing several parameters relevant to the phonon intensities of UC, UN, and US. Al is also included in the table since it is responsible for significant background contribution in our neutron scattering experiments.

In order to gain more insight, a simple 2-force constant model can be used to calculate the phonon dispersion for both US and UC. However, since more comprehensive models for phonon dispersions for UX are available in other publications, we opt not to implement a more sophisticated model. The experimental data shown in Fig. 5.5 has been verified to be consistent with existing publications.

UC, $T = 4\text{K}$

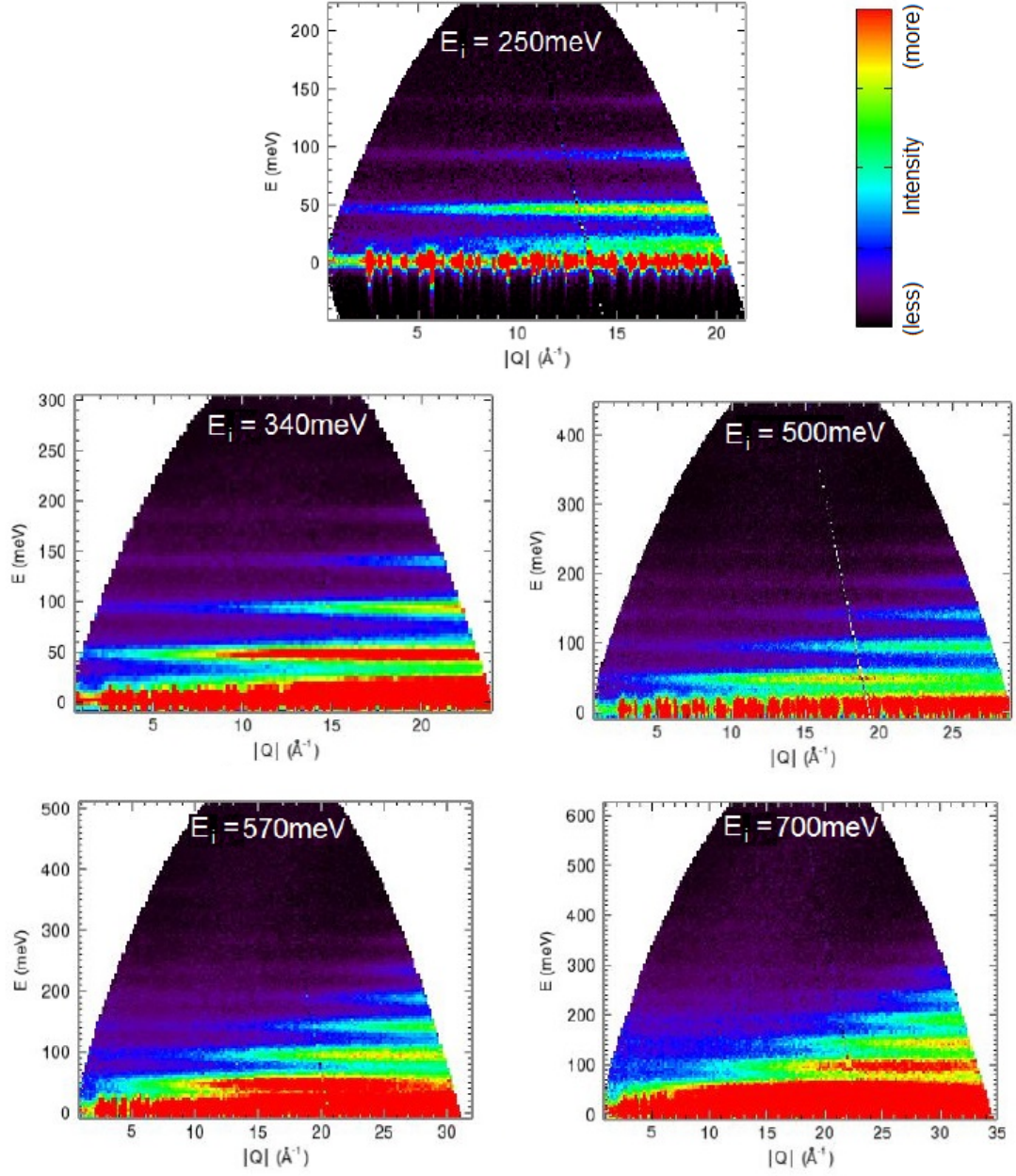


Figure 5.6: Shown here are powder averaged data of energy transferred vs. Q plots for UC at 4 K, collected at SEQUOIA. All E_i used are shown, including $E_i = 250$, 340, 500, 570, and 700 meV .

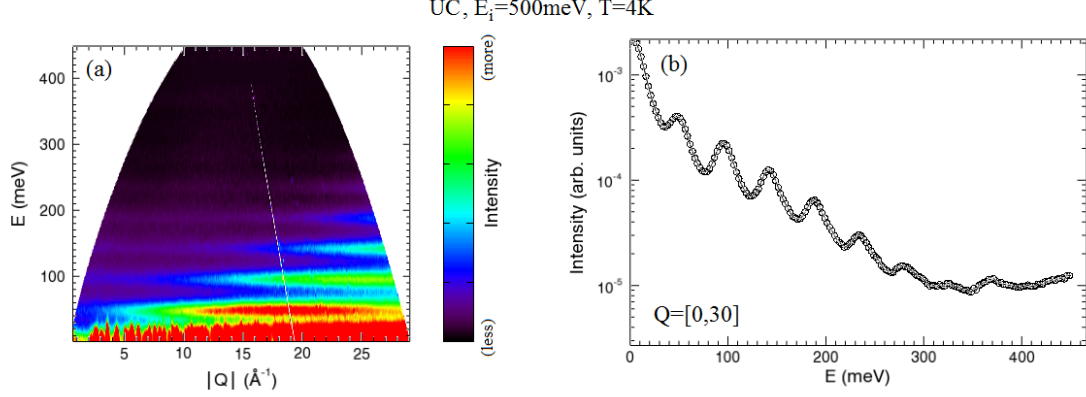


Figure 5.7: (a) A powder averaged data of energy transferred vs. Q plots for UC at 4K collected at SEQUOIA with $E_i = 500$ meV; (b): Intensity vs. energy transferred data, Q is integrated over its full range.

5.3.2 Evenly spaced QHO modes in UC

Fig.5.6 shows all of the powder averaged inelastic neutron diffraction data collected for UC, all measured at $T = 4$ K, with $E_i = 250, 340, 500, 570$, and 700 meV. The QHO modes are visible up to the 9th or the 10th mode in the $E_i = 700$ meV plot, comparable to that observed in UN.

Fig.5.7(a) shows one of the powder averaged inelastic neutron diffraction data for UC, taken at $T=4$ K with $E_i = 500$ meV. One can clearly see the evenly spaced energy levels analogous to the evenly spaced energy levels of QHOs as illustrated in Fig.5.2. Note that the y-axis is the energy transferred $E = E_i - E_f$, for example the bright horizontal mode at $E=50$ meV visible in all the plots of Fig.5.6 corresponds to the energy between the ground state and the first excited state, i.e. 40 meV $= E_1 - E_0 = 3/2\hbar\omega - 1/2\hbar\omega = \hbar\omega$, and not the energy of the first excited state itself. Fig.5.7(b) shows the Q -integrated curve for intensity vs. energy transferred for a closer look at the QHO modes. One can easily count up to the 7th mode, with a spacing of about 40 meV between each mode.

Anisotropy of QHO modes in UC

All QHO data presented to this point for both UC and UN (15) has been powder-averaged, so only Q is considered and not $\mathbf{Q}$. The reason this approximation works so well is because the modes are extremely isotropic. However, to try and quantify any anisotropy or anharmonicity for the QHO modes of UC, we collected a $E_i = 700$ meV dataset with very high statistics along three crystallographic directions, [100], [110], and [111]. The C atoms have nearest neighbour distances along these directions in the ratio of $1:\sqrt{2}:\sqrt{3}$, as one can see from considering the crystal structure shown in Fig. 5.8(a). Constant- Q difference cuts along the three directions are shown in Fig. 5.8(b). The difference cuts were obtained by subtracting a low $Q_{\parallel}$ cut ($-8 < Q_{\parallel} < 0 \text{ \AA}^{-1}$, with the two other mutually orthogonal directions $|Q_{\perp}| = [-2, 2] \text{ \AA}^{-1}$) from a high $Q_{\parallel}$ cut ($-30 < Q_{\parallel} < -20 \text{ \AA}^{-1}$, also with $|Q_{\perp}| = [-2, 2] \text{ \AA}^{-1}$) with the goal of trying to eliminate multiple scattering effects from the ensuing data analysis.

The Q-integrated intensity versus energy data can be fitted to the following functional form to determine the exact energy for each of the QHO mode.

$$I(E) = \sum_n T_n e^{-\frac{(E-E_n)^2}{2\sigma_n^2}} + B_{exp} e^{-\lambda_B E} + B_0 \quad (5.5)$$

A flat instrumental background B_0 and a simple exponential decaying potential $B_{exp} e^{-\lambda_B E}$ which can be expected from a simplified diffusive model of multi-phonon scattering (183; 184), were incorporated into the fit. E_n are the mode positions that were fit independently and the last term incorporates all sources of background.

By fitting the Q-integrated cuts to Eq.5.5, the mode positions were determined along the [001], [110], and [111] directions. The peak positions are listed in Table 5.3(a), and the fits are indicated in Fig. 5.8(b) by the solid curves. Table 5.3(b) shows the peak positions for QHO modes along different directions using a calculated potential, as explained in the next paragraph. Fig. 5.8(c) shows the mode positions determined from the data (E_n^{exp}), with the dashed curve representing the expectation

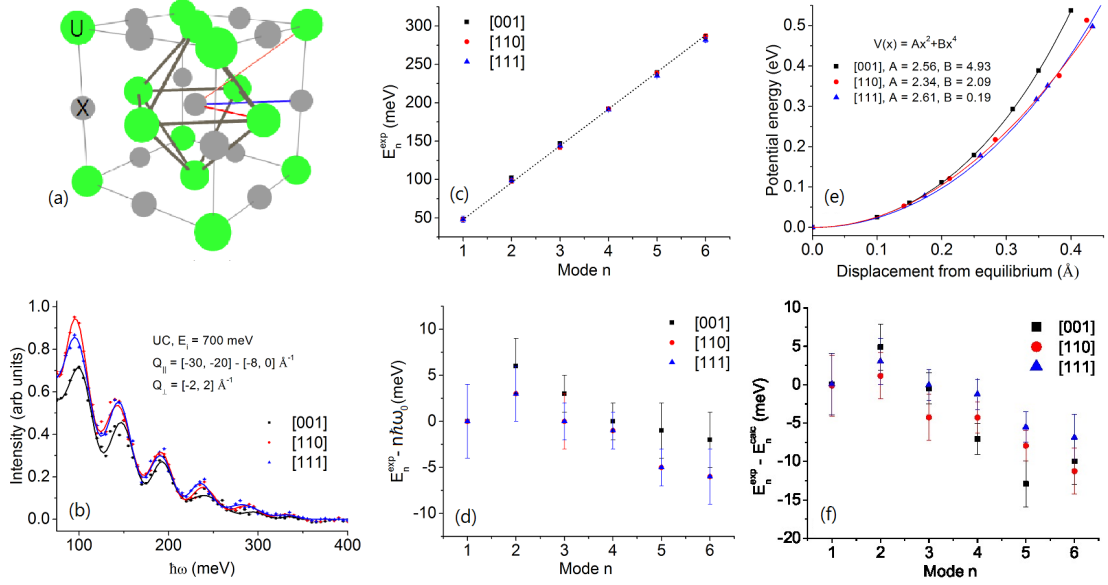


Figure 5.8: (a) The crystal structure of the binary uranium systems UX. The light X atom is in an octahedral cage of U atoms. The colored lines indicates the three primary crystallographic directions, [001], [110] and [111]. The carbon atom nearest neighbor distances in these directions are in the ratio of $1:\sqrt{2}:\sqrt{3}$. (b) Constant- E difference cuts along the major crystallographic directions [001], [110], and [111] for UC. The solid curves are fits of the data to a superposition of Gaussian functions. (c) Peak positions along the three different directions taken from the fits in (b). The dotted line corresponds to the expected peak positions for an isotropic QHO. (d) The difference between the peak positions of the modes from our UC data and a perfectly harmonic potential. (e) Local potential of the carbon atoms calculated by DFT. The solid curves are fits to the anharmonic function $V(x)$ given in the text. (f) The difference between the peak positions of the UC data and the result from the DFT calculations.

Table 5.3: (a): Peak positions of the QHO modes (in meV) extracted from fitting difference cuts of the $E_i = 700$ meV single crystal UC data along three major crystallographic directions. The form of the difference cuts is explained in the text. (b): Peak positions of the QHO modes calculated using first order perturbation from calculated potential of UC as described in text.

(a) Experimental values in meV:

n	[100]	[110]	[111]
1	-	-	-
2	100(5)	98(7)	97(7)
3	148(2)	143(3)	145(3)
4	192(2)	192(2)	191(2)
5	239(3)	239(2)	235(2)
6	296(3)	287(2)	282(3)

(b) Calculated values for each QHO level and the values for the x^4 term using $V(x)$, in meV:

n	100	$\langle x^4 \rangle$	110	$\langle x^4 \rangle$	111	$\langle x^4 \rangle$
1	47.3	1.2	47.8	0.3	46.9	0.09
2	95.8	3.6	95.8	0.8	93.9	0.26
3	145	7.2	144	1.5	141	0.51
4	196	12	193	2.5	188	0.85
5	248	18	241	3.8	235	1.3
6	301	25	290	5.3	283	1.8

for an ideal carbon QHO with $\hbar\omega_0 = 48$ meV. Fig. 5.8(d) shows the difference between the mode positions for the ideal model ($n\hbar\omega_0$) and the experiment. The error bars represent the uncertainty arising from fitting the data to obtain the mode positions.

An attempt was made to model the anisotropy and anharmonicity of the UC QHO modes by considering a potential energy at the C site of the form:

$$V(x) = Ax^2 + Bx^4 \quad (5.6)$$

Assuming that the x^4 term is small in the above expression, the energy levels corresponding to this potential can be calculated according to first order perturbation

theory, with the n th energy level corresponding to:

$$E_n = \hbar\omega_0(n + 1/2) + \frac{3B\hbar^2}{2m^2\omega_0^2}(n^2 + n + 1/2) \quad (5.7)$$

and the energy difference between the n th level and the $n = 0$ ground state given by:

$$E_n - E_0 = 2A\gamma n + \frac{3B\gamma^2}{2}(n^2 + n) \quad (5.8)$$

with $\gamma = \hbar/m\omega_0$. Solving Eq.5.8 for γ yields the fundamental frequency for the anharmonic oscillator as a function of A and B . We have determined these two parameters from density functional theory (DFT) calculations of the carbon atom potential along the [001], [110], and [111] major crystallographic directions, allowing us to predict the shifts of the oscillator levels. The DFT calculations are indicated by the symbols in Fig. 5.8(e), while the fits to Eq.5.6 are indicated by the solid curves.

Fig. 5.8(f) displays the difference between the oscillator mode positions determined from the experiment and the DFT calculations (E_n^{calc}). The data and the model are in fairly good agreement, however, the calculated potential do predict a slightly larger anisotropy than observed. Both also indicate the presence of a small amount of anisotropy, and show that the anharmonicity is maximized along the [001] direction. This is apparent in Table. 5.3(b), which shows the values of the calculated x^4 terms for each of the directions and QHO levels.

5.3.3 Observation of QHO modes in US

Fig.5.9(a) shows the inelastic neutron diffraction data collected for US, measured at T=4K with $E_i = 250$ meV. From the first glance only the first 2 mode can be made out of the $E_i=250$ meV graph, at E=48 and 96 meV. According to previous discussion in 5.3.1 and table 5.2, it is expected that the QHO modes observed in US to be less prominent than in UC. In order to effectively separate the US signal from the background, additional measurements were performed using a close replica of the

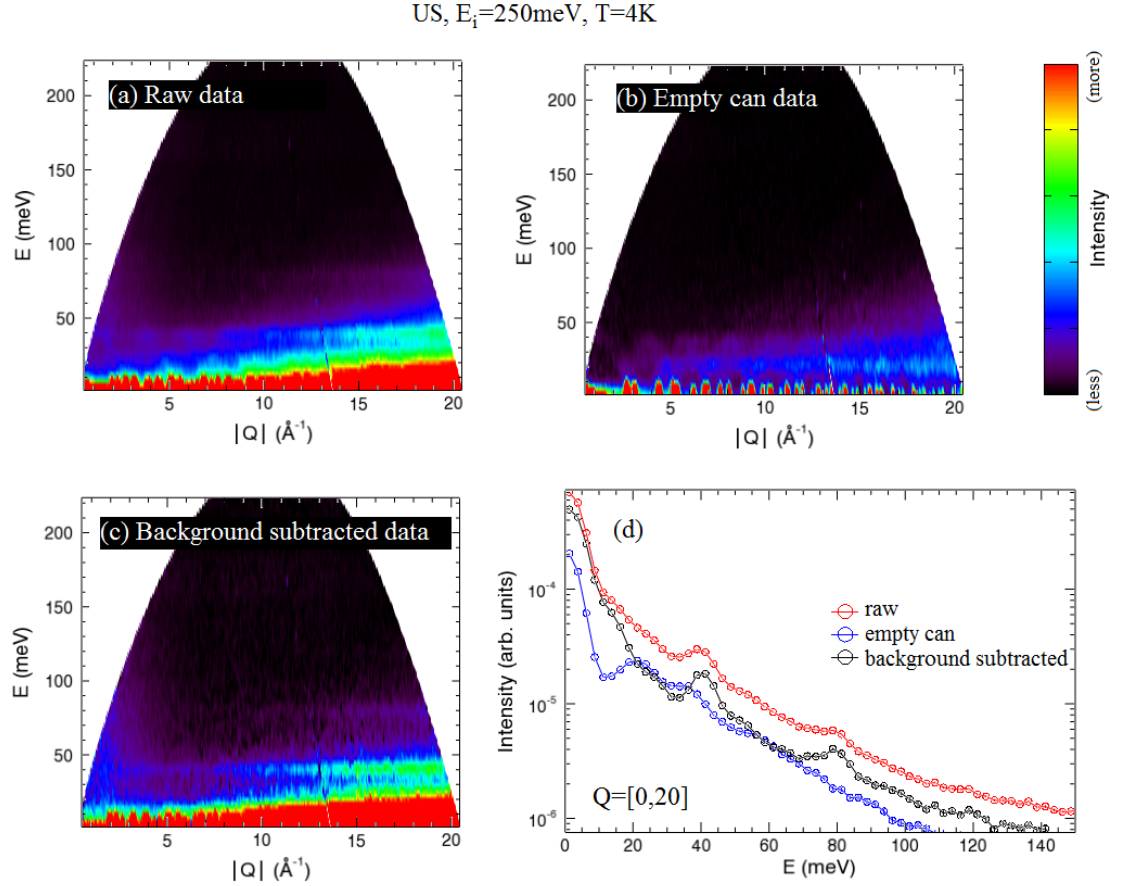


Figure 5.9: (a) A powder averaged data of energy transferred vs. Q plots for US at 4K collected at ARCS with $E_i=250\text{meV}$; (b): Background data collected by repeating the same measurement for an empty Al can, completed with sample holders and brackets; (c): The resulting data after subtracting the empty can data from the raw data; (d): A comparison of intensity vs. energy transferred data for (a), (b), and (c). All Q 's are integrated over the full range.

sample container and mount very similar to that shown in Fig.5.3. The data from this measurement is shown in Fig.5.9(b), and the difference between Fig.5.9(a) and Fig.5.9(b) is shown in Fig.5.9(c). Fig.5.9(d) shows the Q-integrated curves from the three datasets. One can see that the QHO peaks at 48 meV and especially at 96 meV, are sharper for the background subtracted curve than the raw data curve.

Fig.5.10 shows the rest of the inelastic neutron diffraction data collected for US, measured at $T = 4$ K, with $E_i = 250, 500$, and 700 meV. In the $E_i = 500$ meV and the $E_i = 700$ meV no QHO mode can be made out.

Indeed the vibrational modes of the light atoms are much more representative of ideal QHOs in UC and UN (15) than for US. The differences in the U:X mass ratio (U:C = 19.8, U:N = 17, U:S = 7.4) therefore play a major role in dictating when one expects the QHO modes to be visible. As the U:X mass ratio decreases, the dispersion of the optic phonon modes has been shown to increase systematically (172), and therefore the vibrational behavior of the light atoms shifts further away from the localized QHO picture. A smaller U:X mass ratio has also the effect of pushing the optic phonon modes down closer in energy to the acoustic modes, so any resulting QHO excitations would be more closely spaced and therefore harder to resolve for a given instrumental energy resolution.

There are also additional factors to consider, related to the mass m and neutron scattering lengths b_X of the X atoms. As shown in Eq.5.9, the intensity of the optic phonon modes decreases with increasing m . In fact, Table 5.2 shows that the optic modes for US are down in intensity by two orders of magnitude compared to UC and UN. This intensity decrease is partially due to the lower b_X of S compared to C and N. Our previous work on UN also revealed that the positions of maximum intensity in $Q - E$ space for the QHO modes corresponds to the recoil line for the X atoms (15), given by $E = \hbar^2 Q^2 / 2m$. As the mass m increases, these positions are shifted up in Q outside the coverage range of ARCS. The recoil lines for elements of interest are plotted together in Fig.5.11, i.e. C and S, and H, He and Al for background, and also N for comparison. One can easily see that the recoil line for S falls out of the

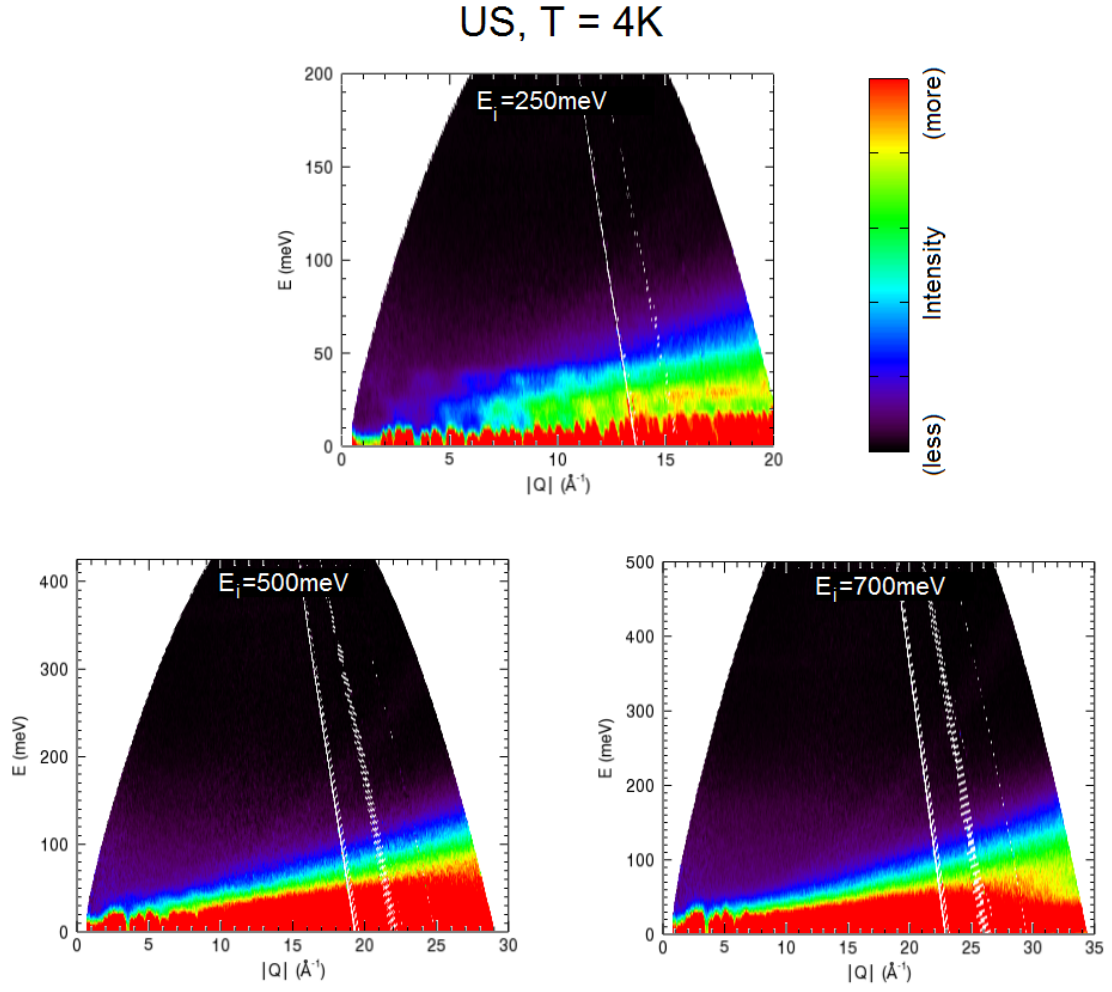


Figure 5.10: Shown here are background subtracted, powder averaged data of energy transferred vs. Q plots for US at 4 K, collected at ARCS. All E_i used are shown, including $E_i = 250, 500$, and 700 meV .

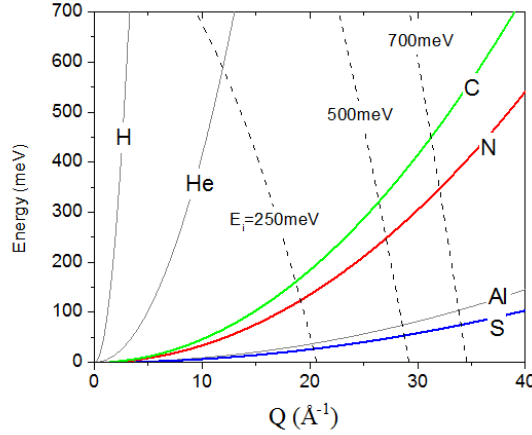


Figure 5.11: Shown here is what the recoil lines corresponding to different elements would look on a E versus Q color contour plot. The detection range of SEQUOIA for different E_i 's are also plotted.

detectable range at much lower energy than C and N. Moreover, the proximity of the Al and S recoil line, together with the relatively smaller scattering cross section of S compared to Al's, further complicate the task to resolve QHO modes in US.

5.3.4 Comparing UC and US

Fig.5.12(a) thru (c) depicts the orientationally averaged, high energy response observed for both UC and US on ARCS, where (d) thru (f) shows the Q integrated data of the data, fitted to Eq.5.5. Several evenly-spaced vibrational modes are found in the UC $E_i = 500$ meV spectrum shown in Fig.5.12(a), with modes up to 7th order clearly visible in the Q -integrated data shown in Fig.5.12(d). The US data with $E_i = 500$ meV yields a drastically different response, with no clear high energy vibrational modes observed, as shown in Fig.5.12(b) and (e). On the other hand, higher resolution $E_i = 250$ meV data depicted in Fig.5.12(c) and (f) shows evidence for two higher order vibrational modes above the optic phonon modes centered around 40 meV.

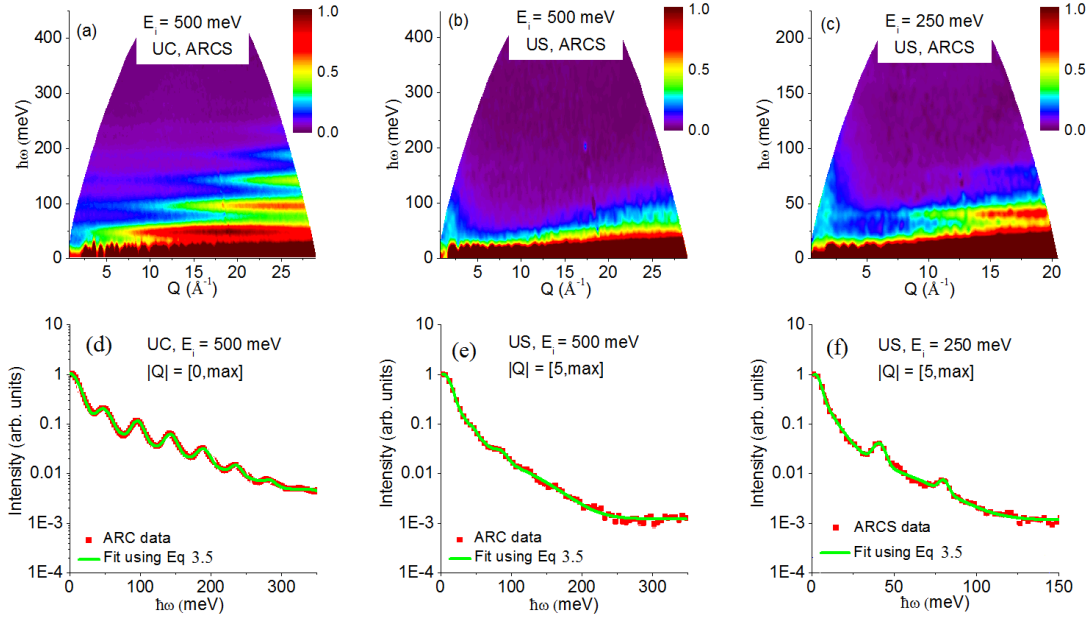


Figure 5.12: Color contour plots of the experimental neutron scattering spectra for (a) UC, $E_i = 500$ meV, (b) US, $E_i = 500$ meV and (c) US, $E_i = 250$ meV. The evenly-spaced, high energy vibrational modes are clearly visible in the UC plot, but hardly noticeable in the case of US. (d), (e), and (f) show the corresponding Q -integrated plots for the three experimental data sets, with solid green lines showing the fitted curve for each of the experimental data using Eq.5.5.

The fitted peak positions of the modes for the different datasets are shown in Table 5.4, and indeed they are extremely evenly spaced. The average spacing between the modes, incorporating all fitted datasets, was found to be $\hbar\omega_0 = 48$ meV for UC and $\hbar\omega_0 = 40$ meV for US.

Table 5.4: Peak positions of the high energy vibrational modes (in meV) for (a) UC and (b) US from fits to data integrated over all Q.

(a) UC, T = 7 K			
$n \backslash E_i$	500 meV	700 meV	800 meV
1	47.7(3)	-	-
2	96.2(3)	98.1(2)	99.7(4)
3	142.8(4)	144.1(3)	146.0(5)
4	189.1(6)	190.9(3)	193.0(4)
5	235.6(1)	237.3(4)	239.0(4)
6	283.8(36)	283.7(6)	284.7(6)
7	-	329.9(7)	331.0(10)
8	-	372.9(12)	375.5(17)
average $\hbar\omega_0$: 48 meV			
(b) US, T = 7 K			
$n \backslash E_i$	250 meV		
1	40.9(3)		
2	79.9(9)		
		average $\hbar\omega_0$: 40 meV	

5.4 A 3D QHO model

Since the vibrational spectra of UC and US are characterized by a series of evenly-spaced modes, the most plausible explanation for these findings is that the light atoms behave like independent 3D QHOs in an analogous way to the nitrogen atoms of UN (15). This hypothesis can be tested quantitatively in a variety of different ways, since the dynamical structure factor for the n th mode of a QHO at low T has a simple analytical form given by the following equation (167).

$$S_n(Q, \omega) = \frac{1}{n!} \left(\frac{\hbar Q^2}{2m\omega_0} \right)^n \exp\left(\frac{-\hbar Q^2}{2m\omega_0}\right) \mathcal{F}(\omega) \quad (5.9)$$

where $\mathcal{F}(\omega) = \delta(\hbar\omega - n\hbar\omega_0)$.

One option is to perform Monte Carlo ray tracing simulations of the neutron scattering spectra with a QHO scattering term as part of the sample kernel (166). This approach worked exceptionally well to describe the neutron scattering spectra observed for UN. Recent advances in the Monte Carlo technique allowed us to include weaker scattering contributions not accounted for within the QHO model, such as the intrinsic broadening of QHO modes as explained by the binary solid model. For this reason, the resulting UN simulations described the experimental data to unprecedented accuracy, and therefore the Monte Carlo ray tracing approach is extended to the cases of UC and US here.

5.4.1 Monte Carlo ray tracing simulation

Monte Carlo (MC) ray tracing simulations of both the UC and US ARCS neutron scattering experiments were performed to try and gain a better understanding of the various factors contributing to the observed scattering intensity. These simulations used the MC ray tracing program Monte Carlo Virtual Neutron Experiment (MCViNE) developed in the Distributed Data Analysis for Neutron Scattering Experiments (DANSE) (185) software development project. In each simulation, the sample was approximated as a cube with a 1 cm³ volume, similar to the sample used in the actual experiment. The source files for the simulations were created through a series of simple modifications to the files used for the UN MC simulations described in detail in Ref. (166). The acoustic phonon density of states in both cases was obtained from a Born-Van Karmen model, with the values for the nearest neighbour U-X and U-U radial force constants given below.

For UC, the electronic structure within the density functional theory (DFT) was obtained using the Quantum ESPRESSO package (186). The calculation was performed using a plane-wave basis set and an ultrasoft pseudopotential (187) optimized in a RRKJ scheme (188). The uranium pseudopotential was obtained from

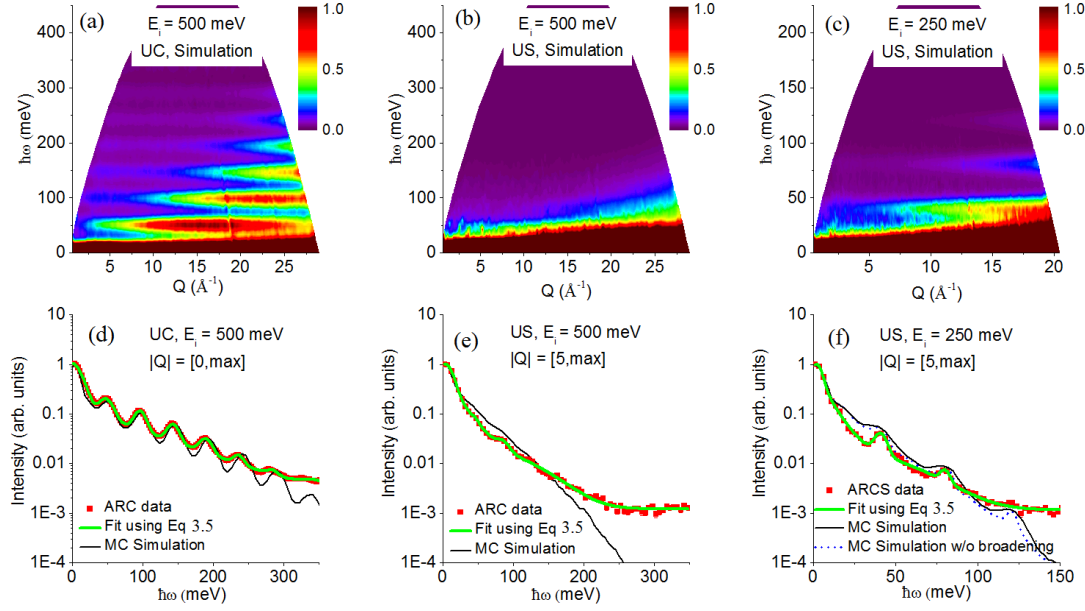


Figure 5.13: (a), (b), and (c) shows the Monte Carlo ray tracing simulations for UC with $E_i = 500$ meV, and US with $E_i = 500$ and 250 meV respectively. (d), (e), and (f) again show the corresponding Q -integrated plots for the three experimental data sets, with comparison to the simulation results. (i) shows simulation results for both including and excluding intrinsic broadening of the model.

an ionized electronic configuration: $6p^6 6d^{15} f^3 7s^1$ with cutoff radii equal to 3.5 atomic units (a.u.), 1.7 a.u., 2.6 a.u. and 1.6 a.u. for s, p, d and f angular momentum. The electronic levels deviate from the all-electron ones by less than 0.1 meV. We used the Perdew, Burke, Ernzerhof (189) exchange-correlation functional. The Brillouin zone (BZ) summations were carried out over a $4 \times 4 \times 4$ supercell. The electronic smearing with a width of 0.02 Ry was applied according to the Methfessel-Paxton method. The plane wave energy and charge density cut-offs were 73 Ry and 1054 Ry respectively, corresponding to a calculation accuracy of 0.2 mRy/atom. The carbon atom potential was obtained from the total energy modification of a $2 \times 2 \times 2$ supercell when one carbon atom was shifted from the equilibrium position in the [100], [110], or [111] directions and the remaining atoms were held fixed in their equilibrium positions.

A Monte Carlo ray tracing simulation for UC with $E_i = 500$ meV is shown as a color contour plot in Fig. 5.13(a) and the Q -integrated result is displayed in

Fig. 5.13(d). This simulation is analogous to the one reported in Ref. (166) for UN and includes various sample kernels accounting for elastic scattering, QHO scattering (from carbon atoms), acoustic phonon scattering, and all forms of multiple scattering. The last contribution, multiple scattering, turns out to be extremely important for accurately simulating the neutron scattering spectra of UN due to the even spacing of the QHO modes.

Fig. 5.14 outlines the difference between the single and multiple scattering processes described above, and explains the origin of the Q -dependence of the multiple scattering. For example, both single and multiple scattering events with a neutron energy loss of $2\hbar\omega$ create two quanta of energy. Since these quanta are created by the same scattering process in the former case, the resulting intensity $I \sim Q^4$ and the vibrational state of the X atom is excited up two levels in the QHO picture. In contrast, since the multiple scattering processes create the two quanta at different locations, the resulting intensity $I \sim (Q_1 Q_2)^2$ and each of the two independent scattering processes excite the vibrational state of the X atom up only one level. Fig. 5.14(b) shows how the multiple scattering associated with these vibrational modes arises even at low Q . In the schematic, special values of $\mathbf{Q}_1$ and $\mathbf{Q}_2$ were chosen such that the total momentum transfer $\mathbf{Q} = 0$ but the scattering intensity is non-zero. In general, there are infinitely many combinations of $\mathbf{Q}_1$ and $\mathbf{Q}_2$ that are realized at random, and therefore this scattering has no Q -dependence.

Intrinsic broadening of the QHO modes is also included in the simulation, as it is observed experimentally and predicted according to the binary solid model (167). The broadening arises from the fact that the heavy U atoms are not completely stationary, and can be modelled by replacing the Dirac-Delta function in the QHO expression with a Gaussian:

$$\mathcal{F}(\omega) = \exp[-(\hbar\omega - n\hbar\omega_o)^2/2\Gamma^2(T)] \quad (5.10)$$

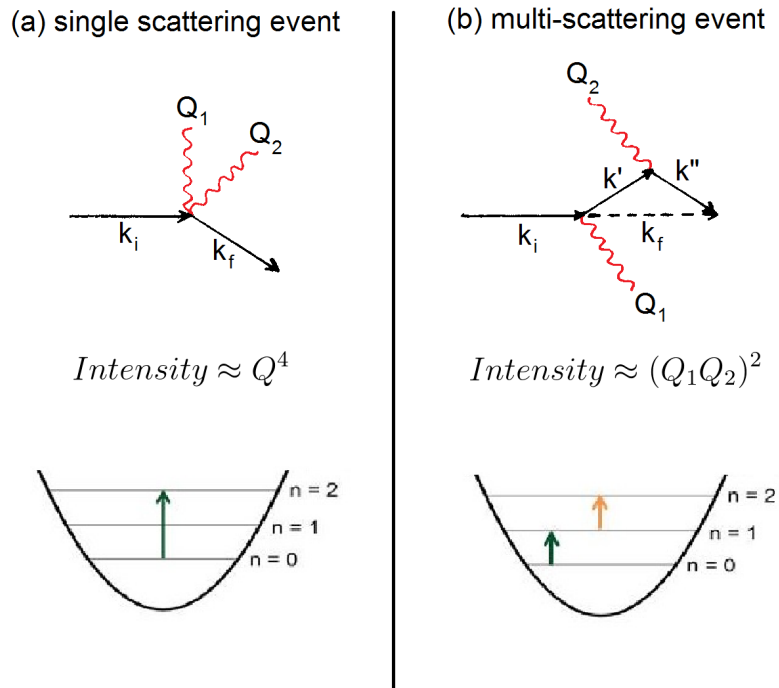


Figure 5.14: Schematics showing the difference between (a) single scattering and (b) multiple scattering processes leading to the observed neutron scattering spectra for UC, UN, and US.

The Gaussian width $\Gamma(T)$ is a function of temperature and given by the following.

$$\Gamma^2(T) = (\hbar^2 Q^2 / 2M) \int_0^\theta du Z(u) u \coth(\hbar u / 2k_B T) \quad (5.11)$$

Here, $Z(u)$ is the acoustic phonon density of states calculated with a Born-Van Karmen model and θ is the maximum band frequency for the acoustic phonon modes. When all of the above factors are taken into account, the resulting agreement between the experimental data and the simulation is quite good, suggesting that vibrational behavior of the carbon atoms in UC is well approximated by independent 3D QHOs. There are only small discrepancies between the simulation and the experiment, which will be discussed in more detail below.

Monte Carlo simulations for US, incorporating the same sample kernels as for UC, are shown as color contour plots in Fig.5.13(b) and (c) with intrinsic broadening included. The Q -integrated results are also presented in Fig.5.13(e) and (f), with (f) showing simulation data for both with and without intrinsic broadening. These simulations do not reproduce the experimental data well regardless of whether or not the broadening is included, suggesting that the vibrational behavior of the sulfur atoms in the system is far from the ideal QHO limit.

In addition, complementary Monte Carlo simulations for Al has also been finished to help visualize Al's contribution to background, especially in the case for US. Fig.5.15 shows the simulated pattern for Al at $T = 4$ K for $E_i = 500$ meV normalized to the simulated US plot in Fig.5.13(b) by both proton counts and color scale of the contour. The volume of the Al stage simulated is a 1 cm thick disk with a diameter of 3cm, comparable in size to the one used during the actual experiment.

5.5 Model versus experimental data

We now discuss the differences present between the experimental and simulation results. Since several well-defined QHO modes were observed for UC, additional

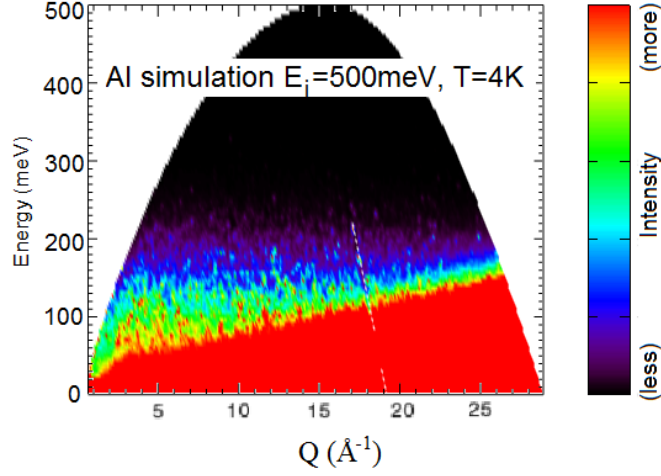


Figure 5.15: (a): a contoured plot for energy transferred vs. Q ; and (b): an Intensity vs. Q plot with curves integrated at energies where the first 3 QHO modes are expected in US.

detailed quantitative analysis is possible. We fit the constant- E cuts of the UC data to the same expression considered for the UN case (15), given by:

$$S_n(Q, \omega) = A_n Q^{2n} \exp(-CQ^2) + B_n \quad (5.12)$$

with C taken as a global parameter and a Q -independent B_n term included to account for the multiple scattering described above. For the ideal QHO model, $A_n = C^n/n!$ is a required constraint, and this was adopted in the simulations. By relaxing this constraint and allowing A_n and C to be independent parameters in the data fitting, one can gain a better sense of how much the UC data deviates from the ideal QHO limit.

Fig. 5.17(a) depicts constant- E cuts from the 500 meV dataset for the $n = 1-5$ modes, centered about $n\hbar\omega_0$ for the n th mode (20 meV integration range). Similar cuts were made for the $E_i = 700$ meV and 800 meV datasets (not shown). The cuts from the $E_i = 500$ meV MC simulation, with C fixed at the value of $0.0036 \text{ \AA}^2$ corresponding to a carbon QHO with $\hbar\omega_0 = 48$ meV, are presented on the same plot as

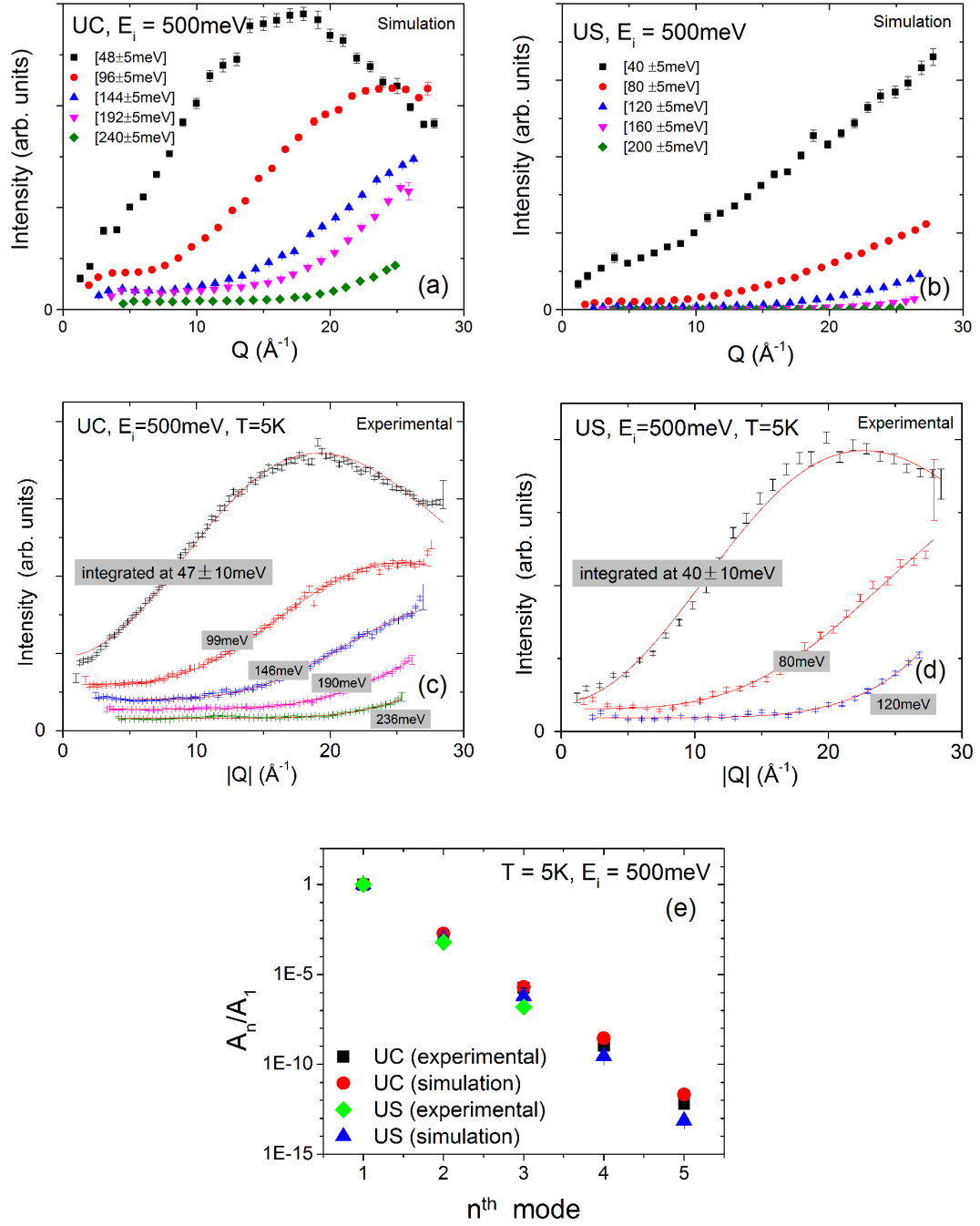


Figure 5.16: Shown here are constant energy cuts centered at each QHO modes for (a): UC, simulation; (b): US, simulation; (c): UC, experimental; and (d): US, Simulation; (e) Parameter A_n/A_1 extracted from each of the dataset.

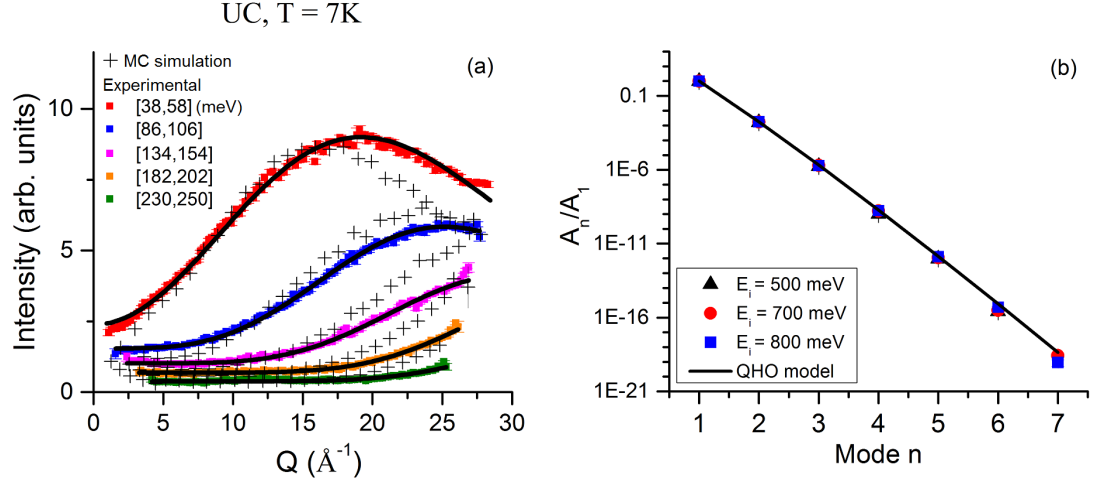


Figure 5.17: (a) The Q -dependence of the intensity for the $n = 1-5$ UC oscillator modes with $E_i = 500$ meV. The solid lines are fits to the QHO model described in the text, while the (+) symbols represent constant- E cuts from the MC simulations. (b) The A_n coefficients for the $n = 1-5$ modes normalized by the values of A_1 . The coefficients are extracted from fits to the $E_i = 500$ meV (black triangles), 700 meV (red circles) and 800 meV (blue squares) ARCS datasets. The solid line is the prediction of the QHO model with $\hbar\omega_0 = 48$ meV and m corresponding to the mass of a carbon atom. The ratio is plotted on a logarithmic scale and spans almost 20 orders of magnitude.

connected brown symbols. There are clearly deviations between the constant E -cuts of the ARCS data and the simulation, suggesting that the assumption $A_n = C^n/n!$ made in the latter is not strictly true, but not too far off.

Fig. 5.17(b) plots the ratios of the fitted parameters A_n/A_1 for the $E_i = 500$ meV, 700 meV, and 800 meV datasets. The solid curve indicates the prediction for the QHO model with $\hbar\omega_0 = 48$ meV, with the non-integer n values interpolated by using $\Gamma(n+1)$ to calculate $n!$. As in the case of UN, there is excellent agreement between the QHO model and the data over 20 orders of magnitude. The experimental C value, corresponding to the zero point motion of the oscillator, also agrees well with the model. By incorporating all three datasets into the fitting, the average value of C was found to be $0.0031(1) \text{ \AA}^2$, which is close to the ideal value given above. These findings are all strong confirmation that the high energy vibrational modes observed in UC correspond to quantum oscillations of the carbon atoms in the system, despite the small discrepancies that arise when one constrains $A_n = C^n/n!$ in the simulations. One can think of the carbon atoms as independent, 3D QHOs.

Chapter 6

Concluding remarks

The ability to construct tools out of materials have long distinguished mankind from the rest of nature, yet perhaps not the ability to construct tools but the ability to engineer materials is the true reflection of mankind's technological progress: the Stone Age, the Bronze Age, the Iron Age, etc. Throughout the ages, we learned how useful it is to be able to manipulate materials to adapt to our needs; from glass, to steel, to plastic, microchips, graphene, and materials of the future. The arrival of new materials, or rather knowledge about new materials, often launch waves of technological advances. For this purpose, we have explored three distinct groups of materials that carry some of the utmost interests shared among the materials science community. These materials are the iron-pnictide $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$, the uranium rock salts UC and US, and the helimagnetic B20 cubic $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$. We have explored and learned about the structural, magnetic, and dynamical properties of these systems. The following paragraphs will briefly summarize our findings for these materials, thus conclude this report.

For the $\text{PrFe}_{1-x}\text{Ru}_x\text{AsO}$ series, we have combined magnetic susceptibility, heat capacity, NPD, and μSR data for x from 0 up to 1. The substitution of diamagnetic Ru for magnetic Fe generates a spin dilution process, which gradually suppresses the ordering in the FeAs layers, in which evidence for static moments persists until

around $x = 0.6$, the magnetic percolation threshold expected under a localized $J_1 - J_2$ model (76; 51). The gradual suppression of the magnetic phase is closely followed by the reduction of the structural tetragonal-orthorhombic phase transition temperature. The lattice distortion and the magnetic ordering are found to be strongly coupled, as predicted for pnictides by many theoretical works (88; 85; 89; 86; 87; 90). The persistence of static moments and possible suppression of magnetic fluctuations, together with disorder introduced in the FeAs plan by Ru atoms may all be related to the absence of superconductivity in the system.

In addition, we found that both the magnetic ordering of the Pr sublattice and the negative thermal expansion of the c-axis phenomena persist up to $x = 1$. We speculate that the abnormal thermal expansion behavior can be linked to the magneto-elastic coupling within the Pr sublattice, which survives despite of the disruption of the ordering of Fe moments.

As for the study on the B20-cubic helical magnet, we discovered that non-cubic phase FeGe can be stabilized by annealing a stoichiometric mixture of Fe-Ge along with as little as 3% of cubic CrGe polycrystals. We investigated the effect of Cr doping on the helimagnetic ordering in FeGe. We found that the magnetic order in $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ is systematically suppressed by Cr doping. Strong temperature dependence is observed for the helix and coherence length of the helical ordering in samples with $x > 0.09$, with increasing temperature dependences for higher doping levels. The base temperature length of the helix k_0 also decreases with doping, with $2\pi/k_0 = 408\text{\AA}$ for $x = 0.33$ compared to $700\text{\AA}$ for FeGe, a 42% change. We interpreted our findings based on the Maleyev model (123), and compared our data with similar studies on $\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ (135), $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ (124), and MnSi under pressure (152; 153). We adapted the analysis method used in Ref. (135) and mapped the principal interaction energies A/a^2 , F/a^2 , and SD/a as functions of Cr concentration. We also mapped the principal interactions as temperatures for comparison with the ordering temperature T_C and found that $A/(a^2k_B)$ shares a similar temperature dependence as T_C as in the case for $\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ (135). Both

T_C and $A/(a^2k_B)$ decrease almost linearly with Cr doping and disappear around $x = 0.4$. Finally, we also observed a broad maximum in the magnetic susceptibility and SANS peak intensity data, which correspond to a similar feature observed in CrGe previously explained by paramagnon theory (132; 143).

The obvious next step for this project is to attempt at the growth of large single crystals of $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$, since according to literature the single crystal growth of FeGe larger than 1 mm^3 have been extremely difficult. $\text{Fe}_{1-x}\text{Cr}_x\text{Ge}$ for low enough x should have very similar properties as FeGe and will provide a great alternative to better understand the system, particularly the skyrmions that were not examined here. We have also already grown some single crystals of CrGe by vapor transfer and the exploration of the paramagnons in CrGe at low temperature can also be interesting.

Moving onto the uranium rock salts studies. For UC, time-of-flight neutron scattering measurements reveal a series of well-defined, equally spaced, high energy vibrational modes that can be attributed to quantum harmonic oscillator behavior of the carbon atoms in this system. Measurements of the QHO modes along the high-symmetry [001], [110], and [111] directions reveal that these excitations are characterized by only a very small amount of anharmonicity and anisotropy. Similar time-of-flight neutron scattering data for US also shows evidence for the high energy vibrational modes, but only a few are clearly observed and they are much weaker in intensity. The U:X mass ratio therefore plays a key role in the observation of quantum harmonic oscillator behavior in these binary uranium crystals, although the mass of the light atoms is also very important. These two parameters are optimal in UN and UC, allowing the QHO modes to be clearly observed. However, this situation is rarely realized in binary crystals, and therefore well-defined QHO modes are generally not apparent in these systems.

For the future of the study of QHOs in physical systems, we can look into other binary heavy-light element systems, most obviously also of the rock salt structure. Heavy metal carbides is one of the obvious candidates. Another systematic study of a series of heavy metal carbides may reveal new information about QHOs perhaps in the

department of its dependence on the heavy-light atom weight ratio. This particular focus was made complicated by extra variables introduced by the change of light atoms in the uranium rock salts' studies. With heavy metal carbides the difference between members is the heavy atom. It will also not have the complications of the light atoms potentially having a scattering cross section that is too small such as Sulfur.

This concludes this thesis. The study of materials is a never-ending task, we have both explored newly discovered compounds, and revisited old ones to learn features previously unbeknown to us. When, or whether any of these materials will one day become part of a consumer product, or a space ship, or the fuel of the space ship, we can only wait and hope and see. Being at the frontier of scientific research, our duty as scientists is to push the boundary of knowledge further and further ahead so that we can have more and more knowledge at our disposal. When a new crisis or challenge come knocking on our doors, we can be as well prepared as possible, armed with the knowledge of the world's materials.

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Vita

Yuen Yiu was born and raised in a blue collar household in Hong Kong. He discovered his love for math and science during his secondary school years at La Salle College. He initially chose Computer Engineering as his major for undergraduate studies at the University of Michigan. However after a few introductory Physics classes, he began to find Physics more intellectually satisfying and challenging, and switched his major to Physics shortly after. He was then introduced to the world of Condensed Matter Physics by Marcus Bennett, a fellow boxer at Michigan's Men's Boxing Club, and started participating in research as an undergraduate assistant.

After earning his Bachelor's degree at the University of Michigan, Yuen began working as a laboratory assistant in Professor Aronson's group at Brookhaven National Laboratory. During that time Yuen had the chance to learn and adopt practical skills around the laboratory, but also realized that he would need more education if he wants to have a serious career in science. Following his pleasant working experience at a national research facility, Yuen applied to the doctoral program in Physics at the University of Tennessee because of its proximity to Oak Ridge National Laboratory. He was admitted into the program and started his doctoral studies during the Fall of 2008. This is the thesis of his doctoral research at the University of Tennessee under the supervision of Professor Stephen Nagler.

Yuen's other passions in life includes foreign languages, philosophy, music, literature, and boxing.