HIGH THROUGHPUT PARAMETRIC STUDIES OF THE STRUCTURE OF COMPLEX NANOMATERIALS

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ABSTRACT

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The structure of nanoscale materials is difficult to study because crystallography, the gold-standard for structure studies, no longer works at the nanoscale. New tools are needed to study nanostructure. Furthermore, it is important to study the evolution of nanostructure of complex nanostructured materials as a function of various parameters such as temperature or other environmental variables. These are called parametric studies because an environmental parameter is being varied. This means that the new tools for studying nanostructure also need to be extended to work quickly and on large numbers of datasets. This thesis describes the development of new tools for high throughput studies of complex and nanostructured materials, and their application to study the structural evolution of bulk, and nanoparticles of, MnAs as a function of temperature.

The tool for high throughput analysis of the bulk material was developed as part of this PhD thesis work and is called SrRietveld. A large part of making a new tool is to validate it and we did this for SrRietveld by carrying out a high-throughput study of uncertainties coming from the program using different ways of estimating the uncertainty. This tool was applied to study structural changes in MnAs as a function of temperature. We were also interested in studying different MnAs nanoparticles fabricated through different methods because of their applications in information storage. PDFgui, an existing tool for analyzing nanoparticles using Pair distribution function (PDF) refinement, was used in these cases. Comparing the results from the analysis by SrRietveld and PDFgui, we got more comprehensive structure information about MnAs.

The layout of the thesis is as follows. First, the background knowledge about material structures is given. The conventional crystallographic analysis is introduced in both theoretical and practical ways. For high throughput study, the next-generation Rietveld analysis program: SrRietveld, is coded in Python. The details of SrRietveld are provided in the thesis. More importantly, two real applications of SrRietveld are demonstrated to show its use cases. For the error analysis on Rietveld refinement, it is found that the results from two popular Rietveld programs are very sensitive to the input errors and the subset sampling method is particularly useful when the errors on diffraction pattern are unknown. In order to show the power of SrRietveld, I did the parametric study on MnAs bulk and nanoparticles. It is found that the magnetostructural property exists in bulk and one type of MnAs nanoparticles. However, when I want to probe the other type of MnAs nanoparticles that has smaller size, the conventional Rietveld method doesn't work and I turn to PDF for help. Using PDF approach, the structures of bulk and nanoparticle MnAs have been explored. Finally the conclusion is that I can either retain or modify the bulk properties by using different synthesis methods.

To my family

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Table of Contents

List	of Tables	vi
\mathbf{List}	of Figures	rii
1	Introduction to material structure and diffraction method1.1Basics of Crystal system	$ \begin{array}{c} 1 \\ 2 \\ 3 \\ 5 \end{array} $
2	Crystallographic Analysis 1 2.1 Theoretical Background 1 2.2 Rietveld Method 1	.0 .1 .4
3	Next-generation Rietveld analysis: SrRietveld	20 20 21 22 25 30
4	The total scattering and atomic pair distribution function method44.1Theory of PDF44.2Corrections of PDF derivation44.3Cases of PDF calculation4	46 47 50 53
5	MnAs: Diverse structural and magnetic properties	55 55 57 51 58
6 Bibl	Conclusion	'9 34

List of Tables

3.1	Refined values, estimated standard deviations for LaMnO ₃ from the GSAS	38
3.2	Difference in the values of refined parameters between FullProf refine- ments on data converted from time-map format using the SE and NSE methods, respectively. The numbers in the parethese are the standard deviations on the differences, calculated as the square-root of the sum of the variances.	38
5.1	The refined structural parameters for bulk and type-A nanoparticles at 295 K and 335 K using α (P6 ₃ mc) and β (Pnma) model. All models are refined with isotropic thermal factor U _{iso} .	62
5.2	The refined structural parameters for type-B nanoparticles at 295 K and 335 K using the α (P6 ₃ mc) and β (Pnma) model. All models are refined with isotropic thermal factor U _{iso} .	65

List of Figures

4	Bragg diffraction [1, 2]. Two beams with the same wavelength and phase approach the sample and are scattered by two different atoms inside it. The lower one travels an length of $2d\sin\theta$ longer	1.1
6	Ewald construction $[3]$	1.2
23	SrRietveld software architecture. The User Interface, SrRietveld, HDF5 Data Structure, PyGSAS, and PyFullprof are python packages in the SrRietveld project. The GSAS and Fullprof represent the underlying refinement engines.	3.1
27	Temperature dependence of SrRietveld refinement results for NaCl us- ing FullProf (blue dots) and GSAS (red squares) engines. (a) lattice parameter, a , and (b) atomic displacement parameters, U_{iso} , at Na (crosses for FullProf, plus markers for GSAS) and Cl (dots for Full- Prof, squares for GSAS) sites. Dashed lines mark fitted Debye model curves.	3.2
35	(a) TOF neutron powder diffraction pattern on LaMnO ₃ (blue circles) with the best fit calculated pattern from FullProf (red line). The low <i>d</i> -spacing, short TOF, region to the left of the dashed line has been zoomed in 6 times for clarity. The green line offset below is the difference between the calculated and measured patterns. The black markers indicate the peak positions. (b) As (a) but the red curve is calculated using GSAS.	3.3
39	The probability distribution functions of refined lattice parameters from FullProf based on data converted using the SE and NSE methods. (a), (b) and (c) show the distributions of lattice parameters a, b and c , respectively. For each subfigure, red, green and black symbols are from the NSE method; blue, orange and brown are from the SE method. Diamonds are from Monte Carlo resampling, squares are from subset sampling and circles are from the standard Hessian matrix method.	3.4

3.5	The probability distribution functions of thermal factors U_{iso} . (a) is for La, (b) is for Mn, (c) is for O1 and (d) is for O2. All colors and symbols have the same meanings as Fig. 3.4	40
5.1	TEM images and particle size distributions of type-A (a) and type-B (b) MnAs nanoparticles.	70
5.2	PDF refinements on bulk (left) and type-A nanoparticle (right) MnAs data. For each subfigure, the bulk circles represent the PDF from the experimental data and the red solid line is the calculated PDF after refinement. The green curve offset below is the difference curve between data and model.	71
5.3	 (a) comparison of the difference (orange curve) between 295 (blue line) and 335 K (red line) diffraction pattern for bulk MnAs. (b) same as (a) but for type-A nanoparticles with violet-colored difference curve. (c) comparison of the difference curves from (a) and (b). The orange is the same as the difference curve in (a) and the violet is the result of scaling the curve in (b) by a factor of 4 for comparison. 	72
5.4	(a) comparison of the difference (orange curve) between 295 (blue line) and 335 K (red line) PDF for bulk MnAs. (b) same as (a) but for type- A nanoparticles with violet-colored difference curve. (c) comparison of the difference curves from (a) and (b). The orange is the same as the difference curve in (a) and the violet is the result of scaling the curve in (b) by a factor of 4 for comparison. The similar comparison based on diffraction pattern is shown in Fig. 5.3.	73
5.5	Lattice parameters ((a), (b)) and atomic displacement factors ((c), (d)) from PDF refinements on bulk and type-A samples using α phase structure model. (a) and (b) are for lattice parameter a and c in unit of Å. (c) and (d) are for Uiso of Mn and As in unit of Å ² . For each subfigure, the blue and red are for bulk MnAs on the cooling and heating runs respectively. The cyan and magenta are for type-A MnAs nanoparticles on cooling and heating runs.	74
5.6	PDF refinements on data acquired on type-B nanoparticles at 295 ((a), (b)) and 335 K ((c), (d)) using the α ((a), (c)) and β ((b), (d)) phase model, respectively. For each subfigure, the symbol and color representations are the same as Fig. 5.2.	75
5.7	Same as 5.3 but for type-B nanoparticles. In (c) the difference curve (violet) of type-B nanoparticles is scaled by a factor of 10 since its amplitude is too small to compare with the bulk one	76

- 5.8 Same as 5.4 but for type-B nanoparticles. In (c) the difference curve (violet) of type-B nanoparticles is scaled by a factor of 10 since its amplitude is too small to compare with the bulk one. The similar comparison based on diffraction pattern is shown in Fig. 5.7.
- 5.9 Real part of the AC magnetization (a) and unit cell volume (b) in bulk, type-A and type-B nanoparticles. All of the unit cell volumes are based on the results of α -model refinements. The blue (cooling) and red (heating) are for the bulk sample; cyan (cooling) and magenta (heating) are for type-A nanoparticles; and the green (cooling) and orange (heating) are for type-B. The dashed lines at 303 K and 317 K show the temperature range of the structural transitions in bulk MnAs as reported in the literature as we mention in the text.

78

77

Chapter 1

Introduction to material structure and diffraction method

All materials are made of atoms. There are about 100 kinds of atoms based on the periodic table. The universe is composed of them. The properties of the materials are determined by the atoms of which they consist and how the atoms are bonded together [4].

The structures of the materials have to be studied so that the researchers can understand the properties of useful materials [5]. Studies of material structures can also help chemists in synthesis and modification of materials with desired properties [6, 7]. In general, solid materials are the most commonly studied by scientists because of their applications [8, 9, 10], for example in the technology of transistors and semiconductors.

Diffraction techniques, including X-ray diffraction, neutron diffraction and electron diffraction, have been developed to investigate the structures of different materials, especially for the crystalline solids where the atoms are composed in an ordered fashion. More details about this topic can be found in many good books [11, 12, 13]. This thesis focuses on high throughput parametric study on the structure of complex nanomaterials.

A brief introduction to the structure of materials is given in the following three sections, with emphases on issues that are relevant to this thesis. Section 1.1 covers some basic knowledge about crystal structure, such as it description and classification. In section 1.2, the foundation of crystallography: Bragg's law is introduced. The last section describes the relationship between the diffraction pattern and material structure.

1.1 Basics of Crystal system

The structures of the materials appear differently in nature. The simplest one of these structures normally is the one with clearly repeated pattern of atomic positions. The material with such structure is called crystal [8, 9, 10], *e.g.*NaCl and diamond. Scientists who study them are focus on their inside geometry. The crystallography [14, 15] is the field that people study the crystal.

The structure of a crystal is made up of a number of points (atoms or molecules) arranged in a ordered way. Inside a crystal, a lattice (a repeated pattern of atoms or molecules) exhibits long-range order and symmetry. The so-called unit cell is formed by the points. The lengths of the edges in the unit cell and the angles between them are called the lattice parameters [8]. The space group [8] is used to represent the symmetry property of the structure. It is a mixture of the translational symmetry of a unit cell, the point group symmetry operations of reflection, rotation, the screw axis and glide plane symmetry operations [16]. In summary, there are seven lattice systems: triclinic, monoclinic, orthorhombic, rhombohedral, tetragonal, hexagonal, and cubic, which includes 14 unique ones. Normally scientists use one of 230 unique space groups to describe the crystal symmetry [17].

The Miller index is usually used to determine the atomic plane. If we choose

the three lattice vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 to determine the unit cell, the corresponding primitive reciprocal lattice vectors are given by [8]

$$\mathbf{b_1} = \frac{2\pi \mathbf{a_2} \times \mathbf{a_3}}{\mathbf{a_1} \star (\mathbf{a_2} \times \mathbf{a_3})} \tag{1.1}$$

$$\mathbf{b_2} = \frac{2\pi \mathbf{a_3} \times \mathbf{a_1}}{\mathbf{a_2} \star (\mathbf{a_3} \times \mathbf{a_1})} \tag{1.2}$$

$$\mathbf{b_3} = \frac{2\pi \mathbf{a_1} \times \mathbf{a_2}}{\mathbf{a_3} \star (\mathbf{a_1} \times \mathbf{a_2})} \tag{1.3}$$

Using the three Miller indices l, m and n, we can define the plane orthogonal to the lattice vectors:

$$\mathbf{g}_{lmn} = l\mathbf{b}_1 + m\mathbf{b}_2 + n\mathbf{b}_3 \tag{1.4}$$

The perpendicular distance d between two closest lattice planes is determined by:

$$d = \left| \frac{2\pi}{\mathbf{g}_{lmn}} \right| \tag{1.5}$$

In order to understand the structures, it is necessary to know the arrangement of atoms relative to each other, the number of the nearest neighbors, a list of interatomic distances and etc.. To detect the structure information in atom level, people have been relying on diffraction technique since about 100 years ago. In the following section, I will describe the basics of the diffraction theory.

1.2 Bragg's Law

Bragg's Law is the fundamental rule of modern diffraction theory. It is also the milestone where people start to understand the diffraction in more profound way. It was discovered by physicist Sir William L. Bragg in 1912 [1, 2], who later won the Nobel Prize with his son because of their work in determining crystal structures [18].

Since then, the X-rays became a power tool to investigate the structure of crystals and other forms of materials.



Figure 1.1: Bragg diffraction [1, 2]. Two beams with the same wavelength and phase approach the sample and are scattered by two different atoms inside it. The lower one travels an length of $2d \sin \theta$ longer.

X-rays can force the cloud of atom's electrons to move when they are incident on an atom. If the cloud movement results that the same-frequency waves are radiated, this phenomenon is known as elastic scattering [19]. In such case, the new waves can be scattered but it is often negligible for the high-order scattering. If the incident beam is made up of neutrons, elastic scattering could also happen when it hit on the nuclei or it flies through the electronic magnetic field around the nuclei. The big difference between these two type of beams is that X-ray scattering is not sensitive to the atom with few number of electrons, *e.g.*, hydrogen, especially when there are heavy atoms with many electrons while neutron scattering does. The fields produced by the scattered waves can interfere with each other. Sometimes it produces stronger signals while other times it could cancel out each other. Therefore, the diffraction pattern are formed and can be observed through a detector or film, which is usually the experimental result. It serves as the first step of diffraction analysis. In general, the constructive interference happens when the following formula is satisfied:

$$n\lambda = 2d\sin\theta \tag{1.6}$$

where n is an integer representing the given order, λ is the wavelength of the incident wave, d is the spacing between two planes, and θ is the angle between the incident beam and the planes. It is called the Bragg's law. As shown in Fig. 1.1, the diffraction pattern is determined by the parameters mentioned in Eq. 1.6. When the equation is satisfied, there will be strong peak appearing in the diffraction pattern. The strength of those peaks relative to each other are determined by the order parameter n.

1.3 Diffraction Method

Diffraction method is one of the most popular scientific techniques to probe the structures of materials. Normally the X-ray, neutron, or electron beam is used as the probed beam. In particular, for the study in this thesis, I am focus on powder diffraction, which was first used by Debye and Scherrer in 1916 [20]. It has advantage over other diffraction techniques because it is relatively easy to prepare the powder sample for common cases. Meanwhile it can still provide the comparable structure information from analyzing the diffraction pattern.

The most common type of radiation used in powder work is X-radiation since the technique was developed a century ago. For later study in this thesis, I also use the X-ray powder diffraction method as the experimental tool. The X-ray we refer here is a high energy electromagnetic radiation with corresponding wavelength in the order of 1 \mathring{A} . In order to access high energy X-ray source, we usually go to synchrotron at national laboratory (*e.g.*, Advanced Photon Source at Argonne National Laboratory) to perform our powder diffraction experiments.

As we know, the powder sample is made of large number of crystals with random orientations. In order to understand the basis of X-ray powder diffraction, we have to study the interaction of X-ray and crystal first. As I mentioned earlier in this chapter, X-rays can be diffracted from crystals since their electric fields interact with the electron clouds of atoms in the crystals. The X-rays scattered from adjacent atoms interfere and a diffraction pattern is produced. In this section, I will introduce the X-ray diffraction on crystal and later powder diffraction in general.





Figure 1.2: Ewald construction [3]

Assume the incident X-ray beam targeting on the crystal has a momentum k_i , and the diffracted beam has a momentum \vec{k}_f . Therefore the momentum difference between these beams is defined as

$$\vec{Q} = \Delta \vec{k} = \vec{k}_f - \vec{k}_i \tag{1.7}$$

where \vec{Q} is known as the scattering factor (the change of momentum). It defines the so-called reciprocal space that the bright spots are shown on in the diffraction experiments. There is direct relationship between reciprocal space and real space that I will talk about later. It is another basis of diffraction theory.

If the amplitude of \vec{k}_i is $2\pi/\lambda$, where λ is the wavelength, and the diffraction is elastic, then we can calculate the amplitude of \vec{Q} by the following equation:

$$|\vec{Q}| = 2k\sin\theta = 4\pi\sin\theta/\lambda \tag{1.8}$$

where $|\vec{k}_i| = |\vec{k}_f| = k = 2\pi/\lambda$. The angle between $|\vec{k}_i|$ and $|\vec{k}_f|$ is 2θ , which is shown on Fig. 1.2. In fact respective to \vec{k}_i , for the elastic diffraction, the \vec{k}_f will always fall on the surface of the sphere in the figure. The sphere is called Ewald sphere.

When Bragg condition is satisfied, it means Eq. 1.6 is established. By substituting it into Eq. 1.5 and comparing it with Eq. 2.11, we can clearly see that the scattering vector \vec{Q} is equal to a reciprocal lattice vector \vec{g}_{lmn} when the order is 1. More importantly, it implies that the diffraction signals can only appear on the surface of the Ewald sphere as shown in Fig. 1.2.

1.3.2 Basic theory of crystal diffraction

For X-ray diffraction, we can use $\vec{k_i}$ to define the momentum of the incident wave. Based on classical wave theory [12], the incident wave can be totally represented by $Ae^{i\vec{k_i}\cdot\vec{r}}$, where \vec{r} is the position with the sample. Notice here, we only consider the static case, where the momentum vector doesn't depend on the time. If we also assume that the electron density as $\rho(\vec{r})$ and ignore constant term here, then the diffracted wave is determined by

amplitude of diffracted wave =
$$Ae^{ik_i \cdot \vec{r}} \rho(\vec{r}) dV$$
 (1.9)

where dV is the volumn that is filled by electron cloud around the position \vec{r} .

For simplicity, we always consider the elastic diffraction case first. It means for both incident and diffracted wave, they have the same amplitude of momentum vector, as $|\vec{k}_i| = |\vec{k}_f|$. Assume that the diffracted wave hits at the position \vec{r}_d on the detector, the phase change of the wave is given by

$$e^{\mathbf{i}\vec{k}_{f}\cdot(\vec{r}_{d}-\vec{r})}\tag{1.10}$$

Since there is no change on the amplitude of diffracted wave after the diffraction, the total wave that arrive at detector is determined by

$$A \int \mathrm{d}\vec{r}\rho(\vec{r})e^{\mathrm{i}\vec{k}_i\cdot\vec{r}}e^{\mathrm{i}\vec{k}_f\cdot(\vec{r}_d-\vec{r})} = Ae^{\mathrm{i}\vec{k}_f\cdot\vec{r}_d} \int \mathrm{d}\vec{r}\rho(\vec{r})e^{\mathrm{i}(\vec{k}_i-\vec{k}_f)\cdot\vec{r}}$$
(1.11)

Plugging Eq. 1.7 into the above equation, we get

$$Ae^{\mathbf{i}\vec{k}_{f}\cdot\vec{r}_{d}}\int \mathrm{d}\vec{r}\rho(\vec{r})e^{\mathbf{i}(\vec{k}_{i}-\vec{k}_{f})\cdot\vec{r}} = Ae^{\mathbf{i}\vec{k}_{f}\cdot\vec{r}_{d}}\int \mathrm{d}\vec{r}\rho(\vec{r})e^{-\mathbf{i}\vec{Q}\cdot\vec{r}}$$
(1.12)

If we define

$$F(\vec{Q}) = \int \mathrm{d}\vec{r}\rho(\vec{r})e^{-\mathrm{i}\vec{Q}\cdot\vec{r}}$$
(1.13)

which means the $F(\vec{Q})$ is the Fourier transform of $\rho(\vec{r})$. The Eq. 1.12 can be simplified as

$$Ae^{\mathbf{i}\vec{k}f\cdot\vec{r}_d} \int \mathrm{d}\vec{r}\rho(\vec{r})e^{-\mathbf{i}\vec{Q}\cdot\vec{r}} = Ae^{\mathbf{i}\vec{k}f\cdot\vec{r}_d}F(\vec{Q}) \tag{1.14}$$

Finally the intensity of the diffraction peak is determined by

$$A^2 |F(\vec{Q})|^2 \tag{1.15}$$

where $F(\vec{Q})$ is called structure factor. Furthermore, the structure factor is the one to connect the real space (\vec{r}) to reciprocal space (\vec{Q}) . Because of this one-to-one direct relationship, the reciprocal and real space analysis potentially can give us the same set of structure information.

For perfect crystal, its electron density $\rho(\vec{r})$ is periodic. Then its counterpart in reciprocal space, $F(\vec{Q})$, has non-zero values only when the Bragg condition is satisfied. It implied that there are only Bragg peaks appearing in the diffraction pattern on the detector. However, in real experiment, all crystals are not perfect. They have different defects and heterogeneity in their configuration. Therefore, Bragg peaks have a finite width and there may be significant diffuse (inelastic) scattering that fall between the Bragg peaks [21].

1.3.3 Powder diffraction

In our experiments, we use the powder samples, which usually contain large number of randomly oriented crystals. By saying that, we assume that each possible orientation is equally represented in the powder sample. For some crystals in the sample, the Bragg condition will be satisfied and the Bragg peak will appear. Because of homogeneity in crystalline orientation, the azimuthal angle of the incident beam doesn't matter in powder case. Therefore, in powder diffraction pattern, we can't directly obtain the phase information but we can get the magnitude from the intensity of the peaks.

For instance, when Bragg's condition is satisfied for any *hkl* plane, the reflections from all crystals in the sample lie on a cone, which is called Debye-Sherrer cone. From the perpendicular view of the detector area, we can see the smooth circles formed on the powder pattern because many bright spots from crystals are continuously connected. The obvious result is that the information from the three-dimensional reciprocal space has been compressed into one dimension. Due to the complexity of such powder patterns, it is usually very difficult to interpret them without further information.

Chapter 2

Crystallographic Analysis

Crystallographic analysis [14] is a method based on diffraction techniques to study the structure information inside crystals [22]. The method for studying crystal structure has been developing since last century [23, 24]. It is focus on analyzing the diffraction patterns coming from the certain sample. In particular, powder diffraction pattern is one of such cases that many scientists are working on. Since most materials can not form large crystals, the powder diffraction [25] overcomes the single crystal technique and becomes one of the most popular techniques to characterize the crystallographic structure, crystallite size, and preferred orientation in polycrystalline or powdered solid samples [26]. There are several databases [17, 23, 27] existing now for scientists to index their diffraction pattern in order to find new phases in the sample. However, it was hard to do when the databases didn't contain many known structures. So powder diffraction was not popular until Rietveld method [28, 29] was developed in 1960s. Rietveld method is also one of the techniques I have been using for the high throughput parametric study during my PhD research.

This chapter focuses on the Rietveld method only as one of major crystallographic analysis methods. Firstly, section 2.1 provides an overview of powder diffraction pattern, as the basis of the crystallographic analysis. Then in section 2.2, The detailed introduction of Rietveld method is presented.

2.1 Theoretical Background

In this section, I will focus on introducing the background knowledge of powder diffraction data. Usually a diffraction histogram is used to present the powder diffraction data. As we discuss in chapter 1, the intensity I in diffraction pattern is a function of the structure factor, which can be the function of scattering vector \vec{Q} or scattering angle 2θ eventually. Normally people use the scattering vector \vec{Q} as the independent variable since it contains the effects of the scattering angle and wavelength λ . Another advantage to use \vec{Q} is that we can measure our diffraction data under different experimental setup, *e.g.*, different scattering angles and different wavelengths. Finally we can compare them in the same space, reciprocal space [25].

As noted in many books [30] on powder diffraction, the total intensity detected from diffracted X-ray or neutron beam, I_T , is composed of the following parts:

$$I_T = I_c + I_{IC} + I_{MC} + I_{BG} (2.1)$$

where I_c is the intensity of coherent scattering, I_{IC} is the intensity of incoherent scattering, I_{MC} is the intensity of multiple-scattering and I_{BG} is the intensity of the background. Next I will explain them one by one in more details.

Normally the intensity of coherent scattering, I_c , is the largest term in Eq. 2.1. Coherent Scattering refers to the elastic scattering. It usually results all the Bragg peaks in the diffraction pattern as function of 2θ in X-ray diffraction or time of flight in neutron diffraction. As the intensity is determined by structure factor as we see in chapter 1, it contains the information about atom and lattice, *e.g.*, atomic coordinates, lattice parameters and *etc.* According to classical books [12, 31] about the coherent scattering, its intensity is determined by scattering cross section, $\frac{d\sigma_c}{d\omega}$, the absorption factor A, and polarization factor P as following the equation below:

$$I_c = APC \frac{d\sigma_c}{d\omega} \tag{2.2}$$

where C is to used for normalizing the cross section term in the unit of intensity per atom. The cross section term, $\frac{d\sigma_c}{d\omega}$, can be computed directly given the charge, mass of the particle in the sample and scattering angle of the incident beam. The analytical determination form for it can be found in many other books [12, 31].

Comparing with coherent scattering, the incoherent scattering is the inelastic scattering. For X-rays, the incoherent scattering is also called Compton scattering [12] while for neutrons it is from nuclear spin scattering [32]. Since it is inelastic, the energy of scattered beam always is less than the energy of incident beam, which means that there is energy transferred from incident beam to targeted atoms. It may lead atoms to diffuse. So it is also part of diffuse scattering, which generally includes all intensity that is outside Bragg reflections. It is usually difficult to directly separate the intensity of incoherent scattering from multiple-scattering and background although it can be calculated approximately in some cases, e.g., if the multiple-scattering is ignored.

Multiple-scattering [33] is very complex process in general. Since it is the term only giving greater contribution to the total intensity than the background, people usually ignore it although it happen in most scattering process. However for some application, *e.g.*, X-ray absorption Spectroscopy data analysis, it becomes especially important. Scientists develop different modeling such as diffusion process [34] to simulate it. Because it is computationally intensive, it also attracts computer scientists to apply different algorithms to solve it numerically [35].

The intensity of the background in Eq. 2.1 refers to all scattering without the sample, e.g., the scattering from the sample holder, air and *etc*. In the experiments,

people always try to get as less background as possible in order to make the data analysis easier. Usually high background implies certain problem and we have to change the condition to solve it. For example, it could be because of the strong fluorescence and then we have to choose different wavelength to do the measurement. If the sample is in amorphous phase, it is likely to produce strong background that make the data analysis more difficult [36]. It is the case where the conventional crystallographic analysis may not work. In common cases, we model the background by using different type of polynomial functions.

From the powder diffraction data, we can extract the structure and phase information [37]. For example, For each diffraction peak, it represents a particular plane denoted by Miller index as we discuss in the first chapter. The peak position contains the information of the size and shape of the unit cell for the crystalline sample [25]. The peak width depends on more factors: the size of the crystallites, the strain in the sample and instrumental parameters. Combining the information of diffraction peaks including their relative intensities, we can identify the sample and determine its structure. More importantly, for high throughput parametric study, we can control the certain parameter, *e.g.*, doping or temperature, to do the powder diffraction experiments in order to see how the sample system response. As one of the possible results, we could discover a new phase appearing during this process. In this way, the *insitu* measurement can help us understand new science in a complex material system.

Overall, powder diffraction is very useful technique in characterizing the structure information of the sample. However, it usually produces highly overlapped diffraction peaks, which leads the analysis on the data becomes very challenging.

2.2 Rietveld Method

2.2.1 Introduction

Rietveld method is a technique to extract structure information based on the experimental diffraction data and given structure model. It was developed by Hugo Rietveld to analyze the experimental data from either X-ray or neutron powder diffraction [28, 29]. It accounts for the instrumental effect and structural factors into the regression model, which make itself very complex. Theoretically, Rietveld method is a non-linear least square optimization process and provides the values of physical parameters by matching the experimental pattern with calculated pattern based on the predetermined structure model [38]. By varying the values of refined parameters during the process, the best fit can be obtained. In this section, I will introduce the mathematical model of Rietveld method and how it is implemented in order to solve real problems.

2.2.2 Mathematics

Within the weighted least square framework, Rietveld method is to minimize the following function based on all the intensities in the experimental dataset [39].

$$M_y = \sum_{i=1}^{N} w_i (y_{oi} - y_{ci})^2$$
(2.3)

where y_{oi} refers the i_{th} data point in measured dataset and y_{ci} is the calculated intensity for the point based on given structure model. The w_i is equal to the inverse of the variance on the i_{th} data point and N is the number of data points in the experimental dataset.

Since Rietveld method itself is a structure refinement method rather than structure solution [26], as part of the setup, it requires the structure model that make both physical and chemical sense and a set of reasonable initial values for the parameters inside the model.

Rietveld method models the intensity at i_{th} point of the diffraction pattern by the following equation, according to Young's book [38]:

$$y_{ci} = As \sum_{g} L_{g} P_{g} |F_{g}|^{2} \phi(2\theta_{i} - 2\theta_{g}) + y_{bi}$$
(2.4)

where A is an absorption factor, s is the scale factor. The g represents the Miller indices, hkl. L_g is a function that contains the factors of Lorentz, polarization and multiplicity. P_g is the preferred orientation function that depends on $g.F_g$ is the structure factor as we discuss in the first chapter. ϕ is the peak profile function that can be selected from a set of available functions based on the sample and experimental setup. As the last one, y_{bi} is the intensity of the background at the i_{th} point, which is often fitted by one of several polynomial functions.

The absorption factor, A, is usually a constant for flat sample in X-ray diffraction. In this configuration, it depends on the wavelength and the scattering angle. Since the absorption factor varies for different instrument and sample geometry, many Rietveld programs provides different functions to calculate it in different setting [40, 41]. For example, normally a exponential polynomial function is used to model the absorption factor for cylindrical sample in the Debye-Sherrer geometry, which I have been used for all the experiments in my PhD study, while there are other nonlinear functions for other instrumental setup in order to consider the surface effect.

Unlike the absorption factor, the Lorentz and polarization factors are rather modelled differently for different type of radiation. The polarization factor only applies to X-rays and the Lorentz factor depends on it while for time-of-flight (TOF) neutrons it depends on the d-spacing and scattering angle [40, 41].

Among all the parameters that are defined above in Eq. 2.4, the peak profile part

is the most popular topic that scientists have been discussing [42, 28, 29, 43, 44, 45] even before Rietveld method was developed since it plays the most important role in Rietveld refinement. Different peak profile functions are provided to deal with time-of-flight neutron diffraction, constant wavelength neutron and X-rays diffraction, respectively [38]. The simplest profile function is Gaussian function although it is proper only when there are no particle size and inhomogeneous strain effects [43]. Specifically, the Gaussian peak function is a function of peak width and scattering angle, which is widely used in the model of X-ray and neutron diffraction profiles. In reality, the peak function is usually asymmetric because of the instrument geometry and strain inside the sample. Lorentzian function is applied to fit the asymmetric feature in the peaks. Combining Gaussian and Lorentzian function, Pseudo-Voigt function is the most useful one among all peak profile functions [45]. It consistently fits better than pure Gaussian or Lorentzian function for diffraction patterns up to now although there may be better function for certain sample and instrument setup [43].

After introducing the structure model, now let us focus on the weighting factor at data point i, w_i , in Eq. 2.3. As we mention above, w_i is the inverse of the variance on observed data point i [39, 46]. For ideal case, we assume the observation is independent of each other and for each point its statistical fluctuation has the Poisson distribution since it is the counting number on certain position of detector screen. As in Eq. 2.3, the probability that we have observed intensity y_{oi} at point iis

$$P(y_{oi}) = \lambda^{y_{oi}} exp(-\lambda) / y_{oi}!$$
(2.5)

where λ is the expected value of the observed intensity at i_{th} point. Furthermore, it is also the variance of y_{oi} . So to get better weighting factor now, we need to estimate the λ . On the other hand, Eq. 2.5 can be view as the the probability distribution of parameter λ given the known intensity y_{oi} . In this case, we can get the unbiased estimation of λ by calculating its mean, which is $y_{oi} + 1$ if we assume λ is a continuous variable [47]. It is the application of Bayesian inference [48]. However, the estimates from Bayesian approach heavily depends on the prior distribution. In the literature, Rainwater *et al.* [49]use an unbiased estimate of λ based on the assumption of the prior distribution is uniform over all possible values. It also leads to the same result as $y_{oi} + 1$. However, Box *et al.* [38] argue that the prior distribution as $\lambda^{-0.5}$ is more proper, which results that the estimate of λ is equal to $y_{oi} + 0.5$. Overall, considering the y_{oi} is much larger positive number from experimental data, y_{oi} is good enough to use as the estimate and still widely used in conventional Rietveld softwares [40, 41].

With understanding the means of all parameters in Eq. 2.3, I am going to describe how Rietveld method works as the following. The purpose of the method is to find the refined values of all variables by matching the calculated pattern with the experimental pattern. In other words, we need to find the minimum of Eq. 2.3. In order to do so, we take the derivative of it respect to parameter p_k and set it to zero if we assume the calculated model is a function of parameters $p_k, k = 1, ..., n$:

$$\frac{\partial M}{\partial p_k} = -2\sum_{i=1}^N w_i (y_{oi} - y_{ci}) \frac{\partial y_{ci}}{\partial p_k} = 0$$
(2.6)

Since the model to calculate y_{ci} is non-linear, it has no analytic solution. So we can apply Taylor series expansion about a_l for parameter p_l to approximate it to the first order:

$$y_{ci}(p_l) = y_{ci}(a_l) + \sum_l \frac{\partial y_{ci}}{\partial p_l} \Delta p_l$$
(2.7)

If we assume that

$$\Delta y_i = y_{oi} - y_{ci}(a_l) \tag{2.8}$$

Then Eq. 2.6

$$2\sum_{i=1}^{N} w_i (\Delta y_i - \sum_l \frac{\partial y_{ci}}{\partial p_l} \Delta p_l) \frac{\partial y_{ci}}{\partial p_k} = 0$$
(2.9)

By rearranging the above equation, we get

$$\sum_{i=1}^{N} w_i \frac{\partial y_{ci}}{\partial p_k} \left(\sum_l \frac{\partial y_{ci}}{\partial p_l} \triangle p_l \right) = \sum_{i=1}^{N} w_i \triangle y_i \frac{\partial y_{ci}}{\partial p_k}$$
(2.10)

Here we get the matrix form

$$\vec{x} = \vec{A}^{-1}\vec{b} \tag{2.11}$$

where the element x_l of vector \vec{x} is equal to Δp_l . The element A_{kl} of matrix \vec{A} is equal to $\sum_{i=1}^{N} w_i \frac{\partial y_{ci}}{\partial p_k} \frac{\partial y_{ci}}{\partial p_l}$, and the element b_k of vector \vec{b} is equal to $\sum_{i=1}^{N} w_i \Delta y_i \frac{\partial y_{ci}}{\partial p_k}$. The matrix A is so-called the Hessian matrix [26, 40, 41]. Given an initial values of every refined parameters, Hessian matrix can be calculated explicitly. Based on final equation 2.11, the increment of the parameter value can be obtained and then the current value of parameter is recalculated. The whole process will run repeatedly until it doesn't decrease the residual M any more or it reaches the termination criterion. This approach is called Gauss-Newton method [50]. Because of the probability of divergence [51, 52], there is a shift factor, f, to control the absolute value of the increment as

$$p_l^{m+1} = p_l^m + f \triangle p_l \tag{2.12}$$

where m is the iteration number. In this way, it avoids some failed cases by decreasing the increment systematically. Still if the initial values of parameters are far from the right ones, it may still come to divergent point.

As one of more efficient ways, Levenberg-Marquardt method is widely used [26, 40, 41]. It has the same procedure as Gaussian-Newton method but instead uses the shift factor it employs the damping factor based on Eq. 2.10. By using this factor, it can force the incremental vector to move along the direction of steepest decent. Although it is implemented in many existing Rietveld programs [53, 54, 40, 41, 55, 56, 57, 58], it can't ensure that the found result is the global minimum of function

M [51, 52]. Usually people always want to plot experimental and calculated patterns during Rietveld refinement to see whether the problems appear.

In practice, Rietveld refinement needs a lot of human effort to get as better result as possible. First we want to check whether there are a lot of sharp peaks in diffraction pattern in order to use the method [38]. Normally Rietveld can't work with the pattern with only broad background that can be obtained from amorphous material. Next an initial structure model that is close to the right model and initial values for parameters in the model are required . Furthermore, we need to select proper peak profile and background functions as I mentioned earlier. During the refinement, we have to consider how to refine so many parameters (in which order or how to group them). Overall for high throughput parametric study, these become especially problematic.

Chapter 3

Next-generation Rietveld analysis: SrRietveld

3.1 Introduction

Currently, many computer programs have been developed for Rietveld refinement [40, 41, 55, 56, 57, 58]. However, most software programs of this type require intensive user inputs and there is also a sharp learning curve for new users. The high data throughput from new generation diffractometers [59, 60, 61, 62], such as POWGEN at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory, is more than the conventional Rietveld refinement software can easily handle. Poor convergence of current programs is another obstacle for accurate determination of refined parameters and conventional refinement software often diverges, requiring significant human intervention to find the optimal structure solution. SrRietveld is designed to improve the user experience in computer aided Rietveld refinement.

The new software makes use of the existing refinement programs GSAS [40] and FullProf [41], which are already widely used. These programs are used by SrRietveld as refinement engines and SrRietveld provides an automation layer and a graphical user interface. The new functionalities are implemented in Python packages that can manipulate and communicate with the refinement engines. The refinement process can be controlled from SrRietveld and the results can be displayed and analyzed. This architecture separates the controlling scripts from the refinement engines and also allows the implementation of other engines in the future. Using SrRietveld, average users can set up high-throughput refinement quickly and save time in analyzing large numbers of data-sets. Meanwhile, advanced users are still able to customize the refinement routines, create their own Python scripts, or even develop new software applications based on SrRietveld's functionalities. The SrRietveld codes are open source and delveloped by a team (in Alphabet order): Chris Farrow, Jiwu Liu, Pavol Juhas, Peng Tian, Simon Billinge, Wenduo Zhou and Yingrui Shang.

3.2 Design Principles

SrRietveld has been developed as part of the NSF-funded distributed data analysis for neutron scattering measurements (DANSE) project in the Python language [63] using object oriented programming (OOP) concepts. Python is extensively used in scientific software development. It is cross-platform and suitable for fast development. Also there are many well designed packages for scientific programming and visualization, such as Matplotlib [64], NumPy [65] and SciPy [66]. The OOP design enables SrRietveld to be easily maintained and extended.

The philosophy of the SrRietveld design is to improve user efficiency during a typical work flow by controlling existing Rietveld refinement engines. For example, human intensive steps to guide a refinement to a local minimum can be automated, and multiple (hundreds or thousands) of refinements can be carried out using the same refinement template. Refinement information and results are stored in a flexible HDF5 data structure [67] allowing easy organization of a large number of refinements. SrRietveld also provides powerful tools for visualizing refinements. Fits can be plotted in real-time during refinement, as can selections of refined parameters plotted against refinement number or some other meta-parameter such as temperature. Pre-written scripts are provided for automating common tasks, such as refining from coarse guesses of initial parameters, sequential refinement, etc. It is also possible for advanced users to develop their own macro scripts and contribute to the development of SrRietveld. Users are supported through an online community where features can be requested and bugs reported.

3.3 Implementation

The architecture of SrRietveld is shown in Figure 3.1. SrRietveld consists of several programmatic units, indicated by boxes in Figure 3.1. The SrRietveld user interface is a full-featured graphical user interface (GUI) that enables the user to conveniently configure the refinement routines, modify inputs, and investigate and analyze the results. The GUI interacts with a control layer that coordinates communication with the refinement engines, PyGSAS and PyFullProf. PyGSAS and PyFullProf are Python libraries that give programmatic access to GSAS and Full-Prof. The implementation of PyFullProf, PyGSAS and the control layer ensures that SrRietveld has consistent behavior even while using different engines, allowing refinements to be readily carried out on the same data using either engine. The HDF5 data structure has been designed to be relatively small in size and quick to load, even when handling thousands of datasets.

As one of the developers, I lead the development of PyGSAS, which is comparable with the earlier developed PyFullProf by Wenduo Zhou. As a team, Jiwu Liu, Yingrui Shang and I have been involving the design and development of SrRietveld control layer and the GUI. Specifically, Jiwu Liu developed the HDF5 data structure and



Figure 3.1: SrRietveld software architecture. The User Interface, SrRietveld, HDF5 Data Structure, PyGSAS, and PyFullprof are python packages in the SrRietveld project. The GSAS and Fullprof represent the underlying refinement engines.

Yingrui Shang is more focus on the GUI while I coded most of the SrRietveld control layer. SrRietveld incorporates most of the major functionality supported by the current versions of FullProf and GSAS. However, some features, such as the refinement of magnetic phases, are not implemented, though this is planned for a later release.

SrRietveld is easy to use. It uses automation processes and intelligent control of the work flow whereby users are relieved of a large number of repetitive inputs. Tools are also provided in SrRietveld for extending and interrogating refinement results. Users are able to carry out a series of Rietveld refinements on one or more data sets automatically. The program captures errors and attempts to recover automatically when a refinement diverges, and thus increases the robustness of this sequential refinement process. In addition to the ease-of-use, SrRietveld provides flexibility and extensibility to advanced users. Since SrRietveld is modular and designed with focus on extensibility, the default behavior of the software can be redefined. Advanced user scripts can be written in Python to give new functionalities. Such a script is demonstrated below, which fits a Debye model for the lattice dynamics to the temperature dependence of the refined thermal parameters. In future releases we will allow easy incorporation of user-defined scripts into the program for easy sharing. Scientific programmers can also implement the application programming interfaces provided in SrRietveld into their own applications so SrRietveld's functionality can be incorporated into other programs.

SrRietveld is open source software distributed under the BSD License [68]. It is free to use, subject to the copyright restrictions and disclaimer, though we ask that papers published from work done using SrRietveld cite our work, as well as the paper describing the particular refinement engine used (FullProf or GSAS). More information can be obtained from the project web pages [69] or by contacting professor Simon Billinge (sb2896@columbia.edu).

SrRietveld is under active development and we encourage users to post bug re-

ports and feature requests on the SrRietveld online community group (details in the documentation). The plans for future releases include support for parallel computation, magnetic diffraction, and features for engineering diffraction analysis.

3.4 Application of SrRietveld I: NaCl

To demonstrate a typical use case, sequential refinements were carried out on xray powder diffraction patterns measured from NaCl at a series of temperatures. The data were collected at beamline 11-ID-B of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). The NaCl powder was obtained from Puratronic® with 99.999%, 5N grade purity. To demonstrate the ability to handle data from a high throughput instrument, many data-sets were collected using a low-resolution high throughput mode [70]. The sample was contained in a 1 mm diameter kapton tube mounted perpendicular to the synchrotron beam and cooled using an Oxford cryostream liquid nitrogen cooler. Data were collected at 307 temperature points between 155 K and 500 K on a 2D Perkin-Elmer amorphous silicon detector mounted 128 mm behind the sample and perpendicular to the beam. The beam energy was 58.26 keV giving an x-ray wavelength of 0.2128 Å. The temperature was ramped continuously at 3 K/min during data collection.

To improve the convergence during the sequential refinement, the refined results from the previous temperature point were used as initial values in the refinement on the data set at the following temperature point. The first point to be refined was the lowest temperature point. A refinement scheme was used whereby parameters were turned on in turn according to normal practice [38] beginning with a Lebail refinement [71] of the lattice parameters and the background, followed by Rietveld refinements where the scale parameter, zero shift parameters, lattice parameter, etc., were switched on in turn. This procedure is automated in SrRietveld and requires no user input after initial setup. Although in principle in a sequential refinement it should not be necessary to follow this scheme at every step since the initial parameters from the previous refinement are used and are already close to the minimum in practice we find that at some temperature points the refinement will still diverge if this scheme is not followed. However, SrRietveld provides great flexibility. For example, if speed of refinement is an issue the scheme could be changed so that all parameters are switched on at once after the first refinement, and the step-by-step scheme only turned on if a refinement diverges. Because SrRietveld controls the engines with scripts, there is great flexibility for automating such a procedure.

In the NaCl refinements, the full-set of refinable parameters used was the scale factor, the zero shift factor, the lattice parameter, the background parameters, the peak profile parameters, and the isotropic thermal displacement parameters. The starting model was taken from the literature [72]. Refinements were carried out on the same data using both GSAS and FullProf engines within SrRietveld. Both temperature series refinements used the same SrRietveld script, with the refinement engine changed from FullProf to GSAS by simply loading a different type of of template in the GUI. The ease of refining using both GSAS and FullProf engines is one of the great strengths of SrRietveld as we show here. Although GSAS and FullProf models are highly similar, there are subtle differences in how they handle experimental effects. For example, the way they handle the background function is quite different. In the FullProf example, user defined points are imported and a linear interpolation is applied between them for background correction. In the GSAS case, the background function is fitted to the data together with Rietveld profile. We have used the background function 6, a power series with negative power terms [40]). Also, the peak profiles are slightly different. The pseudo-Voigt peak profile function was used in the FullProf case. The GSAS refinements used profile function 3, which is also a pseudo-Voigt, but parametrized in a slightly different way [40]. These model


Figure 3.2: Temperature dependence of SrRietveld refinement results for NaCl using FullProf (blue dots) and GSAS (red squares) engines. (a) lattice parameter, a, and (b) atomic displacement parameters, U_{iso} , at Na (crosses for FullProf, plus markers for GSAS) and Cl (dots for FullProf, squares for GSAS) sites. Dashed lines mark fitted Debye model curves.

differences result in slight differences in the physical parameters refined from the data from each engine, as evident in Fig. 3.2.

Another feature of SrRietveld is that the parameters from many refinements are retained in the Python data-structure, allowing post-processing scripts of arbitrary complexity to be written. Here this feature is illustrated by writing a script to fit the Debye model to the refined Debye-Waller factors from Na and Cl from each of the engines. It is possible for advanced users to make plug-ins for SrRietveld, which can be saved and reused by the user, and also readily shared with other users.

The theoretical values of U_{iso} are calculated from [73]

$$U_{iso}\left(T\right) = \frac{1}{8\pi^2} \left\{ \frac{6h^2}{Mk_B\theta_D} \left[\frac{1}{4} + \left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} \frac{xdx}{e^x - 1} \right] \right\} + \sigma_o \qquad (3.1)$$

where the refinable parameters are θ_D and σ_o , the Debye temperature and offset, respectively. Additionally, T is temperature in Kelvin, M is the mass of the ion in question, k_B and h are the Boltzmann and Planck constants, respectively. The fitting to the refined U_{iso} data is carried out with the least square optimization algorithm available in the SciPy Python scientific computing package [66]. The best-fit lines are shown in Fig. 3.2 as dashed lines through the data.

The differences between the Debye temperatures and offsets refined from each engine are much larger than the estimated standard deviations. The esds give a measure of the precision of the fit, and not the accuracy of the Debye temperatures. To understand this, note that the dashed lines fit well to the U_{iso} curves, but the slopes and offsets of the curves are clearly different. The differences in slopes and offsets come from differences in the mathematical model for the line-shapes and backgrounds used in FullProf and GSAS, respectively. This illustrates the advantage of being able to refine data using two refinement engines. If the FullProf and GSAS models are equally valid and we cannot say one or the other is inferior, then the dispersion of results from the two engines gives a realistic estimate of our uncertainty in the accuracy of the refined parameters. In this case we may take into account the result from both engines to get estimate of $\Theta_{D,\text{Na}} = 305 \pm 17$ K and $\Theta_{D,\text{Cl}} = 257 \pm 9$ K where the estimated uncertainties now reflect accuracy rather than precision. The corresponding offset parameters obtained by combining the Rietveld and GSAS results are 30 ± 50 Å⁻¹ and 20 ± 40 Å⁻¹ for Na and Cl, respectively. Therefore there is no evidence for a static offset in the Debye model that would indicate a significant number of static defects in the structure.

In other experiments, the Debye temperature of NaCl can be determined either by measuring the elastic constant or by fitting the specific heat data. The Θ_D values measured with these two methods are 321.2 ± 1.6 K and 320.6 ± 1.5 K, respectively, reported by Lewis et. al. [74]. Broadly speaking the Debye temperatures measured here are in good agreement. Because of the simplicity of the Debye model, and the different way that different measurements weight the phonon density of states, the different approaches are not expected to yield the same Debye temperatures. Furthermore, the thermodynamic measurements give some average of the full density of states whereas the diffraction measurement differentiates the behavior of Na and Cl. The agreement between the values determined from diffraction and those obtained from other methods are therefore quite acceptable.

The refinement engines used in the current release of SrRietveld are FullProf and GSAS. Along with many others in the community, we would like to thank Juan Rodriguez-Carvajal and the other FullProf developers and Robert B. Von Dreele, Brian H. Toby and the other GSAS developers, for their enormous efforts in developing FullProf and GSAS. We would also like to thank the other developers in the DANSE project for useful advice and help. We appreciate the cooperation and valuable suggestions from Emil Božin, Jason Hodges, Ashfia Huq, Ke An, Paolo Radaelli and Laurent Chapon. We thank Timur Dykhne for help with the documentation. In addition to their suggestions, Aziz Daoud-Aladine, Jon Hanson, Vanessa Peterson, and Andrew Studer shared data for testing which we are grateful for. The authors also would thank Christos Malliakas for providing the NaCl sample and assistance on the measurements on this sample. SrRietveld was developed as part of the DANSE (distributed data analysis of neutron scattering experiments) project, which is funded by the National Science Foundation under grant DMR-0520547. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

3.5 Application of SrRietveld II: Error estimations

In Rietveld refinement [75], a non-linear least squares method is applied to refine model parameters in order to give a best fit to experimental data. It is also important to get accurate estimations of the uncertainty on the corresponding parameter values, for example, to differentiate between competing structural models based on the refined parameters. This section explores three different methods for estimating uncertainties, applied using two different popular refinement programs, GSAS [40] and FullProf [76, 41]. To facilitate this process we use the SrRietveld program [77] that automates GSAS and FullProf using Python [63] scripts and a graphical user interface. The bootstrap error estimation methods required many thousands of Rietveld refinements to be carried out which was straightforward in SrRietveld.

Based on the standard least-square weighting schemes built into most of the Rietveld refinement programs, the estimated standard deviations (esd) of refined parameters are calculated through the Hessian matrix [75]. Since the Rietveld method forms a nonlinear multivariate model, it is not possible to get a closed form Hessian matrix and an iterative optimization procedure is used to refine parameters and calculate their standard deviations.

Estimates of uncertainties from Rietveld refinements are widely thought to be problematic. For example, the model is approximate and includes things such as peak profile and details of how the background is calculated, which are often not ideal. It is difficult to tell whether the refinement is converged at the global minimum point, which is a requirement for the estimated uncertainties to reflect the real uncertainty [78, 27, 79]. Even at a global minimum, if the model is inadequate to reproduce all the features in the diffraction pattern, the correct standard deviations cannot be calculated by statistical methods [80].

In this section, in addition to the normal uncertainty estimation coming directly from the least-squares minimization procedure we use a Monte Carlo resampling and a subset sampling approach where we use a pseudo random number generator through SrRietveld [77] to do uncertainty estimation for refined parameters. This is done on LaMnO₃ data from the neutron powder diffractometer, NPDF, at Los Alamos National Laboratory. In the Monte Carlo resampling method, an ensemble of equivalent data-sets are created by fluctuating the intensity on each data-point using a random number generator consistent with the known measurement errors. In subset sampling a subset of data-points is selected randomly and the fit is made to that reduced data-set. This is done many times to determine the distribution of refined parameter values from the many subsets. It works because the number of independent measured points greatly exceeds the number of refined parameters. This method has the advantage that it can estimate uncertainties on refined parameters even when the measurement error is not known.

We find that all three methods yield uncertainty estimates that are comparable to each other. For all parameters we find that GSAS and FullProf yield the same refined values. Therefore, model errors coming from subtle differences in how GSAS and FullProf parameterize peak profiles and backgrounds don't result in larger errors than those from the statistical fluctuations in the data. We also carry out a sensitivity analysis of refined values when different statistical weights are used in the least-squares equation. This is done by setting different, though reasonable, estimated errors on the data-set before refining the data in FullProf. Applying different weights to the same data-set resulted in a number of parameters refining values that sometimes exceed five standard deviations from the values with the correct weights, and so we note a high sensitivity of refined values to the statistical weights used in the least squares equation. The use of both GSAS and FullProf within SrRietveld has yielded a very complete picture of precision and accuracy of all refined parameter values. We also summarize the subtle differences between how GSAS and FullProf calculate and report standard deviations and reconcile the two approaches.

3.5.1 Methods

We carried out the refinements on previously published data [81, 82]. The data are neutron powder diffraction data from LaMnO₃ measured at 300 K on the NPDF diffractometer at the Lujan Center of Los Alamos National Laboratory. The data were refined using the GSAS [40] and FullProf [76, 41] programs controlled by the SrRietveld program [77]. SrRietveld is a highly automated program for Rietveld refinement. It not only can do the conventional refinement by using GSAS and FullProf as the engines but also can automate the refinement of large numbers of datasets with minimal human effort.

The original diffraction data are stored in GSAS time-map format [40]. These files can be read by GSAS but not FullProf. In order to use both engines to refine the data we therefore must transform the data so that it can be recognized by FullProf. To convert the data we used functions in rawplot, part of the GSAS package, controlled by SrRietveld. Rawplot does not propagate the errors on the data and so we estimated the uncertainties using $\sqrt{I_{obs}}/I_i$, where I_{obs} is the observed intensity and I_i is the incident spectrum intensity. During the conversion in rawplot the incident spectrum is smoothed, and our approach assumes that after smoothing the incident spectrum does not contribute error to the normalized intensities, but without having access to details of how this was done we took this as being a reasonable starting point. We refer to this as the no-spectrum-error (NSE) method.

The problem with this calculation is that it doesn't consider the errors on the incident intensity. On the other hand, GSAS uses a fitted function with a few parameters to describe this spectrum. When GSAS carries out a refinement, the variance and covariances obtained from the fitting of the spectrum are used by GSAS to propagate the estimated uncertainty for each point in the incident spectrum and this is then included in the calculation of the statistical weight used in the least-squares equation for each time of flight (TOF) channel. However, this is happening during a GSAS fit but not in Rawplot, which suggests a two step approach is needed for converting timemap data to FullProf compatible data while propagating the errors correctly. First, run rawplot to get the intensities. Then, carry out a GSAS refinement to generate the .LST file [40] which includes the weights for each point in the diffraction pattern. The standard deviation on each point in the .LST file of normalized intensities is the square-root of the inverse weight. Finally, a data file in (x, y, σ) format is created using these values. We refer to this as the spectrum-error (SE) method for converting the time-map data.

The SE method gives more accurate estimates of the standard errors on the data, but it requires a GSAS refinement to be carried out as part of the steps in generating a FullProf input file from the Los Alamos time-map data. It would be preferable if the NSE method works sufficiently well to be used. However, as we see below, this is not the case. The results of Rietveld refinements are highly sensitive to the values used as weights in the least-squares equation. Automated versions of the conversion program for converting GSAS-time-map to FullProf compatible data will be included in future releases of SrRietveld. Before the refinement, instrumental parameters were calibrated using standard nickel data. The standard orthorhombic structure [81, 83] was used for LaMnO₃ in the *Pbnm* space-group. The refinable structural parameters were a, c, La's X and Y fractional coordinates, O1's X and Y, O2's X, Y and Z fractional coordinates and all isotropic thermal factors. The profile used was time of flight convolution pseudo-Voigts with back-to-back exponential function (TOF profile function 3 in GSAS and Npr= 9 in FullProf) and the background function used was a polynomial function for both engines. SrRietveld allows parameters to be turned on sequentially to improve convergence. The refinement strategy used was to turn on scale factor, then background (polynomial function with 6 coefficients), zero shift, lattice parameters, peak profile parameters (sigma1, sigma2), all allowed atom fractional coordinates and finally isotropic thermal factors. Examples of Rietveld fits to the data from GSAS and FullProf are shown in Fig. 3.3.

Standard Uncertainty Estimation in Rietveld refinement

The standard Rietveld method is to calculate the diffraction pattern $y_{calc,k}(p_i)$, on a grid of N points that match the data points, from a model with n parameters, p_i , and vary the parameters in such a way as to minimize the properly weighted sum of squared differences,

$$M = \sum_{k=1}^{N} w_k (y_{obs,k} - y_{calc,k})^2, \qquad (3.2)$$

between the calculated function $y_{calc,k}$ and a measured one $y_{obs,k}$. Here w_k is a weighting factor that depends on the statistical uncertainties on the measured data as we discuss below. If we find the minimum value of the above function, we find the best fit. As described in standard textbooks [75, 30], the minimum is found by taking the first derivative of Eq. 3.2 with respect to the parameters, p_i , and setting it to zero. The



Figure 3.3: (a) TOF neutron powder diffraction pattern on LaMnO₃ (blue circles) with the best fit calculated pattern from FullProf (red line). The low *d*-spacing, short TOF, region to the left of the dashed line has been zoomed in 6 times for clarity. The green line offset below is the difference between the calculated and measured patterns. The black markers indicate the peak positions. (b) As (a) but the red curve is calculated using GSAS.

resulting system of equations that must be solved can be written in the matrix form as Ax = b where A is the Hessian matrix and $A_{ij} = \sum w \frac{\partial y_{calc}}{\partial p_i} \frac{\partial y_{calc}}{\partial p_j}$. Inverting this matrix equation, we get $x = A^{-1}b$. The estimated standard deviation for parameter p_i, σ_i , can be determined from the diagonal elements of the variance-covariance matrix that is the properly normalized form of A^{-1} , thus, $\sigma_i \propto \sqrt{(A^{-1})_{ii}}$ [30].

The standard deviation on refined parameters p_i are calculated using the same formula in both FullProf and GSAS,

$$\sigma_i = \sqrt{(A^{-1})_{ii}\chi_\nu^2},\tag{3.3}$$

where $\chi^2_{\nu} = M/(N_{obs} - N_{var})$ and N_{obs} is the number of observations in all histograms and N_{var} is the number of variables in the least-squares refinement.

As the FullProf manual mentions, it reports two different χ^2_{ν} values. One is computed by considering all points in the fit and the other is computed by summing over only those points that are under Bragg peaks [76, 41]. This latter definition results in slightly larger χ^2_{ν} values since it gives greater weight to regions of the pattern where the fit is less good. For example in our fits this resulted in $\chi^2_{\nu,FP} = 1.77$ compared to 1.63 for the conventional definition that includes all points in the fitted spectrum. It is this definition of $\chi^2_{\nu,FP}$ that FullProf uses in its estimation of the parameter uncertainties in Eq. 3.3, which increases the estimated errors reported by FullProf compared to those from GSAS.

Monte Carlo Resampling of Data Probability Distribution

In a powder diffraction experiment, each observation is assumed to come from a Poisson distribution due to the random nature of the scattering processes. If more than around 20 counts have been measured at a particular point, the Poisson distribution is well approximated by a Gaussian and least-squares analysis is the appropriate minimization procedure for fitting the diffraction pattern [84]. The Gaussian distribution of counts, d, at the *i*th point in the diffraction pattern, with mean μ_i and standard deviation σ_i , is given by

$$p_i(d) = \frac{1}{\sigma_i (2\pi)^{1/2}} \exp\left[\frac{-(d-\mu_i)^2}{2\sigma_i^2}\right].$$
(3.4)

In the absence of a model, our best estimate for μ_i is the measured number of counts. Given that we know σ_i by propagating errors from the raw counts [75], we can create duplicate data-sets that are consistent with the measured data-set by choosing a different value of d from $p_i(d)$ using a pseudo-random number generator. This is not strictly correct since the measured d on the *i*th point is not equal to μ_i . However, when we apply this to a large number of independent points we expect that on average the approximation will hold quite well. An ensemble of 5000 new data-sets was generated in this way. Each data-set in the ensemble was then refined using SrRietveld. A histogram was then made of the refined values for each parameter yielding its probability distribution. The mean and standard deviation of the distribution was then calculated for each parameter. The results are shown in Table 3.1, which show the probability distributions for representative refined parameters. The values in the table for the refined parameters and the standard deviations from the MC resampled data are the values of the mean and standard deviation, respectively, of the probability distributions. The reported profile weighted agreement factor, R_w , and χ^2_{ν} 's were calculated by determining the diffraction pattern using the mean values of the parameters from the probability distributions (the ones reported in the table) and comparing this to the original, non-fluctuated, data-set.

Parameter		Standard			Monte Carlo			Subset		
		value	σ_H	σ'_H	value	σ_M	σ'_M	value	σ_S	σ'_S
a (Å)		5.537938	1.17	0.91	5.537974	1.18	0.91	5.537972	2.24	1.83
b (Å)		5.741537	1.28	1.00	5.741540	1.34	1.04	5.741548	2.09	1.71
c (Å)		7.697324	1.76	1.37	7.697319	1.76	1.36	7.697400	2.82	2.30
La	X	-0.007697	2.15	1.67	-0.007699	2.21	1.71	-0.007665	2.64	2.16
	Y	0.047808	1.80	1.40	0.047801	1.85	1.43	0.047704	2.44	1.99
	U_{iso} (Å ²)	0.00595	2.1	1.6	0.00594	2.1	1.6	0.00609	2.3	1.9
O1	X	0.073758	2.42	1.88	0.073745	2.38	1.84	0.073741	2.88	2.35
	Y	0.488184	2.45	1.91	0.488180	2.52	1.95	0.488044	3.46	2.83
	U_{iso} (Å ²)	0.00743	3.2	2.5	0.00743	3.2	2.5	0.00790	3.3	2.7
O2	X	0.725351	1.86	1.45	0.725352	1.82	1.41	0.725243	1.98	1.62
	Y	0.306210	1.80	1.40	0.306211	1.78	1.38	0.306252	2.45	2.00
	Ζ	0.038524	1.27	0.99	0.038526	1.27	0.98	0.038540	1.65	1.35
	U_{iso} (Å ²)	0.00769	2.1	1.6	0.00769	2.2	1.7	0.00764	2.5	2.0
Mn	U_{iso} (Å ²)	0.00422	3.4	2.7	0.00422	3.5	2.7	0.00445	3.6	2.9
R_w		4.86%			4.89%			4.43(2)%		
χ^2_{ν}		1.65			1.67			1.49(2)		

Table 3.1: Refined values, estimated standard deviations for $LaMnO_3$ from the GSAS.

Table 3.2: Difference in the values of refined parameters between FullProf refinements on data converted from time-map format using the SE and NSE methods, respectively. The numbers in the parethese are the standard deviations on the differences, calculated as the square-root of the sum of the variances.

	*	<u>.</u>		
Parameter		Standard	MonteCarlo	Subset
a (Å)		0.0014(2)	0.0014(2)	0.0014(3)
b (Å)		0.0014(2)	0.0014(2)	0.0014(3)
c (Å)		0.0019(2)	0.0019(2)	0.0019(4)
La	X	0.0001(3)	0.0001(2)	0.0001(4)
	Y	0.0003(3)	0.0003(2)	0.0003(3)
	U_{iso} (Å ²)	0.0015(3)	0.0017(2)	0.0016(4)
O1	X	0.0001(4)	0.0001(3)	0.0001(4)
	Y	0.0002(4)	0.0001(3)	0.0001(5)
	U_{iso} (Å ²)	0.0011(5)	0.0012(4)	0.0012(5)
O2	X	-0.0001(3)	-0.0001(2)	-0.0001(2)
	Y	-0.0001(3)	-0.0001(2)	-0.0001(3)
	Ζ	0.0000(2)	0.0000(2)	0.0000(2)
	U_{iso} (Å ²)	0.0011(3)	0.0012(3)	0.0011(4)
Mn	U_{iso} (Å ²)	0.0010(5)	0.0011(4)	0.0010(5)



Figure 3.4: The probability distribution functions of refined lattice parameters from FullProf based on data converted using the SE and NSE methods. (a), (b) and (c) show the distributions of lattice parameters a, b and c, respectively. For each subfigure, red, green and black symbols are from the NSE method; blue, orange and brown are from the SE method. Diamonds are from Monte Carlo resampling, squares are from subset sampling and circles are from the standard Hessian matrix method.



Figure 3.5: The probability distribution functions of thermal factors U_{iso} . (a) is for La, (b) is for Mn, (c) is for O1 and (d) is for O2. All colors and symbols have the same meanings as Fig. 3.4.

Subset Sampling

In subset sampling we remove some percentage of the measured data-points before carrying out the refinement. This is done by using a pseudo-random number generator to randomly select which data-points to discard. It is done in such a way that sufficient data are retained to carry out a stable refinement. In our case we removed 50% of the data-points to create each sub-sampled data-set. We tested discarding more data-points but it led to unstable refinements. In this way we created 5000 sub-sampled data-sets. We carried out a Rietveld refinement on each sub-sampled data-set using GSAS and FullProf, respectively, running under SrRietveld. In the same way as for the Monte Carlo method described above, the probability distribution for each refined parameter is shown in Figs. 3.4 and 3.5 and the means and standard deviations of the resulting probability distributions are listed in Tables 3.1. In this case we report in the table the average R_w and χ^2_{ν} values from 5000 refinements. We also report the standard deviations of the distributions, which are sharply peaked around the mean value.

3.5.2 Results and Discussion

We first compare the three different methods for assessing uncertainties on the refined parameters by considering the results of the GSAS refinements in Table 3.1. No bias is introduced into the refined values themselves by using the resampling methods as evidenced by the fact that the refined values are the same for each method within the standard deviations. None of the average values are more than one standard deviation from the values refined using a different method. Furthermore, we see excellent agreement between the unweighted (primed) standard deviations obtained from the Hessian matrix and the MC resampling method. The computationally efficient use of the variance-covariance matrix gives the same error estimates as the computationally expensive MC resampling method. The unweighted σ' s from the

sub-sampling method are significantly higher. This is expected because only half of the data has been used in each of these refinements, so we expect that the uncertainty on our results will be higher by roughly $\sqrt{2}$ since half the data have been removed (it won't be an exactly $\sqrt{2}$ change since not exactly half the *counts* have been removed in the sub-sampling). The average value of $\sigma'_S / \sigma'_H = 1.38$, which is close to $\sqrt{2}$ as expected.

The subset sampling method gives good unbiased estimates of the uncertainties but at the expense of yielding lower precision estimates of the refined values themselves. The information content in the data is being used to estimate each number (the mean and standard deviation) independently whereas in the Hessian and MC resampling we are using additional information (the counts and the uncertainties on the counts) to estimate the refined parameters and their standard deviations. If the data uncertainties are known accurately then the standard Hessian matrix approach is best. In principal, the sub-set sampling method is preferable in the case where the data uncertainties are not well known. However, as we discuss later, incorrect weights in the least squares equation result in biased estimates of the refined parameters and in practice it is important to have good uncertainty estimates on the data, as well as good data.

The same overall behavior is seen when we consider the FullProf refinements. There is excellent agreement between the unweighted esd's of the Hessian Matrix and MC resampling methods, with enlarged values on the subset sampled esd's. Of greater interest is to compare the GSAS and FullProf refinement results to check for consistency by comparing the corresponding values in Table 3.1. We see that there is excellent agreement in all the values between the tables, including the refined values and their esds. Despite using subtly different parameterizations for backgrounds and peak parameters, the two refinement methods give excellent agreement with each other.

Here we show the results of refinements to the data when reasonable, but incorrect, weights have been applied in the least-squares equation. In all other respects the refinements are identical to those. The esd's on the refined values from both the Hessian and MC methods are smaller than the those on GSAS and FullProf refinements on SE converted data. This is because the esd's on the data points are smaller in the NSE converted data, where no error was propagated from the spectrum normalization. In this case the Hessian and MC methods under-estimate the true esd's on the refined parameters. However, interestingly the sub-sampling method returns esd's on the refined parameters that are in good agreement with those obtained from from the GSAS and FullProf refinements on the SE converted data. This can be seen by comparing the unweighted σ'_S 's with those in Tables 3.1. This is because the sub-sampling method uses the refinements to sample the *real* fluctuations in the data and does not use the propagated esd values on the data in its estimates of refined parameter esd's (although it does use them as weights in the least-squares equation). The subset sampling method can be relied upon to report unbiased estimates of uncertainties in the data even when the data uncertainties have not been properly propagated, as before at the expense of yielding less precise estimates of the refined values themselves. However, we show below that the sub-sampling method does not prevent biased estimates of the refined values being obtained if the data uncertainties are incorrectly propagated.

The values that are refined using FullProf for the SE and NSE converted data can be compared. For a number of parameters the refined values are significantly different (by more than 5 standard deviations) even though the refinements were done with the same model on the same data. The only difference was the values of the weights used in the least squares equation. This is highlighted in Table 3.2 which shows these differences, and the esd's on the differences, for a number of structural parameters. This effect can also be seen in Figs. 3.4 and 3.5 where the probability distributions for refinements to the NSE and SE converted data are clearly offset.

This result shows a clear sensitivity of refined parameter values to using the correct weights in the least-squares equation. Not only is it essential to have a good model, but also to have accurate uncertainty estimates on the data, in order to refine unbiased values for parameters. An interesting question is whether it is possible to test for the situation that the esd's quoted in a data file are accurate or not. This is possible in principle by comparing the uncertainties obtained from the Hessian and sub-set sampling methods. As we showed above, the ratio of the uncertainties estimated using these two methods should be roughly $\sqrt{1/R}$ where $R = N_{subsampled}/N_{total}$. If this criterion is significantly violated it may indicate the data esd's are not accurate.

3.5.3 Conclusion

We have compared three ways of estimating uncertainties on refined parameters in a Rietveld refinement using two different Rietveld programs, GSAS and FullProf: the estimated standard deviations obtained from the programs themselves, and by resampling the data in two different ways using a pseudo random number generator. There is no apparent advantage of using the computationally expensive Monte Carlo resampling method with respect to using the standard deviations obtained directly from the variance-covarience matrix. However, in certain circumstances the use of the sub-sampling method is warranted. These uncertainty estimation methods will be included as features in future versions of the SrRietveld Rietveld refinement automation program.

We have demonstrated that there is a significant sensitivity of refined parameters to the use of correct data-esd's as weights in the least squares equation. Significantly biased refined values result when incorrect weights are used even when the same model is fit to the same data-set. This underscores the importance in Rietveld refinements of having accurate data-esd's propagated from the raw data or estimated in some other way. The use of the sub-sampling method yields accurate estimates of standard deviations on refined parameters even when the data-esd's are incorrect or unknown. However, it does not correct for the biased values of the refined parameters themselves that result in this case. Comparing the esd's from the sub-sampling method to the values obtained from the variance-covariance matrix may be a useful diagnostic, indicating situations when there may be a problem with the reported data-esd's. In this case, the accuracy of the refined values is certainly lower than the precision which should be reported. This is generally true because of model errors and parameter correlations that are not included in these, but we note an additional contribution due when data uncertainties are uncertain.

Chapter 4

The total scattering and atomic pair distribution function method

Due to the emerging demand for the alternative energy and electronic applications, the more complex materials are synthesized and characterized. They are made of multiple elements, have large unit cells and often low dimensional or incommensurate structures [30, 32]. Commonly, they have aperiodic disorder: some aspect of the structure that is different from the average crystal structure. In the case of nanoparticles, the concept of crystal is invalid as the approximation of infinite periodicity is no longer a good one. It is often critical important to know their structure details in order to explain their special properties. Nevertheless, powder diffraction is an important method for characterizing these materials, but we have to go beyond the Bragg equation and crystallographic analysis.

In this chapter, we present an alternative approach which treats both the Bragg and diffuse scattering on an equal basis, the so-called total scattering technique. Data from throughout reciprocal space, over a wide range of Q-values, are utilized. The technique is both straightforward and intuitively easy to comprehend. Fourier transformation helps us translate the reciprocal space information into real space. For total scattering, Fourier analysis of the data is known as pair distribution function (PDF) analysis.

This chapter will give the background knowledge of PDF and the physical meaning of it. Finally I will introduce the interesting cases for calculating the PDFs that will be used later in the thesis.

4.1 Theory of PDF

Recently, the work of Chris Farrow in Prof. Simon Billinge's group resolves a long-standing ambiguity in the PDF literature by deriving the PDF equations from the beginning. Since the full derivation is not reproduced even in many textbooks on the subject and it leads the precise relationship between the measured correlation function in an X-ray or neutron total-scattering experiment and the underlying model. So this section will briefly go through the procedure as the following to give the clear ideas about the PDF and its application and for more details please refer to Chris's paper [85].

From classical wave theory [12], the scattering amplitude from a set of i atoms at points $\vec{r_i}$ is:

$$\psi(\vec{Q}) = \sum_{i} \psi_{i}$$

$$= \sum_{i} f_{i}(Q) e^{i\vec{Q}\cdot\vec{r_{i}}}.$$
(4.1)

Assume there is no inter-atom contribution on the intensity, the incoherent intensity

is calculated as the following:

$$I_{inc} = \sum_{i} \psi_{i}^{*} \psi_{i}$$

= $\sum_{i} f_{i}^{*}(Q) f_{i}(Q)$
= $N \langle f^{2} \rangle$, (4.2)

where * means the complex conjugate. Also we can define the square of the average scattering power as

$$\langle f \rangle^2 = \frac{1}{N^2} \sum_{ij} f_j^* f_i. \tag{4.3}$$

On the other hand, the coherent scattering intensity is given by

$$I_{c} = \sum_{i} \sum_{j} f_{j}^{*} f_{i} e^{i\vec{Q}\cdot(\vec{r_{i}}-\vec{r_{j}})}$$

$$= \sum_{i} f_{i}^{*} f_{i} + \sum_{i\neq j} f_{j}^{*} f_{i} e^{i\vec{Q}\cdot\vec{r_{ij}}}$$

$$= N\langle f^{2}\rangle + \sum_{i\neq j} f_{j}^{*} f_{i} e^{i\vec{Q}\cdot\vec{r_{ij}}}$$

$$(4.4)$$

From the classical book [32] about PDF, the total scattering structure function is defined as

$$S(\vec{Q}) = \frac{I_c}{N\langle f \rangle^2} - \frac{\langle (f - \langle f \rangle)^2 \rangle}{\langle f \rangle^2}.$$
(4.5)

Based on Eq. 4.4, we get

$$S(\vec{Q}) - 1 = \frac{1}{N\langle f \rangle^2} \sum_{i \neq j} f_j^* f_i e^{\mathbf{i}\vec{Q} \cdot r_i \vec{j}}.$$
(4.6)

For a powder sample, since there is equal probability for all direction, thus we have

$$\overline{e^{i\vec{Q}\cdot r_{ij}}} = \frac{\int_{0}^{2\pi} d\phi \int_{0}^{\pi} d\theta e^{iQr_{ij}\cos\theta} r_{ij}^{2}\sin\theta}{\int_{0}^{2\pi} d\phi \int_{0}^{\pi} d\theta r_{ij}^{2}\sin\theta}$$

$$= \frac{-2\pi r_{ij}^{2} \left[e^{iQr_{ij}\cos\theta}\right]_{0}^{\pi}}{4\pi r_{ij}^{2}iQr_{ij}}$$

$$= \frac{\left[e^{iQr_{ij}} - e^{-iQr_{ij}}\right]}{2iQr_{ij}}$$

$$= \frac{\sin(Qr_{ij})}{Qr_{ij}}.$$
(4.7)

Therefore, based on Eq. 4.6, the reduced total scattering structure function, F(Q) = Q[S(Q) - 1], is

$$F(Q) = \frac{1}{N\langle f \rangle^2} \sum_{i \neq j} f_j^* f_i \frac{\sin(Qr_{ij})}{r_{ij}}.$$
(4.8)

Since we have the following relationship according to Fourier transformation on F(Q)

$$f(r) = \frac{2}{\pi} \int_0^\infty F(Q) \sin(Qr) dQ.$$
(4.9)

This is the common definition of the PDF. Substituting F(Q) by Eq. 4.8 we get

$$f(r) = \frac{2}{\pi} \int_0^\infty \frac{1}{N\langle f \rangle^2} \sum_{i \neq j} f_j^* f_i \frac{\sin(Qr_{ij})}{r_{ij}} \sin(Qr) dQ$$
$$= \frac{2}{\pi N\langle f \rangle^2} \sum_{i \neq j} \frac{f_j^* f_i}{r_{ij}} \int_0^\infty \sin(Qr_{ij}) \sin(Qr) dQ$$
$$= \frac{1}{N\langle f \rangle^2} \sum_{i \neq j} \frac{f_j^* f_i}{r_{ij}} [\delta(r - r_{ij}) - \delta(r + r_{ij})]$$
(4.10)

Assume we have only positive axis, then it becomes

$$f(r) = \frac{1}{rN\langle f\rangle^2} \sum_{i\neq j} f_j^* f_i \,\delta(r - r_{ij}). \tag{4.11}$$

According to Chris's paper [85], we can interpret f(r) by the radial distribution function (RDF), R(r). It means the number of atoms in the shell at a distance r when the thickness of shell is one. So $R(r) = 4\pi r^2 \rho(r)$. On the other hand, by integrating f(r)r along r direction, we also can get the number of atoms as shown in the paper. Therefore, we have

$$f(r) = \frac{R(r)}{r}$$

$$= 4\pi r \rho(r).$$
(4.12)

In our experiments, we can only measure Q down to certain value, Q_{min} due to the experimental setup. So we should consider $f(r; Q_{min})$ function as the following:

$$f(r;Q_{min}) = \frac{2}{\pi} \int_{Q_{min}}^{\infty} F(Q) \sin(Qr) dQ$$

$$= 4\pi r \rho(r) - \frac{2}{\pi} \int_{0}^{Q_{min}} F(Q) \sin(Qr) dQ.$$
(4.13)

4.2 Corrections of PDF derivation

First we consider the simplest case: RDF of an infinite scatterer with uniform density, ρ_0 . In this system the intensity will be a delta function at Q = 0, which results f(r) = 0 based on Eqs. 4.6 and 4.9. This shows the conflict with the assumption as pointed out by the paper [85]. As mentioned in chapter 1, the scattering amplitude can be expressed as $\psi = \langle f \rangle e^{i\vec{Q}\cdot\vec{r}}\rho_0 d\vec{r}$. In this simple system, the intensity is given by

$$I_c(\vec{Q}) = \rho_0^2 \langle f \rangle^2 \int \int e^{i\vec{Q} \cdot (\vec{r} - \vec{r'})} \mathrm{d}\vec{r} \mathrm{d}\vec{r'}, \qquad (4.14)$$

where the integrals are over all space.

Considering the shape of the scatter, we define a shape function $s(\vec{r})$ such that inside the shape s = 1 and outside the shape s = 0. Then,

$$I_{c}(\vec{Q}) = \rho_{0}^{2} \langle f \rangle^{2} \int \int s(\vec{r}) s(\vec{r'}) e^{i\vec{Q} \cdot (\vec{r} - \vec{r'})} d\vec{r} d\vec{r'}.$$
 (4.15)

We redefine variables so that $\vec{r''} = \vec{r} - \vec{r'}$, and $d\vec{r''} = d\vec{r}$, in which case we have

$$I_{c}(\vec{Q}) = \rho_{0}^{2} \langle f \rangle^{2} \int \mathrm{d}\vec{r''} e^{i\vec{Q}\cdot\vec{r''}} \int s(\vec{r'})s(\vec{r'} + \vec{r''})\mathrm{d}\vec{r'}.$$
 (4.16)

If we define

$$\gamma_0(\vec{r}) = \frac{1}{V} \int s(\vec{r'}) s(\vec{r'} + \vec{r}) d\vec{r'}, \qquad (4.17)$$

where $V = \int s(\vec{r}) d\vec{r}$ is the volume. This $\gamma_0(\vec{r})$ is the characteristic function of the shape [86], and is also called the nanoparticle form factor in the PDF literatures [82, 87, 88]. With the above definition and Eq. 4.16, we have

$$I_c(\vec{Q}) = \rho_0^2 \langle f \rangle^2 V \int \gamma_0(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} d\vec{r}.$$
(4.18)

Substituting the above equation into $S(\vec{Q}) - 1 = \frac{I_c}{N\langle f \rangle^2} - \frac{\langle f^2 \rangle}{\langle f \rangle^2}$, we get

$$S(\vec{Q}) - 1 = \frac{1}{N\langle f \rangle^2} \rho_0^2 \langle f \rangle^2 V \int \gamma_0(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} d\vec{r} - \frac{\langle f^2 \rangle}{\langle f \rangle^2}$$

= $\rho_0 \int \gamma_0(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} d\vec{r} - \frac{\langle f^2 \rangle}{\langle f \rangle^2}.$ (4.19)

The second term, $\frac{\langle f^2 \rangle}{\langle f \rangle^2}$, is very small compared to the first term and can be ignored normally.

Since we assume it is isotropic scatter, we can use the result from Eq. 4.7 as the

following

$$S(Q) - 1 = \rho_0 \int_0^\infty dr \int_0^{2\pi} d\phi \int_0^\pi d\theta \overline{\gamma_0(\vec{r})} e^{i\vec{Q}\cdot\vec{r}} r^2 \sin\theta$$

$$= \rho_0 \int_0^\infty dr \int_0^{2\pi} d\phi \int_0^\pi d\theta \overline{\gamma_0(\vec{r})} e^{i\vec{Q}\cdot\vec{r}} r^2 \sin\theta$$

$$= \rho_0 \int_0^\infty dr \int_0^{2\pi} d\phi \int_0^\pi d\theta \gamma_0(r) \frac{\sin(Qr)}{Qr} r^2 \sin\theta$$

$$= \rho_0 \int_0^\infty \gamma_0(r) \frac{\sin(Qr)}{Qr} 4\pi r^2 dr.$$

(4.20)

This gives

$$F(Q) = \int_0^\infty 4\pi \rho_0 r \gamma_0(r) \sin(Qr) \mathrm{d}r.$$
(4.21)

Then we take the inverse Fourier transform to get

$$f_u(r) = \frac{2}{\pi} \int_0^\infty F(Q) \sin(Qr) dQ$$

$$= 4\pi \rho_0 r \gamma_0(r),$$
(4.22)

where the subscript u indicates that this result is based on the assumption that it is an uniform density system.

As Chris's paper [85] shows, for a macroscopic crystal, in the region of Q below the first Bragg peak, the distinct scattering is zero except at very low-Q where small angle scattering region is reached. The *small angle* scattering intensity, I_{sas} from the crystal is identical to that from the solid with uniform density: $I_u^{sas} = I_{crystal}^{sas}$. The small and wide angle scattering regions are well separated in Q and I_{sas} decays to zero before Q_{min} is reached in the crystal. Thus,

$$f_{sas}(r) = \frac{2}{\pi} \int_0^{Q_{min}} F(Q) \sin(Qr) dQ$$

= $f_u(r)$ (4.23)

and therefore

$$\frac{2}{\pi} \int_0^{Q_{min}} F(Q) \sin(Qr) dQ = 4\pi \rho_0 r \gamma_0(r).$$
(4.24)

Finally, by substituting Eq. 4.24 into Eq. 4.13, we get

$$f(r; Q_{min}) = 4\pi r \rho(r) - 4\pi r \rho_0 \gamma_0(r).$$
(4.25)

4.3 Cases of PDF calculation

4.3.1 Calculation of PDF for bulk crystals

In the case of bulk crystals, the region of interest in the PDF is usually $r \ll D$, where D is the smallest dimension of the crystal. In this region, $\gamma_0(r) \approx 1$. Thus,

$$f(r; Q_{min}) = G(r)$$

$$= 4\pi r(\rho_{bulk}(r) - \rho_0),$$

$$(4.26)$$

The pair density function, $\rho_{bulk}(r)$, is calculated from a model with periodic boundary conditions [89, 90], or from a box of atoms that is much larger in extent than the range of r of interest [91]. The average number density ρ_0 is given by the number of atoms per unit volume, which in the case of crystals is the number of atoms in the unit cell divided by the unit cell volume.

4.3.2 Calculation of PDF for nanoparticles modeled as attenuated bulk crystals

The pair density, $\rho(r)$, in Eq. 4.25 is the function for the nanoparticle, which can be approximated as $\gamma_0(r)\rho_{bulk}(r)$ [92]. In this case $\rho_{bulk}(r)$ is determined in the same way as in the above section. Thus,

$$f(r; Q_{min}) = 4\pi r \gamma_0(r) (\rho_{bulk}(r) - \rho_0).$$
(4.27)

If there is a distribution of nanoparticle sizes and shapes, the characteristic function, $\gamma_0(r)$ can be replaced with an appropriately averaged characteristic function

$$\gamma(r) = \int \gamma_0(r; R_1, R_2, \ldots) p(R_1, R_2, \ldots) dR_1 dR_2 \ldots$$
 (4.28)

Here, $p(R_1, R_2, ...)$ is the normalized distribution of nanoparticle shapes parameterized by $R_1, R_2, ...$ For example, for spherical nanoparticles of radius $R, p(R_1, R_2, ...) = p(R)$, the distribution of nanoparticle radii. Finally, we replace Eq. 4.27 with

$$f(r; Q_{min}) = 4\pi r \gamma(r) (\rho_{bulk}(r) - \rho_0).$$
(4.29)

4.3.3 Calculation of PDF from the normalized Debye Function

For this case, the F(Q) function is evaluated using Eq. 4.8 and then Fourier transformed to obtain the desired real-space function. To account for thermal and zero-point motion in reciprocal-space calculations, Eq. 4.8 is replaced using Debye-Waller effects,

$$F(Q) = \frac{1}{N\langle f \rangle^2} \sum_{i \neq j} f_j^* f_i \left(e^{-\frac{1}{2}\sigma_{ij}^2 Q^2} \right) \frac{\sin(Qr_{ij})}{r_{ij}}.$$
 (4.30)

Here, σ_{ij}^2 is the correlated broadening factor for the atom pair [90, 93, 94]. There are more details and other cases presented in Chris's paper [85] that is a good guide on this material.

Chapter 5

MnAs: Diverse structural and magnetic properties

Discrete nanoparticles of MnAs with distinct magnetostructural properties have been prepared by small modifications of solution-phase arrested precipitation reactions. Rietveld and X-ray atomic pair distribution function based approaches were used to explore the evolution of the structure of the samples with temperature and these data were compared to the magnetic response measured with AC susceptibility. Relative to a bulk standard, one type of MnAs nanoparticles was found to demonstrate similar but smaller structural transitions and corresponding magnetic changes. However, both magnetic and structural transitions in the second type of nanoparticles are strongly suppressed.

5.1 Introduction

MnAs has been noted as an attractive candidate for information storage and energy applications due to its interesting magnetic and structural properties. [95, 96, 97] Bulk MnAs has a magneto-structural phase transition in which a first-order magnetic transition occurs from a high-spin ferromagnetic to a low-spin paramagnetic state with a concommitant structural transition from the hexagonal α phase (NiAs-type) to the orthorhombic β phase (MnP-type) [98]. The transition occurs at 315 K upon warming. At a higher temperature 400 K, a reentrant second-order phase transition takes place back to the α phase, but the high-spin state is now paramagnetic. This sequence of transitions is shown in the following.

In studies on bulk MnAs, scientists observed that the structural transition can be driven by the application of a magnetic field [95], which confirms that the coupling between the magnetic transition and structural transition is strong. These properties result in a tunable magnetocaloric effect in bulk MnAs which could be applied in microelectronic circuit [99, 100] applications. A number of theoretical studies [101, 98] have discussed the correlation between structure and magnetism though there is no clear understanding of the details of the relationship.

Compared to bulk materials, nanoscale materials exhibit size and shape tunable physical properties such as electronic, magnetic and catalytic properties. Research on nanoscale MnAs has been largely focused on epitaxially grown MnAs particles or disks on semiconducting thin films [102] or nanowires [103]. Such nanoscale MnAs is a promising material for thermally assisted magnetic recording [102]. However, these epitaxial structures are subject to external pressure due to lattice strain from the substrate, resulting in significant shifts in the magnetostructural transition temperatures. Recently, a method for preparing MnAs as discrete unsupported nanoparticles [104] enables the effect of size on the first order transition to be probed in the absence of external stress. Particles of size 9-23 nm were prepared in solution by reaction of dimanganesedecacarbonyl ($Mn_2(CO)_{10}$) and triphenylarsine oxide ((C_6H_5)₃As=O) in coordinating solvents at temperatures ranging from 523-603 K. Intriguingly, small changes in the synthetic method led to two distinctly different products, as detected by powder X-ray diffraction conducted at room temperature. Notably, in one case, the metastable β structure, rather than the thermodynamic α structure, was observed. Despite the presence of a magnetic transition consistent with the magnetostructural transformation in bulk MnAs, no evidence was observed of a corresponding structural transition in temperature dependent powder X-ray diffraction measurements for either material [104].

Here we perform a detailed structural evaluation of the two types of MnAs nanoparticles using an advanced nanostructure determination method, the atomic pair distribution function (PDF) technique [32, 105, 106, 88], as a function of temperature in the region of the expected magnetostructural transition. The obsestructions from these data are correlated with AC magnetic susceptibility data acquired over the same temperature range. We show that nanoparticles synthesized using one approach behave like the bulk, albeit at a reduced level. Nanoparticles synthesized by the other method appear to be kinetically trapped and do not undergo a magnetostructural transition. This is a dramatic example of the modification of a material's structural and magnetic properties at the nanoscale.

5.2 Methods

5.2.1 Synthesis

The bulk MnAs we used for this study was purchased from Pfaltz and Bauer Chemicals. A chemical etching process was performed to eliminate impurities. Briefly, 1 g of ground bulk MnAs was combined with 20 ml concentrated HCl solution, slowly heated to 80 °C, and kept at that temperature for 20 minutes. The sample was then washed with 50 ml de-ionized water several times to remove the soluble impurities.

The synthesis of MnAs nanoparticles is done by our collaborators, Prof. Stephanie Brock's group at Wayne State University. It can be achieved by either a slow heating method, or a high temperature fast injection method. We call these approaches method A and method B, respectively. The resulting nanoparticles are called type-A and type-B. In method A, 0.256 mmol of $Mn_2(CO)_{10}$ is combined with 0.528 mmol $Ph_3As=O, 8.0 - 10.0$ ml of 1-octadecene (ODE) and 5 g of trioctylphosphine oxide (TOPO) in a Schlenk flask under argon. The mixture is gradually heated up to 250 °C over 2 hours, changing from yellow to orange to black, and then maintained at this temperature for 18 h. The as-prepared nanoparticles are then isolated by centrifugation after dispersing in chloroform and precipitating in absolute ethanol. This dispersion/reprecipitation process is repeated several times to ensure complete removal of TOPO and reaction byproducts.

For method B, the fast-injection method, the same amount of $Mn_2(CO)_{10}$, Ph₃As=O and 1-octadecene are combined together in a Schlenk flask under argon. The mixture is heated slightly using a heatgun until the powder precursors are dissolved. This mixture is then cannulated under inert conditions into hot TOPO (5.0 g) maintained at 330 °C in a second Schlenk flask. The reaction is maintained at 330 °C for 18 hours. The nanoparticles are isolated using the procedure described for type-A MnAs.

Particle size and morphology were assessed using transmission electron microscopy studies performed on a JEOL 2010 HRTEM operating at 200 kV. Samples were prepared by dispersion of solid precipitates in chloroform and then a drop of the colloidal solution was deposited on a carbon-coated copper grid and allowed to air-dry.

5.2.2 Diffraction experiments

Total scattering powder diffraction experiments were performed at the 11-ID-B beam-line at the Advanced Photon Source at Argonne National Laboratory, with 58.26 keV x-rays using the rapid acquisition (RaPDF) mode [70]. A large area 2D GE Revolution 41RT flat panel detector [107] was mounted orthogonal to the beam path. Each sample was packed in a kapton capillary 1 mm in diameter and measured in the temperature range of 295 K - 335 K during heating and cooling. In the heating

(cooling) procedure we continuously increase (decrease) the temperature at 1 K/min rate and collect data frames every 30 s, i.e., every 0.5 K. In the measured range of 295-335 K, this results in ~ 80 data sets for both the heating and cooling runs. The raw 2D data were integrated and converted to intensity versus 2θ using the software Fit2D [108], where 2θ is the diffraction angle.

Rietveld refinements were carried out on the data using the GSAS [40] and Full-Prof [41] programs controlled by the SrRietveld program [77]. SrRietveld is a highly automated program for Rietveld refinement. It not only can do the conventional refinement by using GSAS and FullProf as the engines but also can automate the refinement of large numbers of datasets with minimal human effort. As the first step of the Rietveld refinement, instrument parameters were calibrated using standard silicon data. There are two structural models for the MnAs samples: the α phase model in the P63mc spacegroup and the β phase model in the *Pnma* spacegroup. The refinable structural parameters were a, b and c, Mn's X and Z fractional coordinates, As's X and Z fractional coordinates and isotropic thermal factors on each symmetryindependent atomic site. The peak profile used was the Thompson-Cox-Hastings pseudo-Voigt function (CW profile function 2 in GSAS and Npr=7 in FullProf). The background function used was a Chebyschev polynomial in GSAS and linear interpolation in FullProf. The refinement strategy used was to turn on scale factor, then zero shift, background coefficients, lattice parameters, peak profile parameters, all allowed atom fractional coordinates and finally, isotropic thermal factors.

The PDF, G(r), was obtained by Fourier transformation of the reduced total scattering structure F(Q) = Q(S(Q) - 1) according to the following equation [32].

$$G(r) = \frac{2}{\pi} \int_{Qmin}^{Qmax} Q[S(Q) - 1] \sin Qr \, \mathrm{d}Q, \qquad (5.1)$$

where S(Q) is obtained from a diffraction experiment. The maximum range of Q

used in the Fourier transform was $Q_{max} = 23.0 \text{ Å}^{-1}$. The value of Q_{max} chosen to optimize the PDF was selected by choosing the largest Q_{max} possible without introducing too much statistical noise into the data. The PDFs were modelled using PDFgui [109]. The structural models and refinable parameters are the same as Rietveld refinement discussed above, but the PDF refinements yield information about the local structure rather than the average crystal structure probed by Rietveld refinement. Because of the relatively large size [88] of the nanoparticles in this study, the results from average and local structural refinements matched each other well for all the MnAs samples.

5.2.3 Magnetization measurements

The magnetic measurement of MnAs is done by our collaborators, Prof. Gavin Lawes's group at Wayne State University. AC magnetic susceptibility measurements, which are more sensitive to small changes in magnetization arising from possible impurity phases than dc measurements, were carried out at 10 kHz using a standard option on a Quantum Design Physical Properties Measurement System. The magnetic susceptibility was measured on heating and cooling from 280 K to 340 K at an AC excitation field of 10 Oe with zero DC field. Bulk, type-A, and type-B MnAs nanoparticles were prepared by sealing loose powders in evacuated quartz tubes. The data were normalized to total Mn quantity based on chemical analysis data acquired by atomic absorption spectroscopy using a Perkin-Elmer Analyst 700 instrument. Solid samples were dissolved in nitric acid, diluted, and compared to a calibration curve created using a series of Mn standards (High-Purity Standards).

5.3 Results and Discussion

Discrete nanoparticles of MnAs were prepared from arrested precipitation reactions using either a slow-heating method (method A, yielding type-A particles) or a high-temperature rapid-injection method (method B, yielding type-B particles) [104]. Electron micrographs of the particles are shown in Fig. 5.1, along with a size-distribution histogram. Type-A nanoparticles are well-dispersed and faceted in shape with a size of 22.3 ± 3.9 nm, measured along the small axis. In contrast, type-B nanoparticles show a strong tendency to aggregate and are slightly smaller, at 17.8 ± 3.1 nm. The aggregation of Type-B MnAs particles revealed in the TEM image is not a universal phenomenon for nanoparticles of Type-B MnAs [104] and may be a consequence of surfactant loss due to vigorous washing.

First, I used the Rietveld analysis using α model on bulk MnAs. To compare the quality of the refinements, I plot the zoomed-in figures for both temperatures. It is clearly shown that the 335 K fit is much worse than 295 K at least in the range of 8-16^o as we know from R_w . It implies that bulk MnAs stays at α phase at 295 K but not at 335 K.

In order to know what the transition is for bulk MnAs during the temperature of 295 to 335 K, I do the Rietveld sequential refinements using α model on all datasets of bulk MnAs that we collected. The obvious result is that there is structural phase transition in the temperature range based on the hysteresis shown in the figure. The transition starts at 303 K and ends at 317 K for heating run, which matches the observations in the literature [98]. As we know from Fig. 5.1, the type-A MnAs nanoparticles have relative large particle size so we can still use Rietveld refinement to analyze them. Similarly, we see the transition also happens in type-A nanoparticles for the same temperature range. For the sake of brevity, I only present the results of lattice parameter a together with the ones from bulk. Interestingly, we see the change in type-A is smaller than bulk and dies out broader. However when I want to analyze

Parameter		bulk		Type-A nanoparticles		
		295 K α	335 K β	295 K α	335 K β	
a (Å)		3.724(2)	5.734(3)	3.686(5)	5.728(4)	
b (Å)		3.724(2)	3.684(3)	3.686(5)	3.686(5)	
c (Å)		5.712(5)	6.378(4)	5.731(13)	6.379(9)	
Mn	X	-	0.0021(2)	-	0.0063(5)	
	Z	-0.00014(9)	0.271(7)	0.009(2)	0.27(2)	
	U_{iso} (Å ²)	0.014(3)	0.015(5)	0.021(12)	0.019(9)	
As	X	-	0.231(7)	-	0.23(2)	
	Z	0.25(2)	0.92(9)	0.24(3)	0.9(2)	
	U_{iso} (Å ²)	0.009(2)	0.009(3)	0.013(9)	0.009(7)	
\mathbf{R}_{w}		0.096	0.084	0.203	0.189	

Table 5.1: The refined structural parameters for bulk and type-A nanoparticles at 295 K and 335 K using α (*P6*₃*mc*) and β (*Pnma*) model. All models are refined with isotropic thermal factor U_{iso}.

the type-B nanoparticles, Rietveld refinement doesn't work well since there are less sharp peaks in the pattern. Therefore, we turn to pair distribution function (PDF) for help.

For comparison purpose later on, I repeat the analysis on bulk and type-A MnAs as the first steps here by using PDF technique. Examples of typical total scattering powder diffraction patterns in the form of PDFs are shown in Fig. 5.2. We first verify that our results for the structure of the bulk material are in agreement with the literature [98], i.e., just below room temperature the samples are in the α phase and at just above room temperature in the β phase. In Fig. 5.2(a), we see a good agreement between the best-fit α model and the bulk MnAs data at 295 K, as additionally indicated by the low $R_w = 0.096$. Similarly, there is a good fit of the β model to the bulk data at 335 K as shown in Fig. 5.2(c) and by an $R_w = 0.084$. For comparison, the best fit of the α model to the data at 335 K gives $R_w = 0.196$ and is shown in Fig. 5.2(b). The poor fit shows that the PDF is clearly capable of differentiating between these phases. The refined values of the good fits are presented in Tab. 5.1. Our PDF refinements of the bulk are in excellent agreement with crystallographic results from the literature. [98]
We next consider type-A nanoparticles. In Fig. 5.2(d)-(f) we show the fits of the bulk structural models to the PDFs of the type-A nanoparticles. The fits are good overall indicating that these nanoparticles have similar structures to the bulk material. For the 335 K data (Fig. 5.2(e), (f)) the fit of the β structural model is significantly better than the α model, as in the bulk. The $R_w = 0.189$ for the β model and $R_w = 0.217$ for the α model and the improved fit is evident by comparing the difference curves of (e) and (f) in the figure. However, the overall fit of the β model to the 335 K data is less good than for the bulk material. This is evident from the larger R_w (0.189 vs. 0.084) and the clear features in the difference curves. This shows that there are structural modifications from the purely β structure in the nanoparticles, possibly from the surface region.

Fig. 5.2(d) shows the fit of the α model to the type-A nanoparticle data collected at 295 K. There is a good overall fit, but the $R_w = 0.203$ is somewhat high, and there is some residual in the difference curve in the Figure. However, the β model also fits the 295 K data quite well ($R_w = 0.187$). This could be because the structure is still in the β -form at this temperature and the sample has not transformed. However, another possibility is that the structure has transformed to the α -phase but the β structural model fits better because it has more refinable prameters (12 for β vs. 9 for α). This is possible because the α phase is similar to β and can be obtained in a continuous manner from β by adding some symmetry elements and moving atoms onto special positions. Thus, the observation of a lower R_w is not sufficient to establish that the material is in the α phase and we need to look further. In order to establish definitively whether a structural transition is taking place in the type-A nanoparticles similar to that in MnAs bulk, we consider the *change* in the PDF of the material as its temperature is reduced from 335 to 295 K, shown in Fig. 5.4. The difference curve in Fig. 5.4(a) shows the changes in the PDF of bulk MnAs due to the structural transition and Fig. 5.4(b) shows the same for the type-A nanoparticles. It is clear

that the structural changes in the nanoparticles are smaller than those in the bulk. However, close inspection of the difference curves in Fig. 5.4(a) and (b) shows that they are highly correlated and have similar features. To test the degree of correlation we plot the two difference curves on top of each other in Fig. 5.4(c), multiplying the curve from the nanoparticles by a factor of 4 to account for the smaller amplitude of those changes. Based on the data in Fig. 5.4(c), we calculate the Pearson correlation coefficient [110, 111] to show the degree of correlation between two difference curves. The value of the correlation can fall in the range from 1 (fully correlated) to -1 (anticorrelated), with the middle value zero meaning there is no correlation. For our case, the Pearson correlation coefficient between the two difference curves is 0.959, which clearly shows that the structural changes between 335 K and 295 K of the bulk and type-A nanoparticles are the same. Thus, the type-A nanoparticles are undergoing the same structural phase transition as the bulk, although the amplitude of the changes is less.

Having established that the type-A nanoparticles are undergoing the same transition as the bulk, we next sought to compare the evolution of the transition with temperature and measure the structural hysteresis curves of the two samples. The changes in *a* and *c* lattice parameters, and in *Uiso* for Mn and As of bulk and type-A samples are shown in Fig. 5.5. The hysteresis curves are very similar between the bulk and the type-A nanoparticles. For example, on cooling, the onset temperature of the structural transition is very similar. However, the hysteresis curves of the nanoparticles are less square than those of the bulk, and the size of the structural modifications (for example, the change in lattice parameters) are smaller in the nanoparticles. We conclude that the structural response of the type-A nanoparticles are very similar to the bulk in most respects, but of a smaller magnitude, and the transition is smeared out in temperature on the low-T side. This transition broadening may be expected due to finite size effects of the nanoparticles.

isotropic thermal factor c _{1SO} .					
Parameter		295 K α	295 K β	335 K α	335 K β
a (Å)		3.669(6)	5.702(3)	3.675(6)	5.713(3)
b (Å)		3.669(6)	3.664(4)	3.675(6)	3.672(5)
c (Å)		5.719(12)	6.344(9)	5.724(11)	6.356(9)
Mn	X	-	-0.0023(3)	-	-0.0011(2)
	Ζ	0.008(2)	0.224(12)	0.008(7)	0.227(13)
	U_{iso} (Å ²)	0.03(2)	0.018(16)	0.03(2)	0.019(16)
As	X	-	0.27(7)	-	0.27(7)
	Z	0.24(3)	0.91(2)	0.24(3)	0.91(2)
	U_{iso} (Å ²)	0.017(14)	0.009(7)	0.016(13)	0.009(5)
\mathbf{R}_{w}		0.305	0.201	0.275	0.197

Table 5.2: The refined structural parameters for type-B nanoparticles at 295 K and 335 K using the α (*P*6₃*mc*) and β (*Pnma*) model. All models are refined with isotropic thermal factor U_{iso}.

In our previous published MnAs paper [104], we have described the synthesis of Type-B MnAs with different sizes and compared the structural properties. Type-B MnAs nanoparticles have been prepared in sizes up to 26 nm by this synthetic method by adjusting the reactant concentrations and reaction times. The size in the reported range does not appear to be a primary determiner for the structure being probed. It is also true for this study as we observe that the behavior of the type-B nanoparticles is very different. Structural results from representative temperature points are presented in Tab. 5.2. Fig. 5.6(c) and (d) show the fits of the α and β structural models to the type-B nanoparticle PDFs at 335 K. The β model clearly provides a better fit to the data and a lower R_w (0.197 vs. 0.275) suggesting that at high temperature the material is in the β phase. However, as is the case for the type-A nanoparticles, the fit is far from ideal suggesting additional structural relaxations. Fig. 5.6(a) and (b) show the fits of the two structure models to the 295 K data. The β model provides a significantly better fit than the α model (Rw = 0.201 and 0.305, for β and α -models, respectively), which suggests that the structural transition may have been suppressed in these nanoparticles. As with the type-A nanoparticles, we test this hypothesis by looking at the change in the PDF between

335 K and 295 K for the type-B nanoparticles and compare it to the bulk. The result is shown in 5.8. The first observation is that the overall changes in the PDFs of the β nanoparticles are very small. The changes are comparable to the noise, with some small features that might be explained by a small change in lattice parameter due to thermal expansion. However, there is no indication of any structural phase transition on cooling for these samples. To make sure there is not a smaller magnitude phase transition as was observed in the type-A nanoparticles, we again look for correlations in the difference curves between 335 K and 295 K compared to the bulk, which are plotted on top of each other in Fig. 5.8(c), after scaling up the type-B difference curve by a large factor of 10 to match the amplitude of the fluctuations. Visually there is no evidence of correlation and the Pearson correlation coefficient is -0.197 which indicates the difference curves are essentially uncorrelated. This result indicates that the structural transition has been completely suppressed in the type-B nanoparticles. Furthermore, plots of the temperature dependence of the structural parameters from type-B nanoparticles (not shown) do not show hysteresis similar to those of the bulk and type-A nanoparticles. Interestingly, the unit cell volume of the type-B nanoparticles is significantly less than the bulk or the type-A nanoparticles as shown in Fig. 5.9(b). For example, the cell volume is decreased by 0.89% at 335 K and by 2.71% at 295 K, compared to the bulk. This synthesis method has clearly produced nanoparticles that, although similar in size and composition, are structurally distinct.

Finally, we would like to establish the relationship between the magnetic and structural transitions. This comparison is shown in Fig. 5.9. In agreement with the literature [98] we see a strong correlation between the structural and magnetic transitions in the bulk as can be seen by comparing the red and blue curves in Fig. 5.9(a) (magnetic) and 8(b) (structural), where the structural parameter we choose to plot is the unit cell volume. The cyan and magneta curves show the same comparison

for the type-A nanoparticles. Again, the magnetic and structural transitions appear to be coupled, although the hysteresis in the magnetic data is far smaller than that observed in the structural data. The increase in the magnetization on cooling is decreased in the type-A nanoparticles, relative to the bulk, and this correlates to a smaller increase in cell volume. Most significantly, the width of the thermal hysteresis in the magnetization is much smaller for the type-A nanoparticles, on the order of only 1 K, than for the bulk sample, close to 10 K. This is observed despite the structural hysteresis being broader in the nanoparticles than in the bulk. Thus, the structural and magnetic transitions are related, but not completely dependent on each other.

The volume of the type-A nanoparticles in the low-spin β phase is the same as for the bulk material, though the increase in the volume on entering the α phase is less, consistent with the decreased magnetization in that phase. The small suppression in the magnetic signal can perhaps be attributed to surface effects in the nanoparticle sample. This suggestion is supported by the observation that the high temperature susceptibility in the type-A nanoparticles is smaller than that of the bulk sample, so that the relative change in magnetic susceptibility, $\chi'(T = 295K) - \chi'(T =$ $335K)/\chi'(T = 335K)$, is approximately equal. These measurements support the conclusion that the magnetostructural transition in the type-A nanoparticles is qualitatively similar to that occurring in bulk MnAs, but involving a smaller amount of distortion.

The temperature dependence of the magnetic susceptibility for the type-B nanoparticles, also plotted in Fig. 5.9, differs strikingly from the behavior of the type-A nanoparticles and bulk MnAs. The type-B nanoparticles have a negligible magnetic susceptibility at 335 K, consistent with a weakly paramagnetic low-spin state. There is a small, but distinct increase in susceptibility at lower temperatures. This transition can be seen most clearly in the data collected on warming, which suggest a transition from a weakly ferromagnetic to paramagnetic state at a temperature similar to what is observed in the type-A nanoparticles. In addition to the magnitude of the susceptibility being greatly suppressed from that of the type-A nanoparticles, the thermal hysteresis in the susceptibility is also much broader for the type-B nanoparticles, extending over at least 30 K. The fact that the susceptibility in the type-B nanoparticles is a significant fraction of that found in the type-A nanoparticles together with the different temperature dependence of the two samples makes it unlikely that the magnetic response in the type-B nanoparticles arises from some type-A impurity that was not detected by our other techniques.

This magnetic transition in the type-B nanoparticles does not appear to be linked to a structural transition but may be connected to an observed irreversibility in the unit cell volume on cooling. This evidence for a magnetic transition in the type-B nanoparticles in the absence of any clear structural transition suggests that the interplay between magnetism and crystal structure in MnAs may be more complex than previously believed.

5.4 Conclusion

Structurally distinct samples of MnAs nanoparticles have been prepared using either slow-heating (method A) or high-temperature rapid-injection (method B) arrested precipitation reactions, and their temperature-dependent structure and magnetic characteristics have been probed. Using Rietveld and PDF methods, we confirm that the structure transition in bulk MnAs is highly correlated with the magnetic transition, as previously reported. Type-A nanoparticles have a similar structural transition that happens in the same temperature region as bulk, but the changes are smaller in amplitude. Once again, a clear magnetic transition correlates with what is happening structurally. This is in contrast to previous reports wherein no structural transformation was observed for type-A nanoparticles by traditional temperaturedependent powder X-ray diffraction methods, despite the persistent observation of a magnetic transition [104] and highlights the sensitivity of the PDF approach in probing structural transformations in nanoscale materials. Type-B nanoparticles are distinct from both the bulk and type-A nanoparticles adopting the β structure over the entire temperature range. The fact that type-A particles predictably cycle between α and β , whereas type-B nanoparticles are kinetically trapped, suggests the structure is pinned, possibly by impurity ion inclusion during the rapid nucleation inherent in the method B synthesis. Previous studies have demonstrated a slow conversion over time to the thermodynamic α phase. Partial conversion during the data acquisition could explain some of the irreversibility observed in both the structural and magnetic data. A detailed study of the kinetic stability of type-B nanoparticles as a function of particle size is underway.



Figure 5.1: TEM images and particle size distributions of type-A (a) and type-B (b) MnAs nanoparticles.



Figure 5.2: PDF refinements on bulk (left) and type-A nanoparticle (right) MnAs data. For each subfigure, the bulk circles represent the PDF from the experimental data and the red solid line is the calculated PDF after refinement. The green curve offset below is the difference curve between data and model.



Figure 5.3: (a) comparison of the difference (orange curve) between 295 (blue line) and 335 K (red line) diffraction pattern for bulk MnAs. (b) same as (a) but for type-A nanoparticles with violet-colored difference curve. (c) comparison of the difference curves from (a) and (b). The orange is the same as the difference curve in (a) and the violet is the result of scaling the curve in (b) by a factor of 4 for comparison.



Figure 5.4: (a) comparison of the difference (orange curve) between 295 (blue line) and 335 K (red line) PDF for bulk MnAs. (b) same as (a) but for type-A nanoparticles with violet-colored difference curve. (c) comparison of the difference curves from (a) and (b). The orange is the same as the difference curve in (a) and the violet is the result of scaling the curve in (b) by a factor of 4 for comparison. The similar comparison based on diffraction pattern is shown in Fig. 5.3.



Figure 5.5: Lattice parameters ((a), (b)) and atomic displacement factors ((c), (d)) from PDF refinements on bulk and type-A samples using α phase structure model. (a) and (b) are for lattice parameter a and c in unit of Å. (c) and (d) are for Uiso of Mn and As in unit of Å². For each subfigure, the blue and red are for bulk MnAs on the cooling and heating runs respectively. The cyan and magenta are for type-A MnAs nanoparticles on cooling and heating runs.



Figure 5.6: PDF refinements on data acquired on type-B nanoparticles at 295 ((a), (b)) and 335 K ((c), (d)) using the α ((a), (c)) and β ((b), (d)) phase model, respectively. For each subfigure, the symbol and color representations are the same as Fig. 5.2.



Figure 5.7: Same as 5.3 but for type-B nanoparticles. In (c) the difference curve (violet) of type-B nanoparticles is scaled by a factor of 10 since its amplitude is too small to compare with the bulk one.



Figure 5.8: Same as 5.4 but for type-B nanoparticles. In (c) the difference curve (violet) of type-B nanoparticles is scaled by a factor of 10 since its amplitude is too small to compare with the bulk one. The similar comparison based on diffraction pattern is shown in Fig. 5.7.



Figure 5.9: Real part of the AC magnetization (a) and unit cell volume (b) in bulk, type-A and type-B nanoparticles. All of the unit cell volumes are based on the results of α -model refinements. The blue (cooling) and red (heating) are for the bulk sample; cyan (cooling) and magenta (heating) are for type-A nanoparticles; and the green (cooling) and orange (heating) are for type-B. The dashed lines at 303 K and 317 K show the temperature range of the structural transitions in bulk MnAs as reported in the literature as we mention in the text.

Chapter 6

Conclusion

This thesis work has been motivated by the following quote that was publish in Science magazine by Prof David Waltz and Bruce G. Bruchanan [112]: "The main goals of automation in science have been to increase productivity by increasing efficiency (*e.g.*, with rapid throughput), to improve quality (*e.g.*, by reducing error), and to cope with scale, allowing scientific treatment of topics that were previously impossible to address." By automating scientific activities and making them high throughput, it is possible to understand new science about a system. In material science, one such problem is the study of the structure of complex material, the topic of this thesis.

New powerful X-ray and neutron source are now becoming available allowing us for the first time to do high throughput parametric studies on the structure of complex material. For example, the most intense pulsed neutron beams are available at Spallation Neutron Source (SNS) at Oak Ridge, TN. Inside SNS, as one of worldclass diffractometers, POWGEN, has been built to target for such research studies through powder diffraction method.

Powder diffraction method was first used nearly a century ago. However, until the introduction in 1967 by Rietveld of a method for the refinement of crystal structures

from powder data, interest in powder methods increased dramatically. However, the main problem of Rietveld method is that it is non-linear least squares and is notoriously convergent. To find the minimum, you have to carry out a complex set of refinement steps, manually guiding the refinement to the minimum. For high throughput studies, this become especially problematic.

To overcome the above problem, a new Rietveld analysis program: SrRietveld, was developed in Prof. Billinge's group. SrRietveld is a python program that wraps two legency Rietveld refinement programs: GSAS and FullProf. By using hierarchic data structure, it allows more flexibility and it is easy to use. As one of the developers, I lead the development of PyGSAS and involve the development of other components. The detailed description of SrRietveld has been described in the chapter 3 of the thesis.

As part of this research, I use SrRietveld to do bootstrap error estimation in Rietveld analysis in order to test the accuracy of the error estimation in Rietveld method. I have compared three ways of estimating uncertainties on refined parameters in a Rietveld refinement using two different Rietveld programs, GSAS and FullProf: the estimated standard deviations obtained from the programs themselves, and by resampling the data in two different ways using a pseudo random number generator. There is no apparent advantage of using the computationally expensive Monte Carlo resampling method with respect to using the standard deviations obtained directly from the variance-covarience matrix. However, in certain circumstances the use of the sub-sampling method is warranted. These uncertainty estimation methods will be included as features in future versions of the SrRietveld.

Besides I have demonstrated that there is a significant sensitivity of refined parameters to the use of correct data-esd's as weights in the least squares equation. Significantly biased refined values result when incorrect weights are used even when the same model is fit to the same data-set. This underscores the importance in Rietveld refinements of having accurate data-esd's propagated from the raw data or estimated in some other way. The use of the sub-sampling method yields accurate estimates of standard deviations on refined parameters even when the data-esd's are incorrect or unknown. However, it does not correct for the biased values of the refined parameters themselves that result in this case. Comparing the esd's from the sub-sampling method to the values obtained from the variance-covariance matrix may be a useful diagnostic, indicating situations when there may be a problem with the reported data-esd's. In this case, the accuracy of the refined values is certainly lower than the precision which should be reported. This is generally true because of model errors and parameter correlations that are not included in these, but I note an additional contribution due when data uncertainties are themselves uncertain.

Finally, applying next-generation Rietveld and PDF analysis softwares that I mentioned above, the bulk and nanoscale MnAs have been studied. It is confirmed that the structure transition in bulk MnAs is highly correlated with the magnetic transition as reported in the literature [101, 98]. Type-A nanoparticles have a similar structural transition that happens in the same temperature region as bulk, but the changes are smaller in amplitude. Type-B nanoparticles are distinct from both the bulk and type-A nanoparticles adopting the β structure over the entire temperature range. The fact that type-A particles predictably cycle between α and β , whereas type-B nanoparticles are kinetically trapped, suggests the structure is pinned, possibly by impurity ion inclusion during the rapid nucleation inherent in the method B synthesis. A detailed study of the kinetic stability of type-B nanoparticles as a function of particle size is underway.

I believe that the high throughput Rietveld tool: SrRietveld, can contribute more to the community by providing a way to probe the phase transition and other scientific problems. The error estimation methods that I develop here have potential application in PDF or other methods. More importantly, combining these techniques, more new structure information from complex materials can be discovered in the future.

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