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UNIVERSITY OF CALIFORNIA SAN DIEGO

**Coherent X-ray Studies of Nanoscale Defects and Domains in Functional
Materials**

A dissertation submitted in partial satisfaction of the
requirements for the degree
Doctor of Philosophy

in

Physics

by

Boyan K. Stoychev

Committee in charge:

Professor Oleg G. Shpyrko, Chair
Professor Richard D. Averitt
Professor David Fenning
Professor Alex Frano
Professor Tenio Popmintchev

2023

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The dissertation of Boyan K. Stoychev is approved, and
it is acceptable in quality and form for publication on
microfilm and electronically.

University of California San Diego

2023

DEDICATION

To my wife, family, and friends, for their endless support and
encouragement.

EPIGRAPH

Life is like riding a bicycle. To keep your balance, you must keep moving.

—Albert Einstein

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ABSTRACT OF THE DISSERTATION

Coherent X-ray Studies of Nanoscale Defects and Domains in Functional Materials

by

Boyan K. Stoychev

Doctor of Philosophy in Physics

University of California San Diego, 2023

Professor Oleg G. Shpyrko, Chair

Functional materials with tunable chemical, electronic, and magnetic properties play a pivotal role in advancing modern technology and addressing critical global challenges. A detailed understanding of the structure-property relations in these materials can unlock breakthroughs in their development. Nanoscale structures can have profound effects on the functionality of a material. This dissertation presents how advanced coherent X-ray techniques can be used to probe these nanoscale structures. In particular, Bragg coherent diffractive imaging is used to map lattice strain and defects, while resonant

elastic X-ray scattering can probe nanoscale magnetic domains. The results in Chapter 3 demonstrate the superior electrochemical homogeneity of cathode material fabricated using a novel dry approach, compared to the conventional slurry method, helping to explain observed performance improvements. We further observe a gradient in the electrochemical performance of the cathode as a function of distance from the battery separator. Chapter 4 is an investigation of the strain and defects found in a novel Na-Y-Zr-Cl solid-state electrolyte, as well as the co-existence of two competing crystalline phases. Finally, Chapter 5 presents the discovery of an anomalous order in Fe electrons in magnetite (Fe_3O_4) thin films with a strong magnetic signature. Based on the modeling of the observed reciprocal space structure, this order is likely to be ultra-thin spin domains with a thickness of 0.5 unit cells.

Chapter 1

Introduction

1.1 The Importance of Nanoscale Properties of Materials

Nanoscale structures are ubiquitous in materials and devices around us, including batteries [6] and data storage devices [7]. The intricate arrangements of matter fundamentally shape the operational dynamics and inherent properties of these components. Recognizing that nanoscale architecture exerts a profound influence, it becomes imperative to explore the intricate relationships between structure and properties

In the case of batteries, the positive terminal, known as the cathode, is composed of nanoparticles of layered, spinel, or other crystal structures [8]. Individual nanocrystals known as primary particles (0.1 - 1 μm) are densely packed into spherical secondary particles ($\approx 10\mu m$), and this arrangement is critically important to the reactivity of the cathode,

and by extension, the performance of the battery [9]. Fig. 1.1 contains Scanning Electron Microscopy (SEM) images showing the nanoscale structure of a battery cathode. Smaller particle sizes have been shown to improve rate performance through reduced Li^+ transport distance, but this comes at the cost of a larger surface-area-to-volume ratio, leading to more side reactions [10, 11, 12]. Furthermore, a narrower distribution of particle size and shape can improve energy density and cycling performance but comes at a higher manufacturing cost [11]. Similarly, nano-sized or thin-film magnetite crystals exhibit significant differences in magnetic properties and phase transition temperature depending on their size, shape, and thickness [13, 14]. A more complete understanding of these dependencies can unlock new possibilities for tunable magnetic properties.

Unraveling these complex working mechanisms and the underlying intricate structures of functional materials holds the key to further development in their performance. Through the exploration of structure-property relations on the nanoscale, we gain insights into how to best approach the future development of next-generation devices.

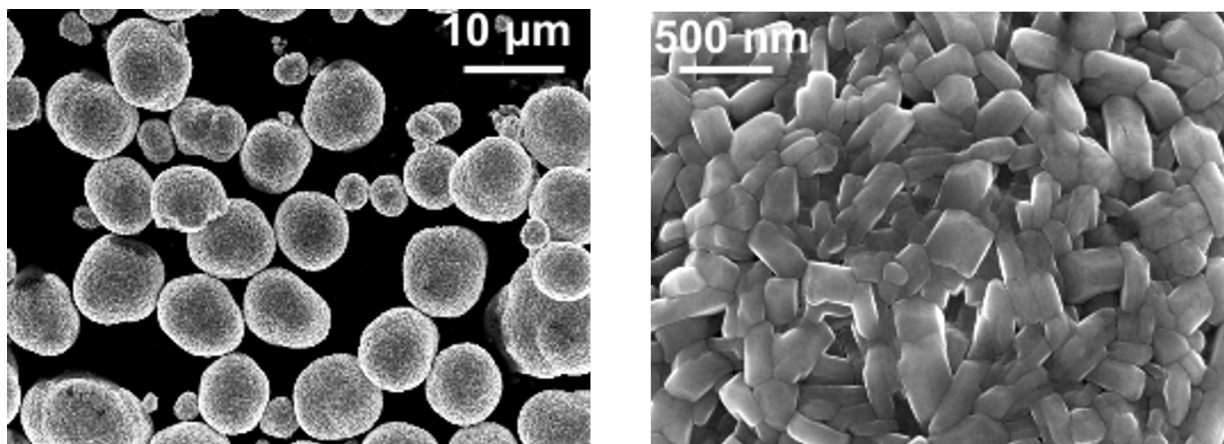


Figure 1.1: SEM images of spherical secondary cathode particles (left), consisting of tightly-packed single nanocrystals also known as primary particles (right).

In order to study these structure-property relations in more detail, advanced experimental techniques that can probe a device during operation are required. In recent years, significant efforts have been made towards the development of *in-situ/operando* characterization methods [15]. For example, researchers used neutron scattering to investigate role of temperature and current in the phase evolution of a LiFePO_4 cathode using *operando* neutron scattering [16, 17]. Other *in-situ* approaches applied to batteries include Atomic Force Microscopy [18, 19], Scanning Electron Microscopy [20, 21], Raman Spectroscopy [22, 23, 24] and X-ray Absorption Spectroscopy [25, 26].

The techniques described above can provide unique insight into the complex processes inside a battery, but they present several limitations. The obtained information is often averaged over a large number of individual particles, and it is restricted to two dimensions. Researchers developed an alternative approach called Bragg Coherent Diffractive Imaging, making use of the coherence of synchrotron X-rays to image strain and defects of micron-sized single crystals in 3D [27, 28]. This technique was successfully applied to *operando* studies of nanoscale evolution of single cathode nanoparticles, revealing that the formation of strain and edge dislocations during battery charging/discharging play a key role in capacity degradation [29, 30, 31].

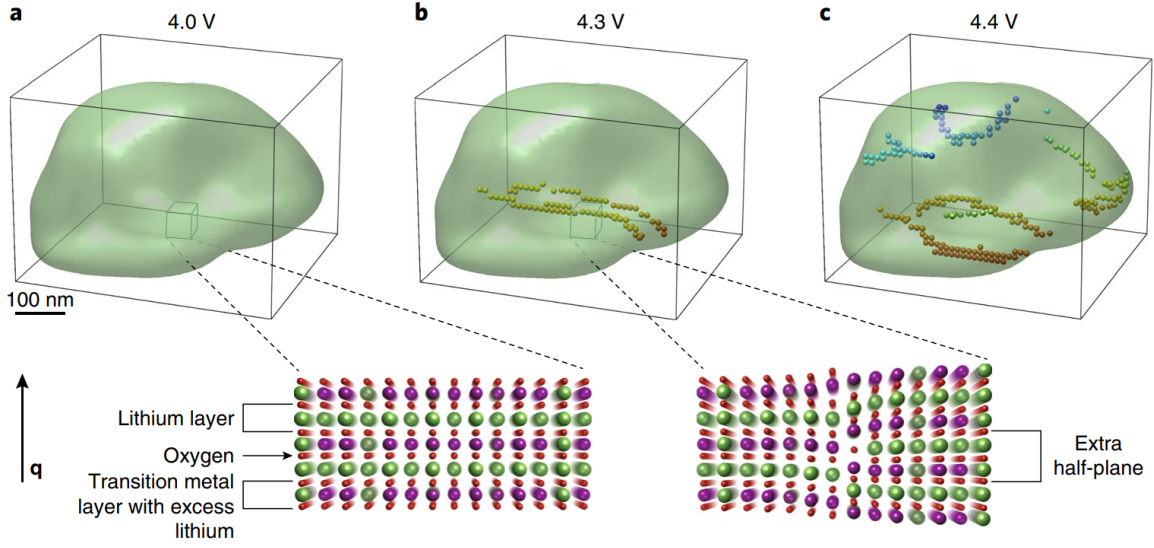


Figure 1.2: Formation of a dislocation network during battery charging. At 4.0V, no dislocations are present in the particle (a), while at 4.3V two edge dislocations can be observed as a result of lithium extraction. At 4.4V (c), a dislocation network emerges. Adapted from [31].

1.2 X-rays as Electromagnetic Waves

Quantum Mechanics tells us that electromagnetic radiation can exhibit both particle and wave behavior, depending on the phenomenon. The wave form became apparent when Maxwell derived the famous set of 4 partial differential equations describing the classical interplay between electricity and magnetism [32]:

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0} \qquad \nabla \cdot \mathbf{B} = 0 \qquad (1.1)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \qquad \nabla \times \mathbf{B} = \mu_0 \mathbf{j} + \epsilon_0 \mu_0 \frac{\partial \mathbf{E}}{\partial t} \qquad (1.2)$$

where ρ is charge density, $\mathbf{j}$ is current density, $\mathbf{E}$ is the electric field, $\mathbf{B}$ is the magnetic field, ϵ_0 is the vacuum permittivity and μ_0 is the vacuum permeability. It turns

out that the two fundamental electromagnetic physical constants, ϵ_0 and μ_0 , are directly related to the speed of light in a vacuum via:

$$c = \frac{1}{\sqrt{\epsilon_0 \mu_0}} \quad (1.3)$$

A solution of Maxwell's equations for $\rho = \mathbf{j} = 0$ exists in the form of a transverse wave of perpendicular oscillating $\mathbf{E}$ and $\mathbf{B}$ fields, propagating at speed c in the third perpendicular direction (see Fig. 1.3). This solution represents the wave description of light, and has the form:

$$\mathbf{E}(\mathbf{r}, t) = \hat{\epsilon} E_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \quad (1.4)$$

where E_0 is the amplitude of the electric field, $\hbar$ is the reduced Planck constant, and $\hbar \mathbf{k}$ and $\hbar \omega$ are the quantized momentum and energy of a single X-ray photon respectively.

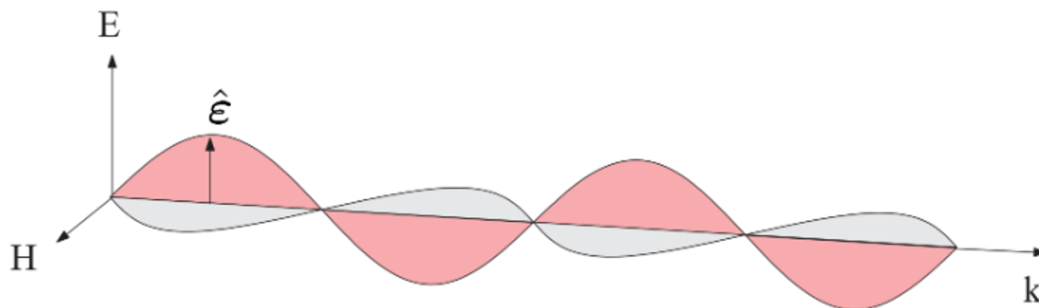


Figure 1.3: An X-ray as a transverse electromagnetic wave, where electric and magnetic fields are perpendicular to each other and to the direction of propagation. Adapted from [1].

1.3 Interactions of X-rays with Matter

X-rays have been widely used as a probe of matter for over 100 years [1]. They are defined as a region of the electromagnetic spectrum corresponding to a wavelengths ranging from 0.1 - 10 nm, or an energy of 100 eV - 10 keV. For comparison, our eyes are sensitive to a significantly narrower range of longer-wavelength electromagnetic radiation, 400 - 700nm. X-rays have several distinct advantages as probes of matter. First of all, they can have significant penetration depth, allowing us to access information beneath the surface of a material. The wavelength of X-rays is also the same order of magnitude as the sizes and distances between atoms (see Fig. 1.4). This means that using X-rays, we can observe interference effects based on scattering between neighboring atoms in a material, which in principle makes it possible to obtain 3D information about their relative positions with sub-nanometer resolution.

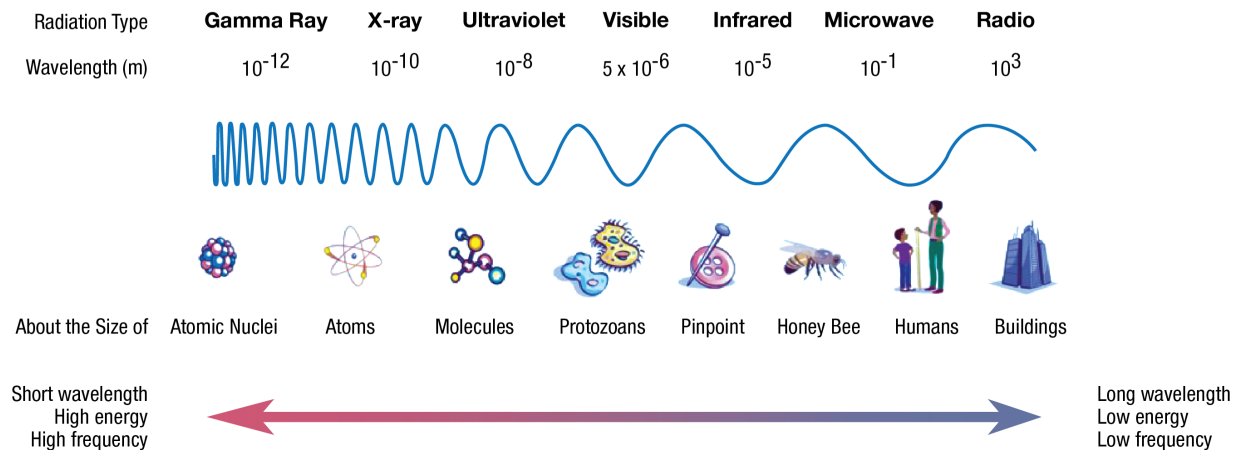


Figure 1.4: The electromagnetic spectrum [2].

In equation 1.4, the wavelength λ is related to the wavenumber $\mathbf{k}$ by:

$$\lambda = \frac{2\pi}{|\mathbf{k}|} \quad (1.5)$$

The energy ϵ of a photon is also directly related to its wavelength and momentum:

$$\epsilon = \frac{hc}{\lambda} = c(\hbar|\mathbf{k}|) \quad (1.6)$$

X-rays primarily interact with the electrons within matter. When an X-ray is incident on an atom, it can either transmit through it, be absorbed and eject an electron, or undergo elastic (Rayleigh) or inelastic (Compton) scattering. In Rayleigh scattering, the X-ray energy $\hbar\omega$ (and therefore magnitude of momentum $|\hbar\mathbf{k}|$) remains conserved, while in Compton scattering this is no longer the case. The experimental techniques in this dissertation are all based on elastic Rayleigh scattering, so we turn our attention to the theory behind this interaction.

1.4 Elastic X-ray Scattering

The simplest scenario in X-ray scattering is to consider an X-ray incident on a single, free electron. The fundamental quantity which describes the strength of this interaction is the differential scattering cross section:

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{I_{sc}}{\Phi_0\Delta\Omega} \quad (1.7)$$

It is a measure of the efficiency with which an X-ray is scattered along a given

infinitesimal solid angle away from an object. The derivation of the results below is beyond the scope of this dissertation, for more details see [1]. Starting from Maxwell's equations, it can be shown that the fundamental length scale in the problem of an X-ray scattering from a single electron is given by the Thomson scattering length, also known as the classical radius of the electron:

$$r_0 = \left(\frac{e^2}{4\pi\epsilon_0 mc^2} \right) = 2.82 \times 10^{-5} \text{Å} \quad (1.8)$$

The differential scattering cross section for an electron is directly related to the square of r_0 :

$$\left(\frac{d\sigma}{d\Omega} \right) = r_0^2 |\hat{\epsilon} \cdot \hat{\epsilon}'| \quad (1.9)$$

where $\hat{\epsilon}$ and $\hat{\epsilon}'$ represent the polarization of the incident and scattered X-ray beam respectively. It is interesting to note that a classical derivation and a quantum mechanical derivation of the scattering by a single electron yield the same result. For a bound electron, an additional frequency dependence appears, which can lead to significant resonance enhancement of the scattering cross section:

$$\left(\frac{d\sigma}{d\Omega} \right) = r_0^2 |\hat{\epsilon} \cdot \hat{\epsilon}'| \frac{\omega^4}{(\omega^2 - \omega_s^2)^2 + (\omega\Gamma)^2} r_0^2 \quad (1.10)$$

where ω is the X-ray frequency, $\omega_s = E/\hbar$ is the electron frequency, and Γ is a damping frequency, typically much smaller than ω_s . Electrons in a material can exist at

different energy levels, and this resonance enhancement can be used to study details of electronic structure. In Chapter 5, we apply these ideas to explore an interesting domain structure in Fe_3O_4 .

When considering scattering from multiple electrons, superposition between X-rays from multiple sources becomes important. In the case of scattering from an atom with Z electrons, we can classically describe it in terms of an electron number density $\rho(\mathbf{r})$. The phase difference between X-rays scattered from two sources can be expressed in terms of the incident wavevector $\mathbf{k}_0$, the scattered wavevector $\mathbf{k}$ and the relative position vector $\mathbf{r}$ as follows:

$$\Delta\phi(\mathbf{r}) = (\mathbf{k}_0 - \mathbf{k}) \cdot \mathbf{r} = -\mathbf{q} \cdot \mathbf{r} \quad (1.11)$$

where $\mathbf{q} = \mathbf{k} - \mathbf{k}_0$ is known as the scattering vector. Fig. 1.5 illustrates this scenario.

Integrating over the volume of the entire atom, the atomic scattering length becomes:

$$r_0 f^0(\mathbf{q}) = r_0 \int \rho(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r} \quad (1.12)$$

Remarkably, $f^0(\mathbf{q})$, also known as the atomic form factor, is exactly the Fourier transform of the electron density $\rho(\mathbf{r})$, signifying the important role that Fourier transforms and Fourier space play in X-ray scattering.

Extending this idea to a molecule with several atoms, the molecular form factor can

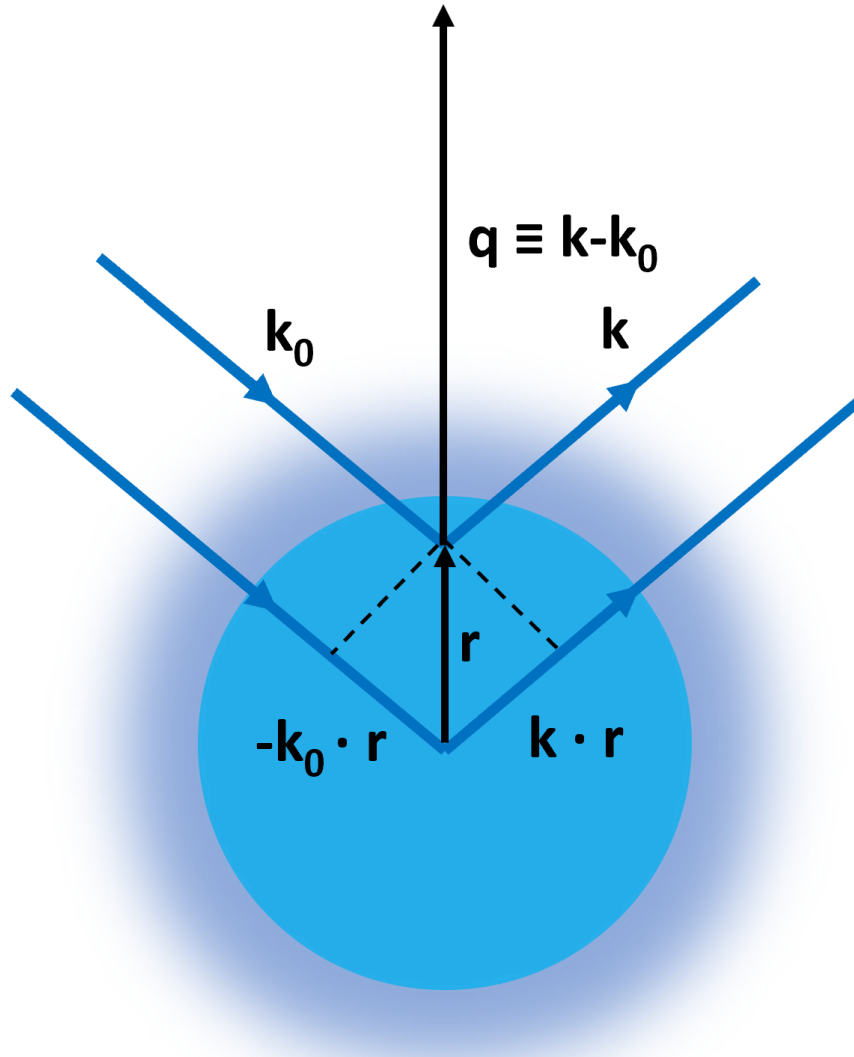


Figure 1.5: Elastic scattering from an atom. The additional path that the bottom X-ray travels is equal to $\mathbf{q} \cdot \mathbf{r}$.

be expressed as :

$$F^{\text{mol}}(\mathbf{q}) = \sum_j f_j(\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{r}_j} \quad (1.13)$$

where $\mathbf{r}_j$ is the position vector of each atom within the molecule. Finally, scattering

from a periodic arrangement of molecules, also known as a crystal, can be factorized as follows:

$$F^{\text{crystal}}(\mathbf{q}) = \sum_j f_j(\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{r}_j} \sum_n e^{-i\mathbf{q} \cdot \mathbf{R}_n} \quad (1.14)$$

Here, the first term is known as the structure factor for a crystal's unit cell, and the second term considers the phase-dependent sum of contributions from each unit cell located at $\mathbf{R}_n$ within a crystal lattice. Since even a micron-sized crystal contains more than 10^9 unit cells, scattering from a crystal strongly depends on the second term in Eq. 1.14. In a crystal, the lattice vectors $\mathbf{R}_n$ can be expressed as:

$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (1.15)$$

Here, $\mathbf{a}_i$ are the lattice basis vectors and n_i are integers. For an arbitrary $\mathbf{q}$, the second term in Eq. 1.14 will vanish as the sum over random values that lie on the complex unit circle. However, thanks to the periodicity of crystal lattices, there exist unique values of $\mathbf{q}$ for which $\mathbf{q} \cdot \mathbf{R}_n = 2\pi m$ for an integer m , leading to constructive interference of the scattered X-rays. We define a reciprocal lattice spanned by the vectors:

$$\mathbf{a}_1^* = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \quad \mathbf{a}_2^* = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \quad \mathbf{a}_3^* = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

Every site on the reciprocal lattice is then given by a linear combination of these

vectors for integer (h, k, l) :

$$\mathbf{G}_{hkl} = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^*$$

It follows that the dot product of a real-space lattice vector $\mathbf{R}_n$ with a reciprocal lattice vector $\mathbf{G}_{hkl}$ is

$$\mathbf{G}_{hkl} \cdot \mathbf{R}_n = 2\pi(hn_1 + kn_2 + ln_3)$$

which is an integer multiple of 2π , meaning that the scattering from each unit cell will constructively interfere and scale with the number of unit cells N . The values of the reciprocal lattice vector $\mathbf{G}_{hkl}$ are directly related to scattering angles θ for which constructive interference occurs. In particular, for a set of lattice planes defined by Miller indices $\{hkl\}$, the $\mathbf{G}_{hkl}$ reciprocal lattice site corresponds to an angle θ for which the path length difference between X-rays scattering from neighboring lattice planes is equal to an integer multiple of the wavelength. This is known as Bragg's law (Fig. 1.6):

$$n\lambda = 2d\sin(\theta) \tag{1.16}$$

where n is an integer, θ is the incident angle, and d is the spacing between the hkl lattice planes.

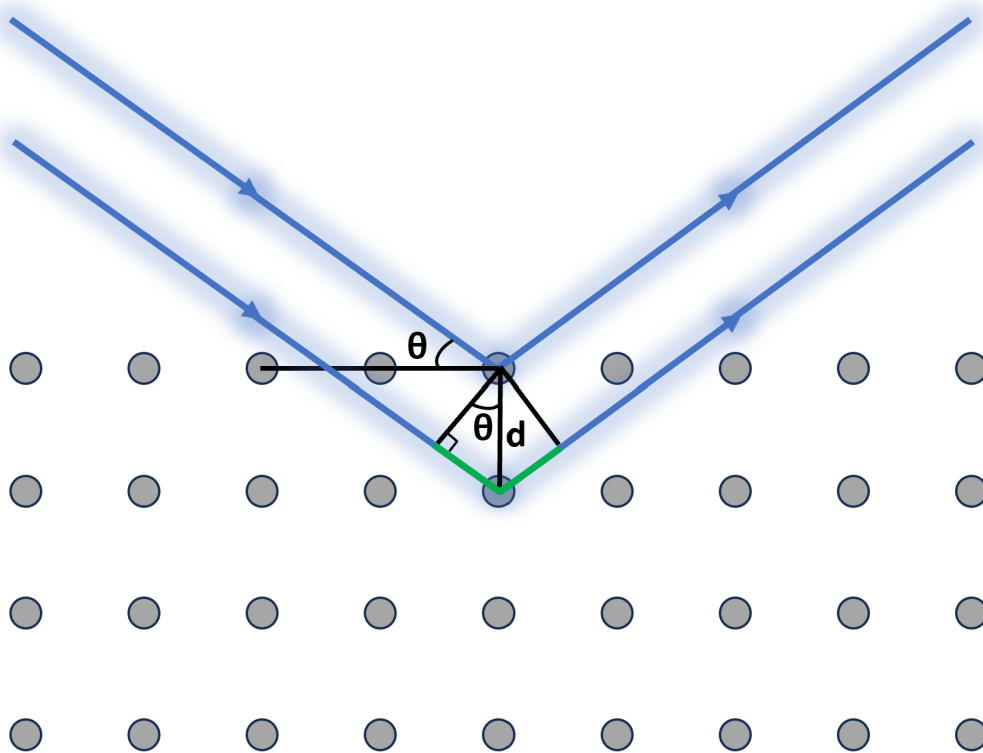


Figure 1.6: Schematic showing the scattering of X-rays from two neighboring lattice planes in a crystal. Constructive interference occurs for particular values of θ and d such that the path length difference (green segment) is equal to an integer multiple of the wavelength. This is known as Bragg's law.

Chapter 2

Synchrotron X-rays

2.1 Limitations of lab-based X-ray instruments

Conventional lab-based X-ray systems make use of the principles described in Chapter 1 to obtain important structural information about samples of interest. When a macroscopic X-ray beam is incident on a crystalline powder, numerous micro-crystals with random orientations will diffract the beam along cones of constant 2θ deflection angle. By setting up an X-ray detector to measure the diffracted intensity as a function of 2θ , one can obtain what is known as Powder X-ray Diffraction (XRD) pattern. In this pattern, the values of 2θ for which intensity peaks appear correspond to can be attributed to lattice spacing values for which Bragg's law (Eq. 1.16) has a solution. Furthermore, Rietveld refinement has been used for over 50 years as a method to model powder XRD patterns based on contributions from the background, the crystal lattice, instrumental factors, and more [33, 34]. Using Rietveld refinement, the exact crystal structure can be determined for

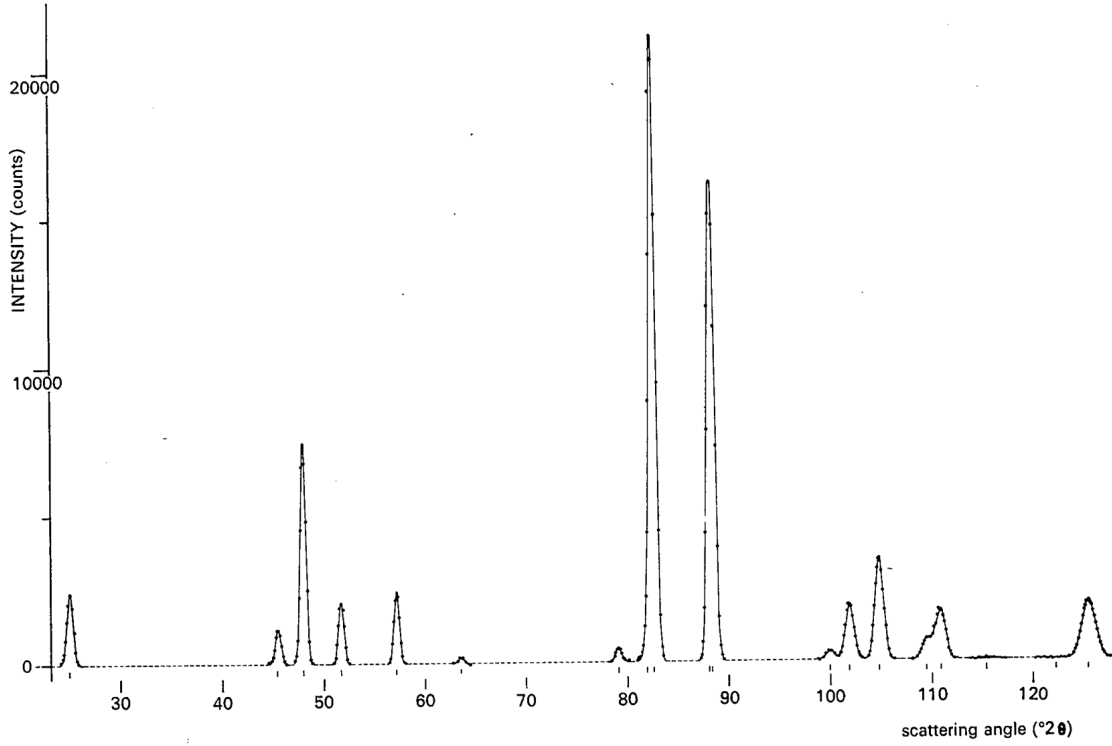


Figure 2.1: The first instance of Rietveld refinement on powder diffraction data of CaUO_4 . In this example, neutrons were used instead of X-rays, with a wavelength of 2.565 Å. The points represent data while the line is based on the refined structural model. Adapted from [33].

a material [35].

Traditional lab XRD instruments have a beam size on the order of $100\ \mu\text{m}$. In order to extract finer details regarding the strain and defects found in individual micro- and nanocrystals, as well as study nanoscale domains within a larger crystal, X-rays need to be focused to a smaller size. The issue that lab-based sources run into is that X-rays are incredibly difficult to redirect since their index of refraction is very close to 1 [36]. To carry out studies that aim to explore structure-property relations on the nanoscale, as well as probe the electronic structure of materials, a highly intense source of X-rays is required.

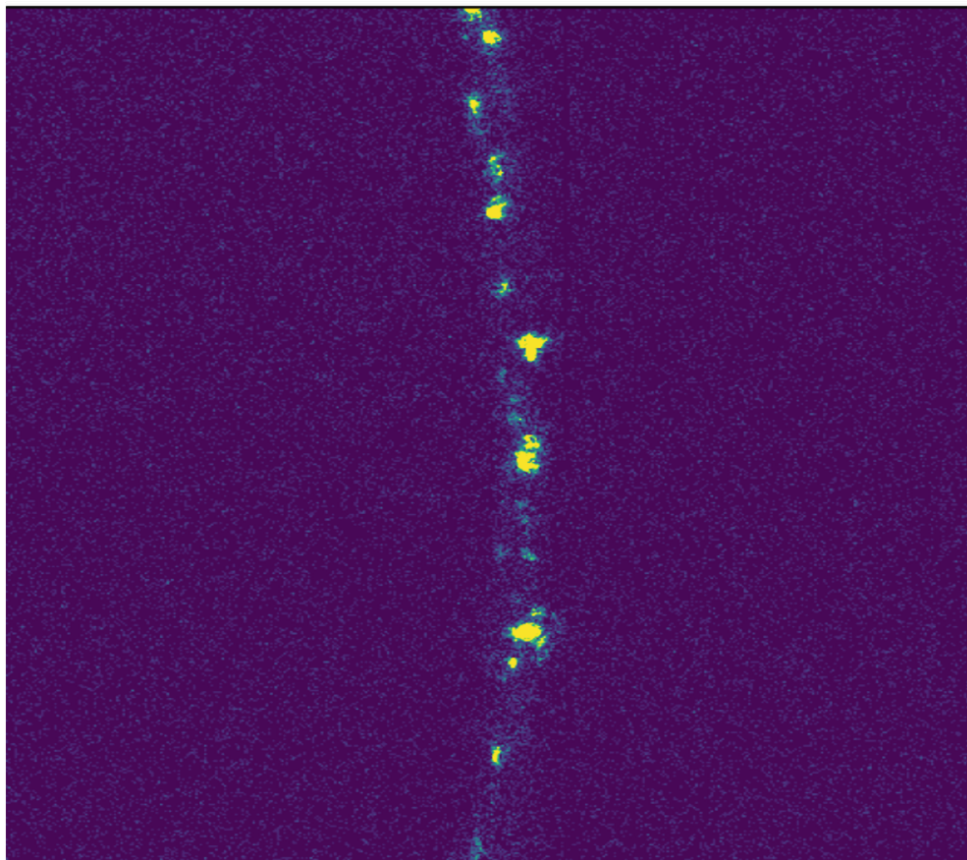


Figure 2.2: Example detector image showing the scattering of a micron-sized X-ray beam from a crystalline powder of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ battery cathode material. The bright spots are Bragg peaks emanating from individual cathode nanocrystals. The Bragg peaks lie along a segment of the diffraction cone for a given deflection angle 2θ .

These types of experiments can be performed in large-scale facilities such as third-generation synchrotron light sources. These facilities make it possible to focus X-ray beams to several hundred nanometers and below while controlling X-ray energy and maintaining a high degree of spatial and temporal coherence. For example, synchrotrons enable us to resolve Bragg peaks from individual nanocrystals, making it possible to probe structure, strain, and defects on a single-particle basis. This is in contrast to lab-based XRD, which provides average structural information for a large number of individual crystals.

2.2 Overview of Synchrotrons

Synchrotron sources harness the principles of synchrotron radiation, a phenomenon arising when charged particles, typically electrons, are accelerated to nearly the speed of light within a circular path by strong magnetic fields. As these high-energy electrons change direction, they emit intense X-ray radiation tangentially to their trajectory, providing a tightly focused X-ray beam. For a non-relativistic electron, the synchrotron radius is related to the magnetic field strength based on the equation for circular motion:

$$F = \frac{mv^2}{r} \quad (2.1)$$

The force in this case is the Lorentz force $F = e|\mathbf{v} \times \mathbf{B}|$, where e is the electron charge. Since $\mathbf{v}$ and $\mathbf{B}$ are perpendicular, we get:

$$\frac{mv^2}{r} = evB; \quad mv = p = erB \quad (2.2)$$

In modern synchrotrons, electrons are accelerated near the speed of light, $v \approx c$. In this relativistic scenario, the momentum p becomes equal to γmc , where $\gamma = \epsilon_e/mc^2$ is the electron energy in units of its rest mass energy. We therefore get:

$$r = \frac{\gamma mc}{eB} = \frac{\epsilon_e}{ceB} \quad (2.3)$$

Electrons/positrons moving in a circle experience a constant acceleration and radiate electromagnetic radiation. At typical synchrotron storage ring energies on the order of

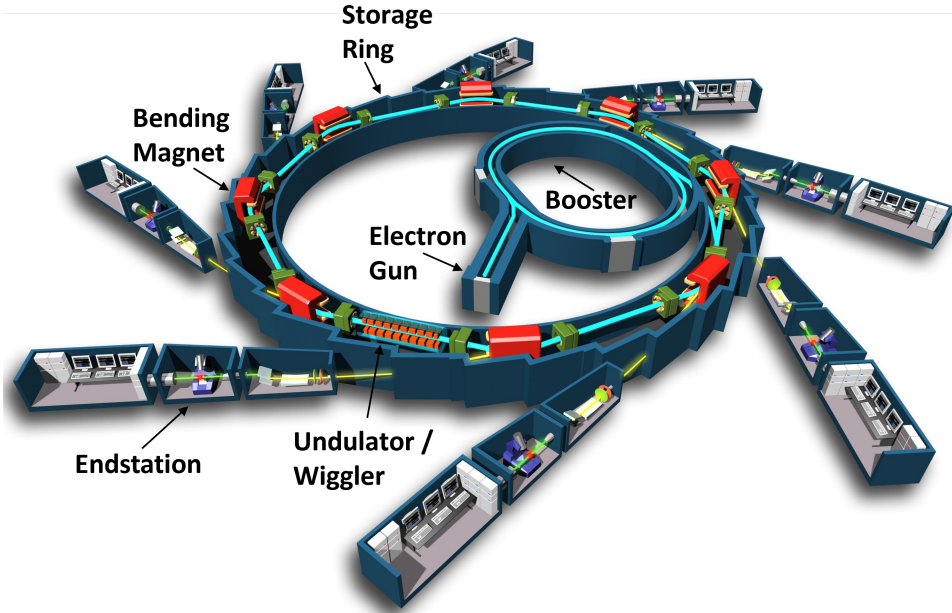


Figure 2.3: Schematic of the main components of a synchrotron. An electron gun emits electron bunches that are accelerated to GeV energies in the booster. These bunches are then injected into the storage ring, where bending magnets control their trajectory. Insertion devices in the forms of wigglers or undulators cause the focused emission of X-rays to experimental endstations [38].

GeV, the spectrum of the emitted radiation peaks at X-ray frequencies. Furthermore, due to relativistic effects, this radiation is compressed into tightly collimated cones defined by the angle $1/\gamma$. For a thorough review of this phenomenon, see [37].

The main components of a synchrotron can be seen in Figure 2.3. Once inside the storage ring, undulators consisting of alternating magnetic dipoles drive oscillations in the electron beam, which leads to further focusing of the X-ray emission. For a number of oscillations N , the opening angle of the radiation cone for an undulator is $1/\sqrt{N}\gamma$, so a further collimation by a factor of $\sqrt{N}$ is achieved. Downstream from each undulator, an experimental endstation uses further optics and instruments to focus and/or select a

particular X-ray energy tailored to a specific technique and sample of interest.

An important measure of the quality of X-rays produced by a synchrotron source is the brilliance, defined as follows:

$$\text{Brilliance} = \frac{\text{Photons/sec}}{(\text{mrad})^2(\text{mm}^2 \text{ source area})(0.1\% \text{ Bandwidth})} \quad (2.4)$$

A source brilliance is high when it produces a high flux of X-rays [Photons/sec] from a small source area [mm^2], with high collimation [mrad^2] within a narrow energy bandwidth [0.1%]. It is worth noting that over the past decades, the rate of increase of X-ray source brilliance exceeds the rate of increase of computer speed as described by Moore's law (Figure 2.4). The research presented in this dissertation is entirely based on synchrotron X-ray experiments, and therefore we will next describe the relevant experimental techniques utilized.

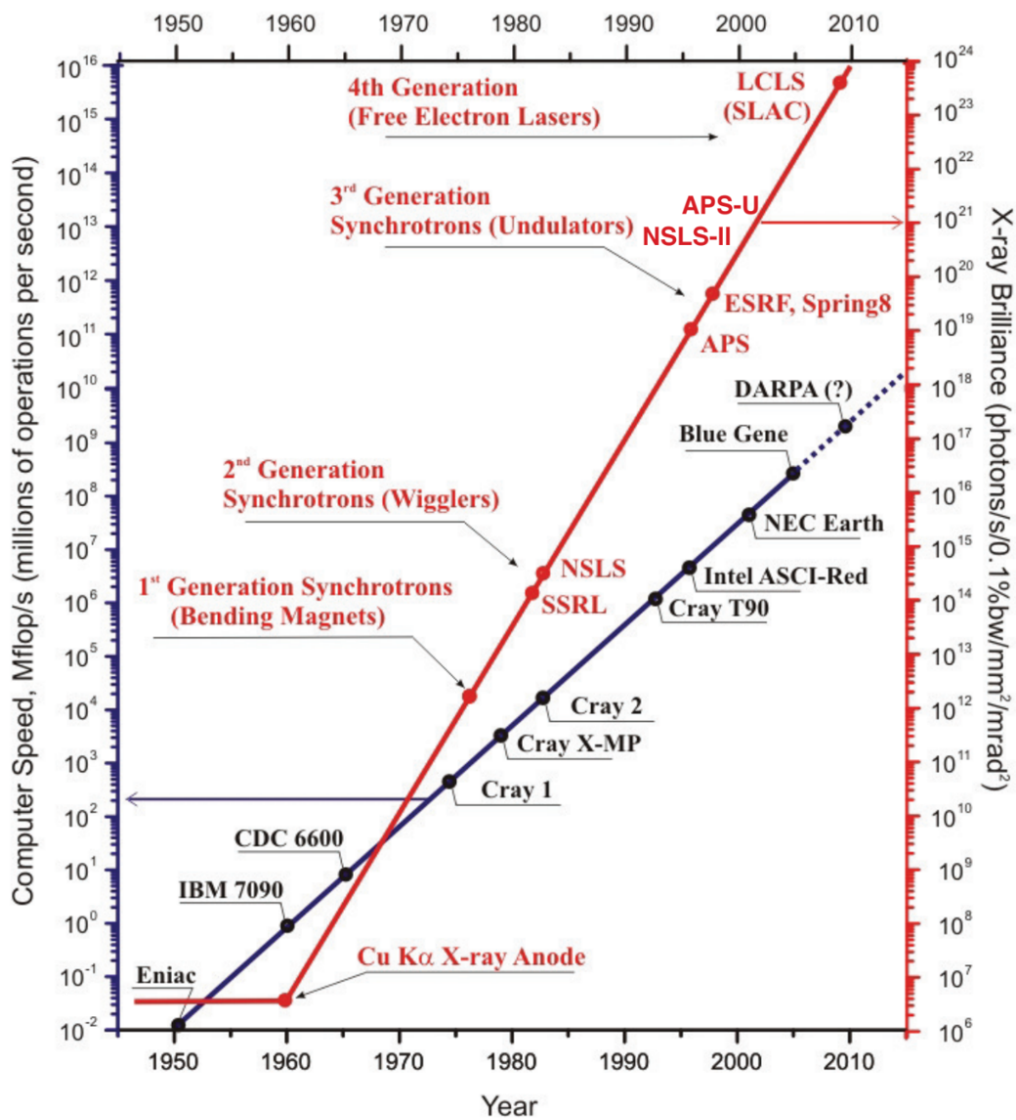


Figure 2.4: The brilliance of X-ray sources over time, compared to computer speed as described by Moore's law. From 1960 onwards, X-ray source brilliance has increased by 18 orders of magnitude, while computer speed has increased by 10 orders of magnitude. Adapted from Oleg Shpyrko.

2.3 Coherence of Synchrotron X-rays

Most electromagnetic radiation around us is emitted in a wide range of directions and follows a continuous distribution of energies. For example, all objects emit thermal electromagnetic radiation known as blackbody radiation, in a wide, continuous spectrum of wavelengths and in all directions [39]. This is known as incoherent radiation, and in that regime interference effects cannot be resolved. In contrast, a perfectly coherent beam would be perfectly collimated and have an infinitely narrow bandwidth. In real synchrotrons, there exists a high, but not perfect, degree of coherence. As alluded to in Eq. 2.4, the coherence of a synchrotron X-ray source is an important component of its brilliance.

The concept of coherence length is used to define the degree of coherence in an X-ray beam. The first scenario to consider is that of two plane waves traveling in the same direction but with different wavelengths λ and $\lambda - \Delta\lambda$. The longitudinal coherence length is defined as the distance it takes these two plane waves to go from fully in-phase to fully out-of-phase. Fig. 2.5 (a) illustrates how L_L is defined:

$$2L_L = N\lambda = (N + 1)(\lambda - \Delta\lambda) \quad (2.5)$$

For a large N , we get that $(N + 1)\Delta\lambda = \lambda$, or $N \approx \lambda/\Delta\lambda$, which gives the following form of the longitudinal coherence length in terms of λ and $\Delta\lambda$:

$$L_L = \frac{\lambda^2}{2\Delta\lambda} \quad (2.6)$$

L_L is a direct measure of how monochromatic an X-ray beam is. The other scenario we consider is of two plane waves with the same wavelength, but a difference in propagation angle of $\Delta\theta$. The transverse coherence length L_T is then defined as the distance in the transverse direction where the two waves change from fully in-phase to fully out-of-phase. Fig. 2.5 (b) demonstrates that $2L_T\sin(\Delta\theta) \approx 2L_T\Delta\theta = \lambda$ for small $\Delta\theta$. In terms of the distance between source points D and distance to observation point R , this becomes:

$$L_T = \frac{1}{2} \frac{\lambda}{(D/R)} = \frac{\lambda R}{2D} \quad (2.7)$$

At third generation synchrotrons, D is on the order $100 \mu m$ while $R \approx 20 m$, which gives a value of L_T of $10 \mu m$ for $1 \text{ \AA}$ X-rays. Similarly, perfect-crystal monochromators can achieve $\Delta\lambda/\lambda \approx 10^{-5}$, which yields $L_L \approx 5 \mu m$. This implies that we can observe interference effects between domains/objects that are closer to each other than these coherence lengths, while the total scattered intensity from objects that are farther apart will simply be the sum of the individual scattering intensities. Interference effects give rise to further modulations in the diffracted intensity, and this additional complexity can be used to extract information about the diffracting crystal. The next section discusses a technique that makes use of this fact.

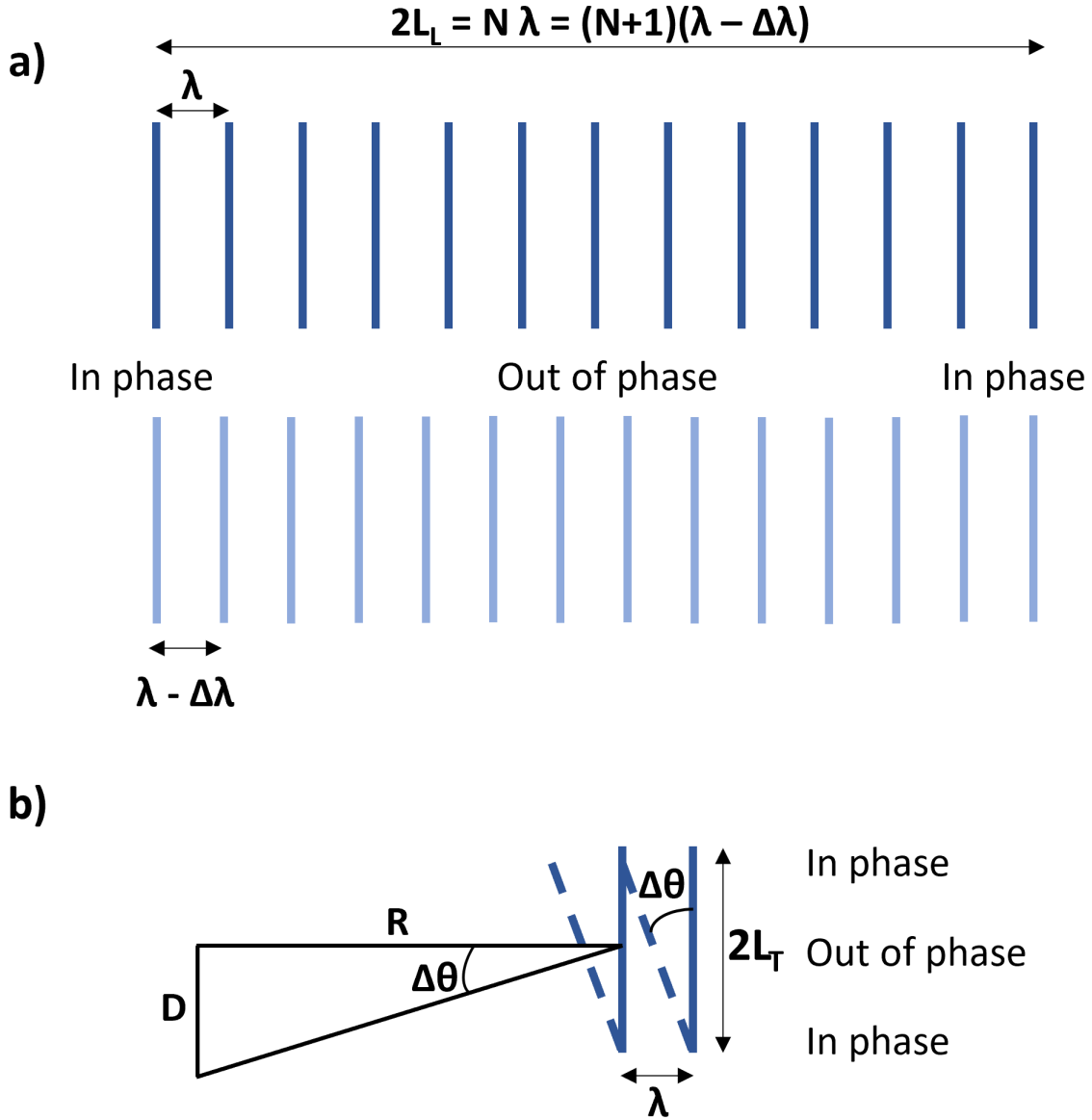


Figure 2.5: Longitudinal and transverse coherence lengths. (a) For two plane waves with different wavelengths emitted in the same direction, the longitudinal coherence length L_L is defined as the distance after which the relative phases of the two waves change by π . (b) For two waves with the same wavelength but emitted from the ends of a finite source in different directions, the transverse coherence length L_T is given by the transverse distance after which the relative phases change by π .

2.4 Synchrotron X-ray Techniques

2.4.1 Bragg Coherent Diffractive Imaging

As described in Eq. 1.12, the far-field diffraction pattern is directly related to the Fourier transform of the electron density of the illuminated electrons. Naturally, one may wonder whether we cannot directly obtain the electron density from an inverse Fourier Transform of the diffraction pattern. The issue is that the intensity that we measure is equal to the square of the amplitude, and we are unable to measure the phase of the diffracted X-rays - this is known as the phase problem in X-ray diffraction. However, it turns out that when coherent X-rays from Synchrotron sources are incident on an object that is fully illuminated by the beam, it is possible to retrieve the missing phases and reconstruct the real-space object in 3D.

To illustrate this idea, let us consider the well-known Young's double slit experiment. When a beam of light is incident on a single slit, the far-field intensity pattern will be equal to the square of the Fourier transform of the slit, which can be described as a "top hat" function:

$$\Pi(x/b) = \begin{cases} 1, & -b/2 \leq x/b \leq b/2 \\ 0, & \text{otherwise} \end{cases} \quad (2.8)$$

The recorded intensity will then be:

$$I(q) = |F(q)|^2 = \left| \int_{-\infty}^{\infty} \Pi(x/b) e^{-iqx} dx \right|^2 = \left| \int_{-b/2}^{b/2} e^{-iqx} dx \right|^2 \quad (2.9)$$

$$= \left| \frac{1}{-iq} (e^{-ibq/2} - e^{ibq/2}) \right|^2 = (b \operatorname{sinc}(bq/2))^2 \quad (2.10)$$

The single-slit diffraction pattern will have the form of the square of the sinc function. In the case of two slits, if the incident waves are incoherent, the resulting intensity will be an average of the two single-slit intensities. However, when the incident waves are coherent, we can consider the two slits as two top-hat functions, formed by convolving a single top-hat function with two Dirac delta functions ($\delta(x - a/2) + \delta(x + a/2)$). The convolution theorem then tells us that the Fourier transform of the two slits will be equal to the product of the Fourier transform of a single slit (sinc function), and the Fourier transform of the two Dirac delta functions:

$$\int_{-\infty}^{\infty} [\delta(x - a/2) + \delta(x + a/2)] e^{-ixq} dx = e^{-iaq/2} + e^{iaq/2} = \cos(aq/2) \quad (2.11)$$

Note that $a \gg b$, which is to say that the spacing between the slits is significantly greater than the width of each slit. The resulting intensity will then be equal to the square of the product of a lower-frequency sinc function with a higher-frequency cos function. We have shown that constructive and destructive interference leads to the formation of higher-frequency modulations known as fringes. While the width of the sinc envelope

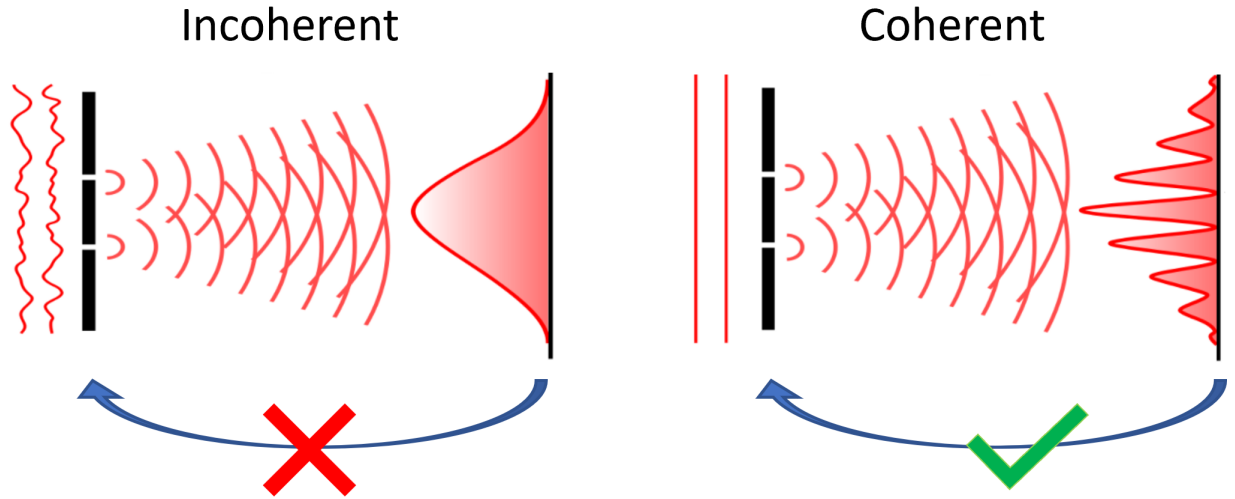


Figure 2.6: Diffraction from two slits in the case of an incoherent and coherent source. In the incoherent case, the resulting diffraction pattern is simply an average of the diffraction from each slit and contains no information about the fact there are two fringes. When the incident beam is coherent, constructive and destructive interference from waves diffracted by the two slits gives rise to a fringe pattern. This pattern contains enough information to recover the separation and width of the two slits.

contains information about the slit size b , the fringe spacing is directly related to the separation between the two slits a . This example, illustrated in Fig. 2.6, demonstrates that in principle, the coherent diffraction pattern contains enough information to overcome the phase problem and reconstruct the real-space electron density and displacement field.

Extending this idea to 3D, it has been demonstrated that if a sufficiently small crystal is fully illuminated by an X-ray beam with a larger coherence volume than the crystal size, a far-field Bragg diffraction peak will similarly exhibit fringes. A rocking curve around a Bragg peak allows us to obtain 3-dimensional data. A variety of iterative algorithms can then be used to retrieve the missing phases, allowing for the full 3D reconstruction

of the measured crystal. The first such is the Gerchburg-Saxton algorithm, also known as the error reduction (ER) algorithm, first introduced in 1972 [40]. In this algorithm, a random phase is combined with the measured amplitude, and an inverse Fourier transform is taken. Constraints are then resulting real-space object, such as requiring it to fit inside a "box" known as the support, and the modified real-space object is taken back to reciprocal space via a Fourier transform. At this stage, the transformed amplitude is replaced with the measured amplitude, while the transformed phase is kept, and the process is repeated. Each iteration gets closer and closer to reproducing the measured diffraction pattern, but this algorithm can often get stuck at a local minima [41]. Fig. 2.7 shows a sketch of a generic iterative phase retrieval algorithm.

A popular modification of the ER algorithm is known as the hybrid input-output (HIO) method. In HIO, an additional parameter β is introduced such that a fraction of the previous cycle's results are combined with the current result. Furthermore, the real-space constraint is relaxed by allowing a fraction of the amplitude to exist outside the support [42]. In practice, recipes that include combinations of ER and HIO steps often produce the best results. Furthermore, a genetic algorithm can be applied to produce generations of reconstructions, with each next generation taking the best reconstructions from the previous generation as a starting point.

Thanks to phase retrieval algorithms, coherent diffractive imaging allows us to directly measure the electron density of a single nanocrystal. Furthermore, the phase of the reconstructed real-space object is directly related to a projection of the displacement field along the scattering vector, such that a phase difference of 2π corresponds to one unit

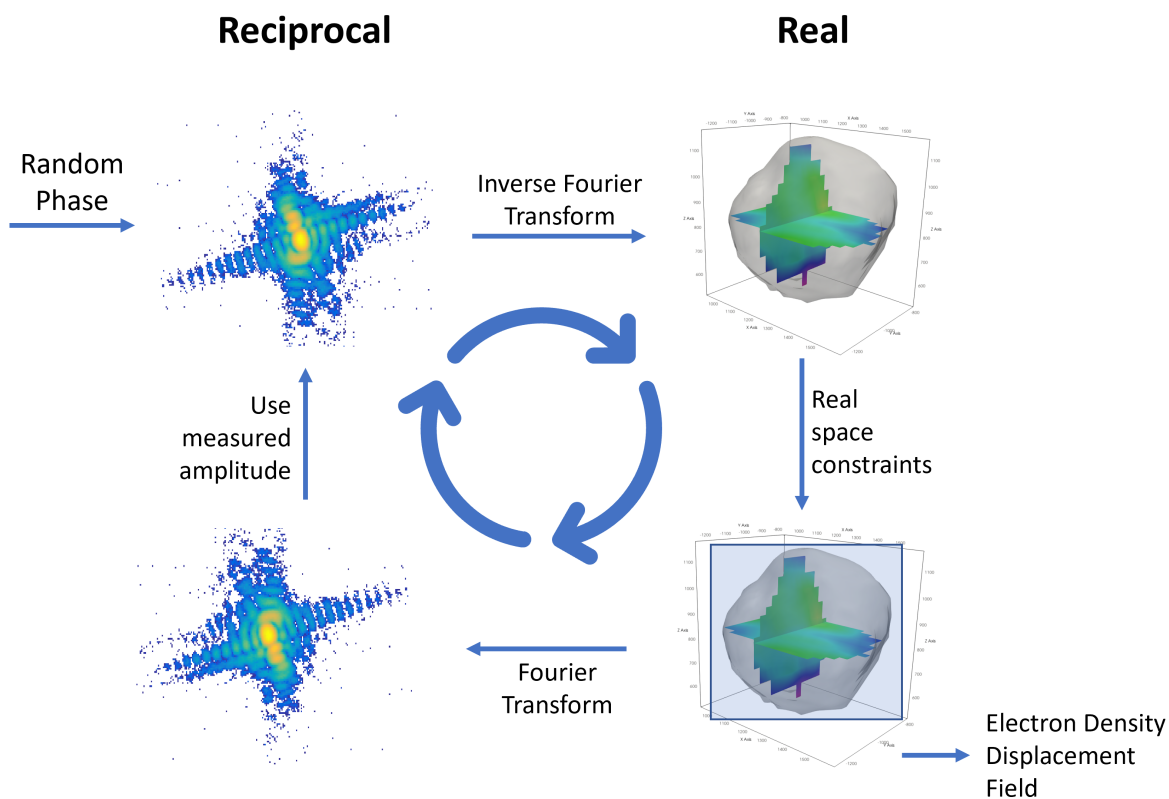


Figure 2.7: A sketch of a generic phase retrieval algorithm. The measured amplitude is combined with an initial random phase and an inverse Fourier transform is taken. Constraints such as size are applied to the resulting real-space object. The constrained object is then taken back to reciprocal space via a Fourier transform. The transformed amplitude is replaced by the measured amplitude, and the process is repeated again.

of spacing for the scattering lattice planes.

An important question is, how do we evaluate the quality of a reconstruction that these phase retrieval algorithms produce? The first method is by use of the Phase Retrieval Transfer Function (PRTF), defined as follows:

$$PRTF(q) = \frac{\langle |FT(\rho(\mathbf{r}))| \rangle}{\sqrt{I(q)}} \quad (2.12)$$

where FT denotes a Fourier transform, and averaging is done over multiple reconstructions as well as over spheres of constant $|\mathbf{q}|$. This function essentially compares the degree to which fringes in the data can be reproduced from the reconstructed object. Fringes closer to the Bragg peak can often be reproduced, but as we go farther and farther in $\mathbf{q}$, artifacts in the predicted amplitude will appear that are not based on the data. As such, the PRTF starts around 1 and decays to 0, and the point at which its value crosses 0.5 (or more liberally, $1/e$) determines the overall length scale to which reconstructed features are trustworthy. Fig. 2.8 shows an example measured Bragg peak, together with the reconstructed real-space crystal, the predicted intensity, and the PRTF.

While the PRTF gives a good general idea of the quality of a reconstruction, the spherical averaging makes it less reliable for data where the fringes are not regular, such as highly-strained materials with high defect density. In these scenarios, it is also important to consider the reproducibility of individual reconstructions, as well as the total error between the predicted and measured intensity.

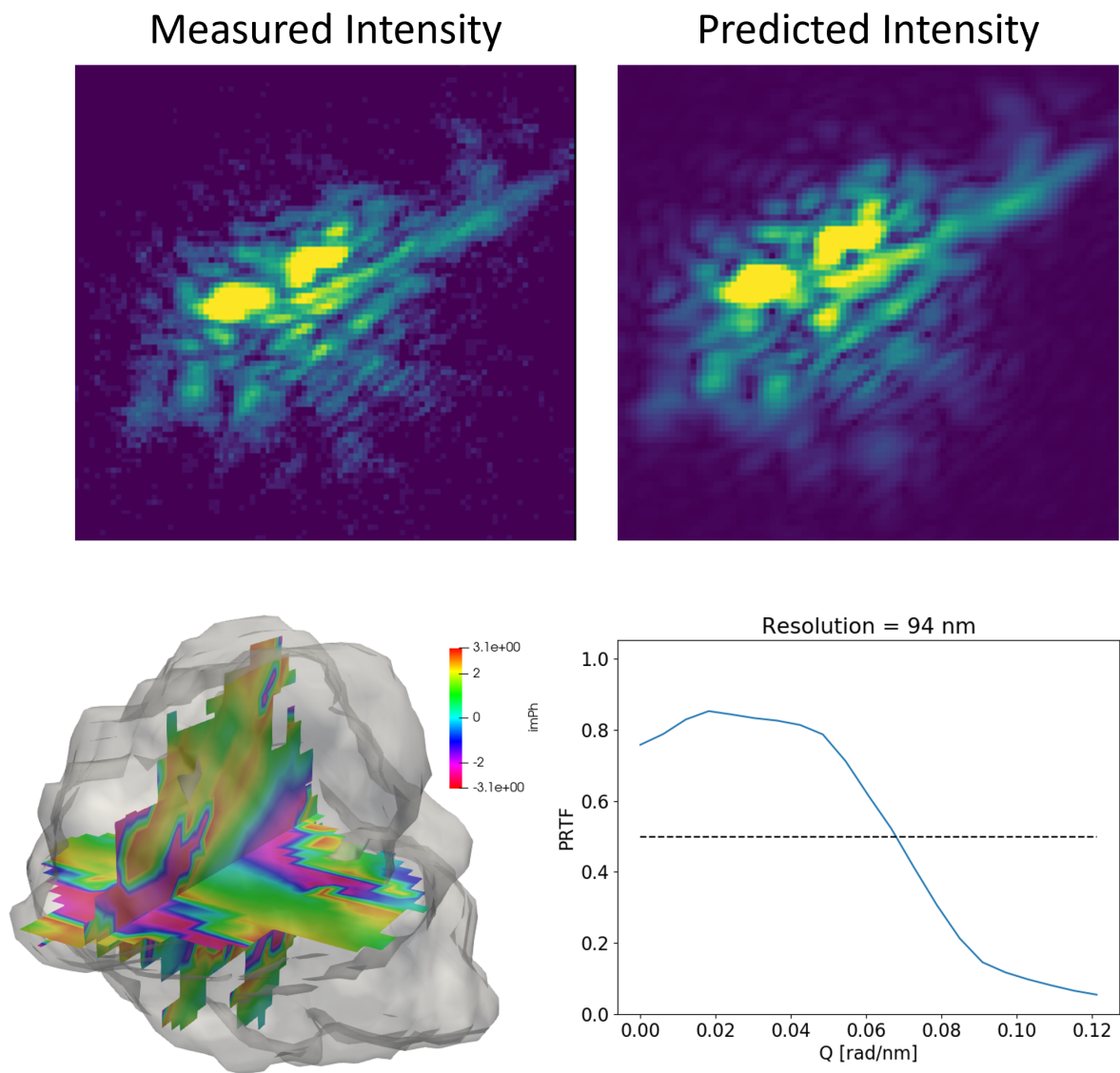


Figure 2.8: Measured intensity compared to predicted intensity for a slice of a 3D dataset. The real-space reconstructed nanocrystal is visualized as a grey isosurface, with colored slices indicating the phase. The PRTF decreases below 0.5 for a q value corresponding to a length scale of 94 nm.

2.4.2 Resonant Elastic X-ray Scattering

Resonant Elastic X-ray Scattering (REXS) is another important coherent X-ray probe. We recall Eq. 1.10, showing the resonant enhancement that appears in the atomic scattering cross-section. Since w_s is specific to particular electron energy states for a particular atom, tuning the incident X-ray energy near one of these frequencies will significantly enhance the scattering from a particular element. Specifically, soft X-rays can be tuned to match the energy difference between a transition metal's $2p$ orbital and an unfilled d orbital, and as such can probe the electronic structure of that element in a material. These particular energies give rise to absorption edges, which are sharp increases in the absorption of X-rays at resonant energies that correspond to electron excitations. For example, in Fe_3O_4 at $(001/2)$ in reciprocal space, where the purely structural scattering signal would fully cancel out, a charge-orbital ordering in Fe gives a measurable signal [43].

The mechanism behind resonant scattering is the following. A photon is absorbed by a core electron, prompting a virtual transition of the electron from its core level to an available state within the valence band [44]. Eventually, the electron returns to its core level, resulting in the emission of a photon with precisely matching energy. Figure 2.9 illustrates this mechanism.

In addition, using X-rays with different polarizations can give rise to contrast in the signal known as X-ray dichroism [45]. Of particular interest is X-ray magnetic circular dichroism (XMCD), which is caused by the difference in absorption of left vs. right circularly-polarized X-rays exhibited by ferromagnetic materials. This technique was first

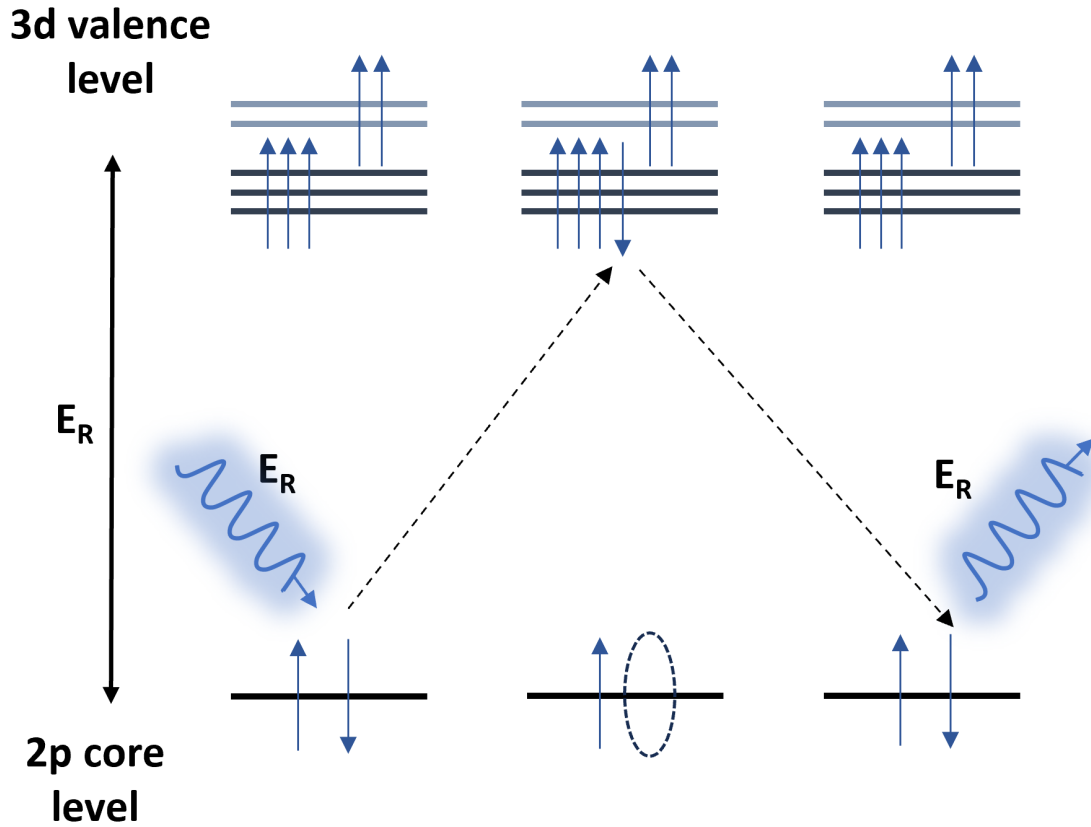


Figure 2.9: Schematic of resonant elastic x-ray scattering for a Fe^{3+} ion. An incoming X-ray photon with energy E_R is absorbed by a core 2p electron. The electron is virtually excited to the 3d orbital and then re-emits a photon of the same energy E_R . This mechanism is entirely separate from scattering and enhances measured X-ray intensity from the resonant orbital state by up to an order of magnitude.

established in 1987, demonstrating a spin-dependent absorption effect in Fe [46]. The XMCD principle is typically explored in absorption experiments, but Chapter 5 shows how an XMCD experiment in scattering geometry can yield unique information about magnetically ordered domains.

Chapter 3

Understanding Nanoscale Cause of Performance Deterioration of Thick-Cathode Batteries Using Coherent X-rays.

3.1 Abstract

Thick electrode batteries can theoretically achieve higher energy density, but their performance has been unable to keep up with the stringent requirements of many use cases. Dry cathode fabrication has shown promise in making thicker cathodes feasible at lower charge rates, but many open questions on the cause of performance deterioration with thicker cathodes remain. In this work, we use coherent X-ray scattering to demonstrate

that the dry fabrication process results in a more homogeneous electrochemical performance in 120 μm thick cathode batteries compared to conventional slurry-based cells at a C/10 charging rate. We further find that at a C/3 charging rate, individual cathode particles perform better the closer they are to the separator. This result is confirmed via modeling, which revealed that the local Li^+ flux follows a similar gradient and plays a key role in single-particle electrochemical performance.

3.2 Introduction

With the increasing demand for long-range electric vehicles, cutting-edge lithium-ion battery technology has become a critical bottleneck. Improvements in energy density are unable to keep up with tightening requirements around weight, size, capacity, and cycle life. Increasing active material loading and electrode thickness is a promising avenue to improve energy density, however using electrodes thicker than 70 μm results in degradation in electrochemical performance [47, 48]. To design an optimal thick electrode, a detailed understanding of why this performance loss occurs is necessary. It is well known that both ionic and electronic conductivity are critical factors for electrochemical performance in thick electrodes. The porosity, tortuosity, and conductive material distribution in thick electrodes vary significantly along the depth direction, which largely determines the overall electrode conductivity [49]. This variation indicates some diversity in the behavior of nanoparticles at different locations in the thick electrode. To address these issues, a novel solvent-free cathode coating method has the potential to solve the issues around thicker cathodes, but

the difference in homogeneity compared to traditional slurry methods remains an open question [50].

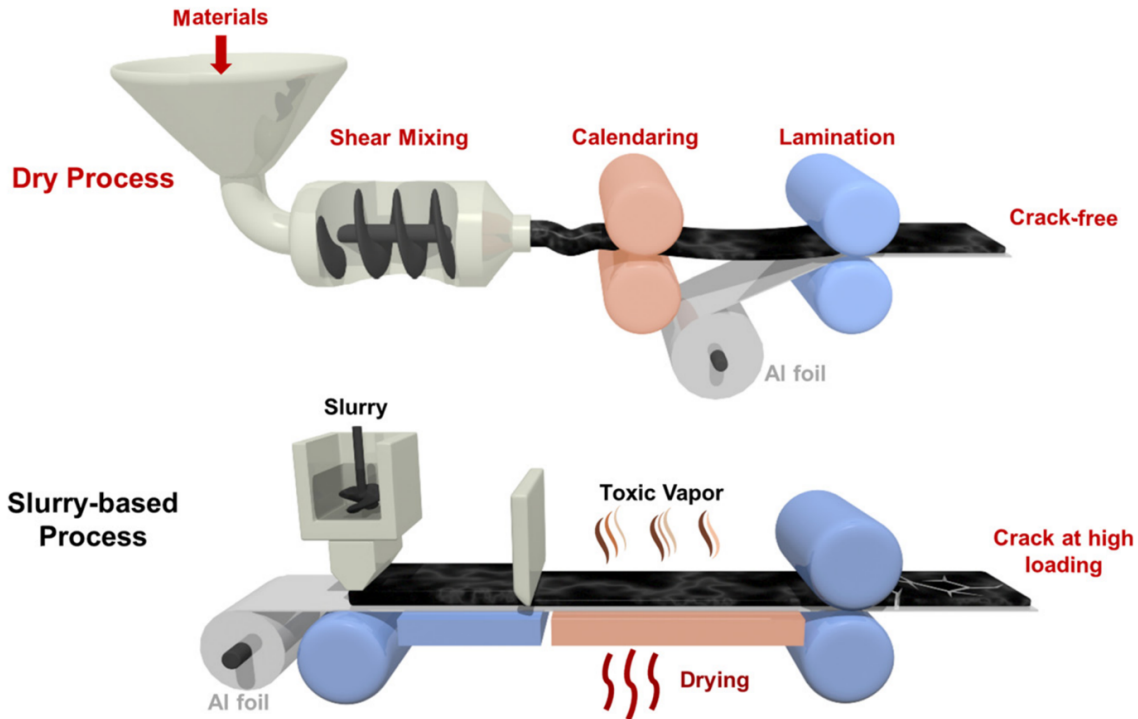


Figure 3.1: Comparison of dry and slurry-based electrode fabrication. Adapted from [3].

One important metric of a battery’s theoretical maximum energy density is the Active Material Ratio (AMR). In the cathode context, it is defined as the mass ratio of energy-storing material divided by the total mass of the cathode, which includes organic binder and carbon fibers. We observed that the electrochemical performance of a $120\text{ }\mu\text{m}$ cathode slurry-based cell significantly deteriorates when the AMR is increased beyond 93%. In contrast, using the novel dry approach, electrochemical performance remains consistent up to 97% AMR. Fig. 3.2 shows voltage curves of slurry and dry cells with AMR ranging

from 93% to 97% as a function of Li content, which is directly related to a cell's capacity. In the slurry case, we observe an increase in hysteresis and a decrease in capacity, as well as kinks in the voltage curve with increasing AMR. In contrast, the dry cells show consistent electrochemical performance up to 97% AMR.

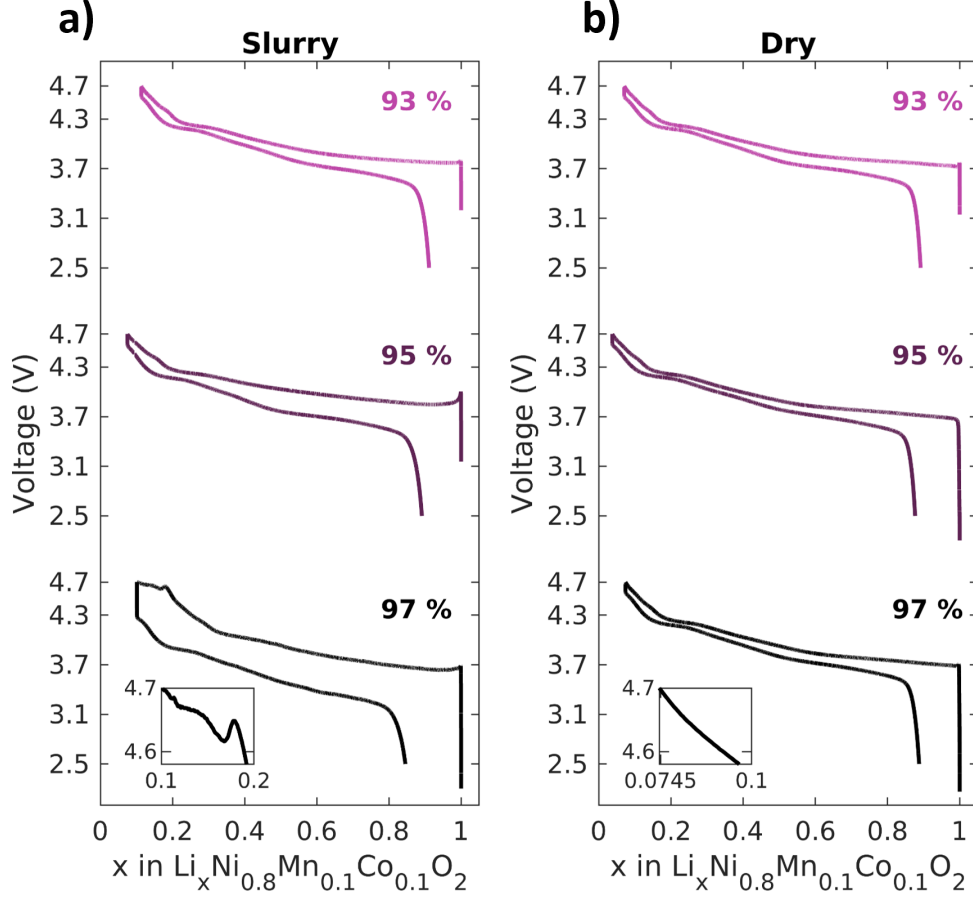


Figure 3.2: Voltage curves of cells using a slurry (a) and dry (b) cathode fabrication method, with an active material ratio of 93%, 95%, and 97%. For 97%, the insets show the curves near peak voltage.

In this work, we investigate the interplay between cathode preparation methods, variability in single-particle electrochemical performance, and its dependence on particle depth within the electrode. We use a focused synchrotron X-ray beam to track the lattice

parameter evolution of individual cathode primary particles in operando conditions. Our study focuses on $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) cells that use a 120 μm thick cathode during C/10 and C/3 charge-discharge cycles.

We first compare the homogeneity of cells prepared using the novel dry manufacturing method against those prepared using a conventional solvent-assisted slurry approach. We report that cathode primary particles in dry cells undergo delithiation more uniformly when compared to slurry cells, where we observed a fraction of the particles exhibit a significant delay in their phase transition. We also observe a sharper change of the lattice parameter with increasing voltage for the dry case, which further points to a more uniform electrochemical process.

We also employed a novel experimental approach to determine the depth within the cathode of individual primary particles, while simultaneously tracking how their lattice parameter evolves during a C/3 charge-discharge cycle. We observed a clear trend between particle depth and electrochemical performance - the closer a particle was to the separator, the better it performed. Our results were verified via modeling, which revealed that the higher Li^+ flux closer to the separator can explain this trend. Overall, this study reveals important details about the reasons behind the performance degradation of thick cathode batteries and will guide the future development of more energy-dense batteries.

3.3 Experiment

Coin cells were assembled in the glove box with moisture control ($\text{H}_2\text{O} < 0.5$ ppm), using a casting with a 5mm opening sealed with kapton film to allow X-rays to pass through [29]. $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}$ (NCM811) was used as the cathode active material, while Li metal was used as the counter electrode. The mass ratio of NCM811: PTFE binder: vapor-grown carbon fibers (VGCF) is 90:5:5. Between the positive electrode and Li metal, a Celgard separator is used to prevent direct contact between two electrodes. After placing cathode electrodes, separator, and Li metal in order and adding electrolyte (1M LiPF_6 in EC: EMC = 3:7 wt%), the cells were closed and sealed using a crimping machine. For voltage cycling, a charging rate of 1C is defined as 180 mA/g. All the electrochemical testing was carried out at room temperature using a MACCOR Cycler System.

The operando X-ray experiments were performed at Argonne National Laboratory’s Advanced Photon Source, beamline 34-ID-C. Coin cells were placed inside a 3D-printed coin cell holder and mounted at the experimental hutch. We used a coherent 11.5 keV X-ray beam focused to several microns and focused our study on the (003) NMC811 Bragg reflection. Our experimental setup allowed us to measure Bragg peaks from multiple individual cathode primary particles at different parts of the (003) Debye-Scherrer ring on a single CCD detector image. Furthermore, we used a Si wafer as a wedge placed immediately downstream from the sample to determine the depth of individual NMC811 primary particles (Fig. 3.3).

As Fig. 3.3 illustrates, the wedge will selectively cut off X-rays that scattered from

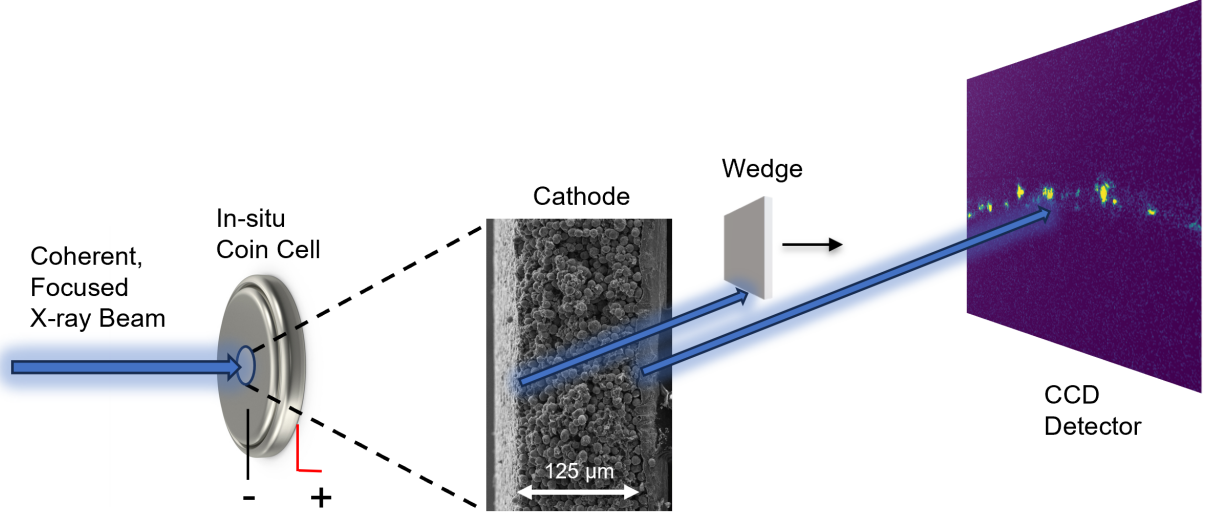


Figure 3.3: A schematic of the experimental setup. A focused, coherent X-ray beam is incident on a coin cell as it is being charged/discharged. X-rays scatter off individual cathode primary particles that match the (003) Bragg condition. A motorized wedge downstream from the cell cuts off scattered X-rays for some particles depending on their position, allowing us to measure the depth of individual particles within the cathode.

farther upstream in the cathode, while allowing X-rays from further downstream to reach the detector. The exact depth for which this crossover occurs depends on its position. As the wedge is scanned in the downstream direction, we can track the exact point at which the intensity of each Bragg peak drops off due to this effect. This drop-off is then fitted with a piecewise function of the form:

$$I(x) = \begin{cases} A + m(x - x_0) + c & \text{if } x < x_0 \\ A \exp((x - x_0)/\sigma) + c & \text{if } x \geq x_0 \end{cases} \quad (3.1)$$

This is a linear function up until the crossover point x_0 , and an exponential decay after that point, defined in a way to maintain continuity across x_0 . This form was chosen

since once the wedge begins to cut off the beam, it will cause an exponential drop in intensity according to the Beer-Lambert law. The fitted value of x_0 is then directly related to the depth of the scattering particle for a particular Bragg peak. Fig. 3.4 shows an example of wedge scans and corresponding fits for two nanoparticles.

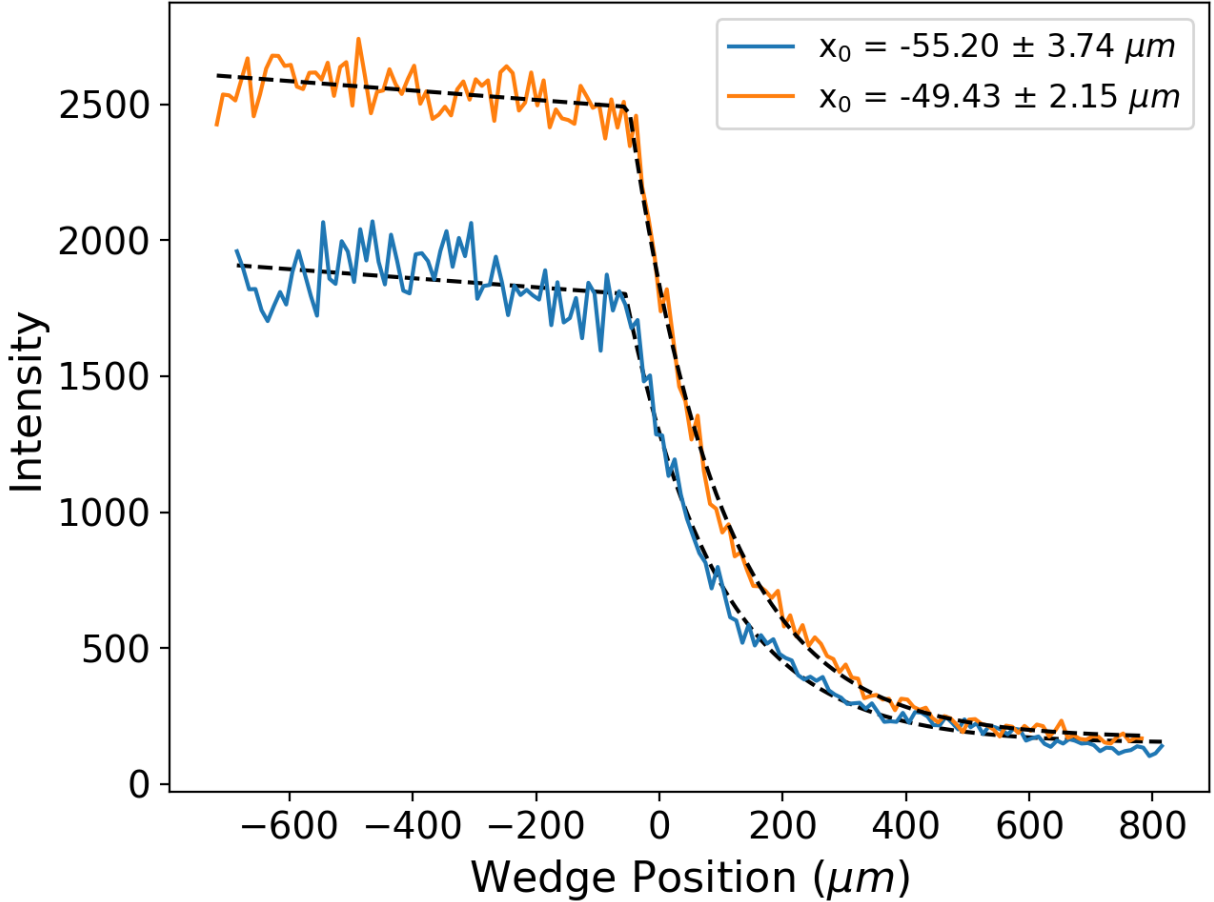


Figure 3.4: Example wedge scans show how the intensity of two separate Bragg peaks suddenly decreases as the wedge enters the path of the scattered X-ray beam. The fits are used to determine the cutoff point, from which we can extract the scattering particle's depth.

To extract the depth from the x_0 value, there is an additional important step. With our setup, the wedge is only sensitive to the scattering angle along the "vertical" direction

as illustrated in Fig. 3.3. In reality, scattering happens along a cone, and each Bragg peak has a total 2θ scattering angle that can be separated into a horizontal component δ and a vertical component γ . The schematic in Fig. 3.5 demonstrates a scenario in which the wedge just begins to block scattered X-rays from two particles at different depths simultaneously due to a difference in their horizontal scattering angle. To correctly account for this effect, the wedge cutoff position for each Bragg peak measured needs to be offset by:

$$dx = x \frac{\sin(\gamma_2 - \gamma_1)}{\sin(\gamma_1)} \quad (3.2)$$

where x is the distance from the sample to the wedge, γ_1 is the horizontal scattering angle of particle 1, and γ_2 is the horizontal scattering angle of a chosen reference particle. Finally, it is important to note that our approach has no explicit reference point for what wedge cutoff position corresponds to what depth. However, by measuring sufficiently many nanoparticles we obtained values with a range of $106 \mu m$, the mean of which can serve as a fairly precise reference point for the center of the cathode.

The depth determination adds a new dimension of data to this experiment which can provide unique insights into the inner workings of cathode nanoparticles, and how their performance varies depending on where they are located within the electrode. In principle, it is possible to determine the depth of a nanoparticle without the use of a wedge, by only relying on the alignment of the center of rotation [51]. However, the approach described in [51] is limited to a single particle at a time, and is therefore more suitable

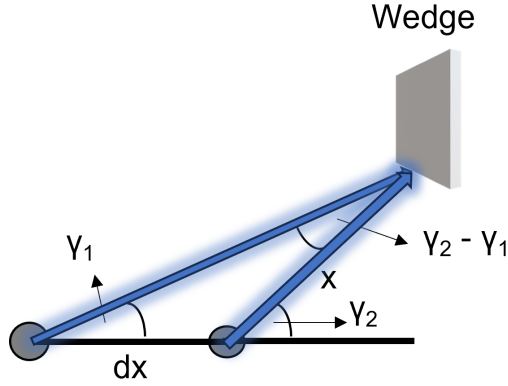


Figure 3.5: Schematic showing the role of the horizontal scattering angle γ in correctly determining the depth of a nanoparticle. A difference in γ can cause scattered X-rays from particles at different depths to be cut off at the same wedge position. To correct for this, an offset is applied to each particle depth based on the observed horizontal scattering angle relative to a reference particle.

for single-particle Coherent Diffractive Imaging studies. In this work, we aimed to track multiple nanoparticles in parallel, and our depth profiling approach proved faster and more reliable.

3.4 Results

Our first goal was to use our experimental setup to study how the NMC811 cathode material responds to charging and discharging. It is well established that the c lattice parameter of NMC811 nanoparticles shows a slow increase followed by a sudden decrease during charging [52]. This evolution is caused by Li ions diffusing away from the lattice, and therefore the lattice parameter can be an indirect measure of the lithiation state of a particular nanoparticle. We tracked the evolution of multiple cathode nanoparticles during a C/10 charge/discharge cycle based on the shifting of their (003) Bragg peaks. Fig. 3.6

contains example detector images showing how several Bragg peaks evolve with voltage for a dry cell. In parallel to the change in lattice parameter, the Bragg peaks broaden and become more diffuse, indicating that the lattice is becoming more strained and disordered.

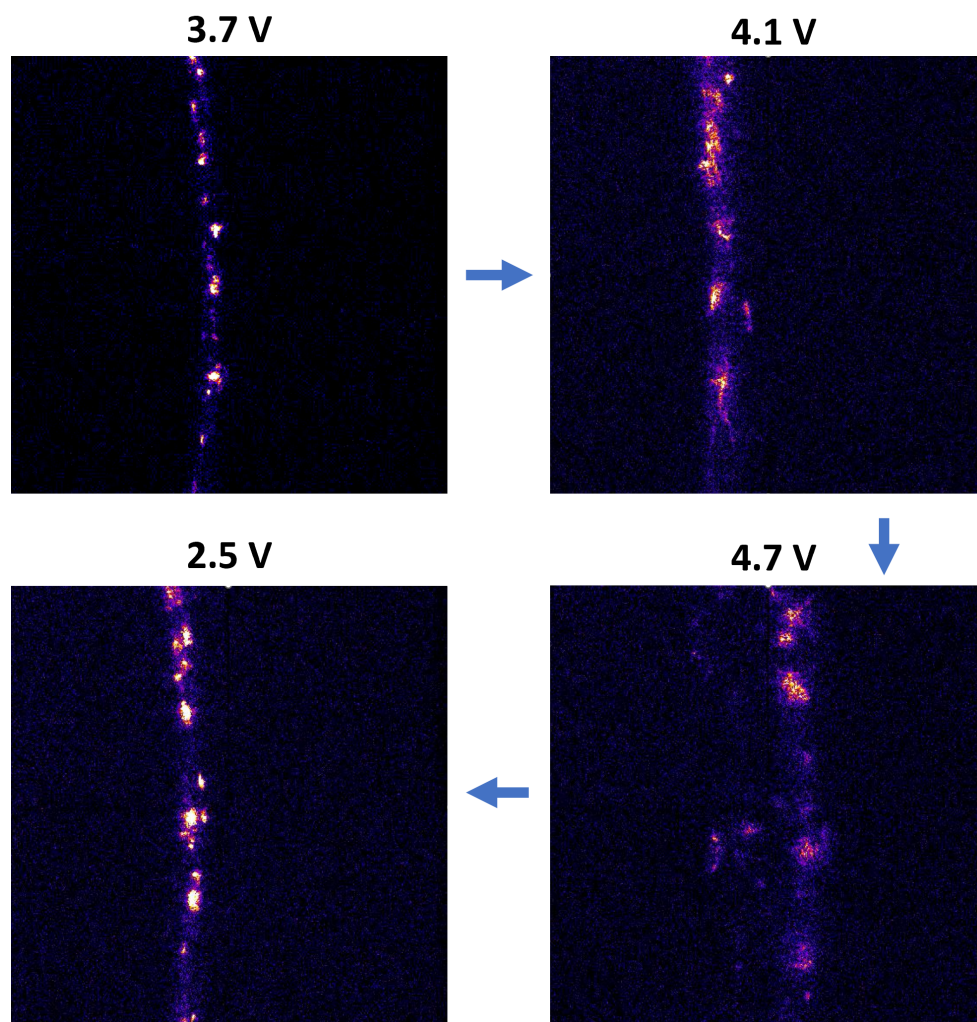


Figure 3.6: Example detector images of a dry cell at different voltages during a C/10 charge-discharge cycle.

We observed a significant delay in the phase transition of some cathode nanoparticles of the slurry-based cell. In contrast, the phase evolution of NMC811 in a dry cell showed

a more homogeneous response (Fig. 3.7). This observation serves as an experimental confirmation that the slurry approach leads to significant inhomogeneity in the electrochemical performance of individual cathode particles. Our results demonstrate that the dry electrode fabrication approach leads to superior homogeneity, which can explain the observed electrochemical improvement at slower C/10 charge/discharge rates.

At a faster C/3 charge rate, the dry thick-cathode cell also exhibited increasing inhomogeneity in the response of individual particles to charging. We tracked multiple particles during a C/3 charge-discharge cycle and determined their depth within the cathode using our novel approach. We define a single-particle electrochemical performance score as the ratio of average measured X-ray intensity in the region in 2D lattice parameter - voltage space where the phase transition is expected to occur, divided by the X-ray intensity measured in a region where a delay in the phase transition would show high intensity. Unlike macroscopic tests and probes, our unique experimental data allowed us to examine how an individual particle's electrochemical performance is dependent on its depth within the cathode.

We report a clear trend relating the electrochemical performance of individual nanoparticles to their depth. Our results show that the closer a particle is to the current collector, the worse it performs electrochemically. In contrast, particles closer to the separator exhibit a more uniform phase transition at the expected voltage, signifying consistent electrochemical performance. This result provides a unique experimental verification of

the importance of the local morphology and ionic conductivity within the cathode on the performance of individual NMC811 primary particles.

This trend was further explored via modeling. A 120 μm positive electrode was stochastically generated with NMC811 particles and conductive fibers as described in [53]. Then, using the open-source toolbox Iso2Mesh, a 3D mesh was generated from the simulated electrode, and an electrochemical simulation was set up. The simulation considered the same parameters as our experiment - C/3 charge up to 4.7V, starting from a fully lithiated electrode. A matching trend was observed between the state of charge of individual model particles and their distance from the separator. Furthermore, the Li^+ flux within the model cell was found to correlate to this trend, suggesting that a difference in Li^+ flux can explain the depth dependence of cathode performance that we observed experimentally. Fig. 3.8 summarizes this result.

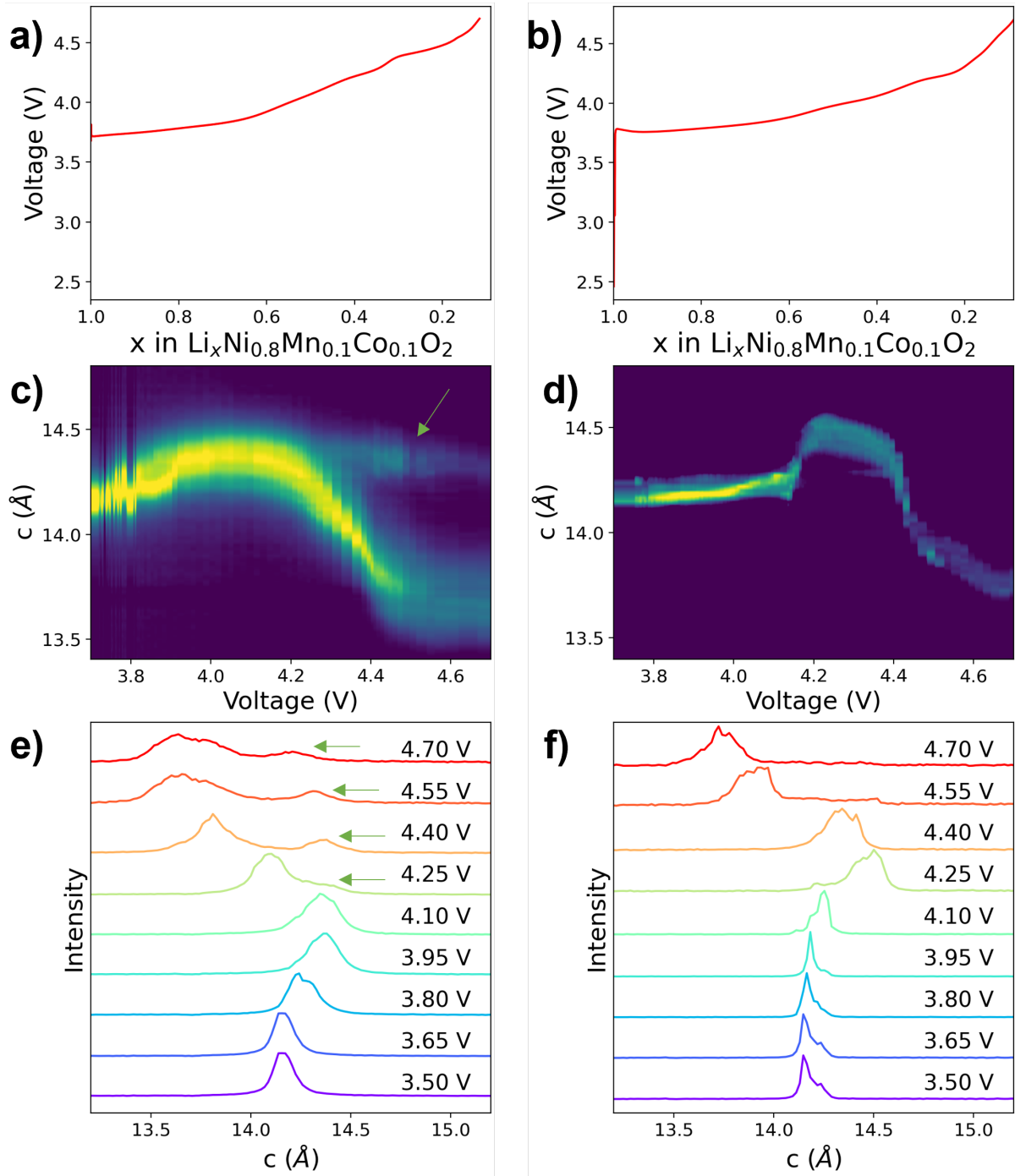


Figure 3.7: Voltage curves for the slurry (a) and dry (b) NMC811 electrode operando cells. Synchrotron X-ray Intensity maps of the evolution of the c lattice parameter as a function of voltage during C/10 charging, for slurry (c) and dry (d) NMC811 cathode. Intensity vs. c lattice parameter curves at different voltages (vertical cuts across intensity maps), for slurry (e) and dry (f) electrodes. The arrows emphasize the delayed phase transition observed in the slurry electrode above 4.2 V.

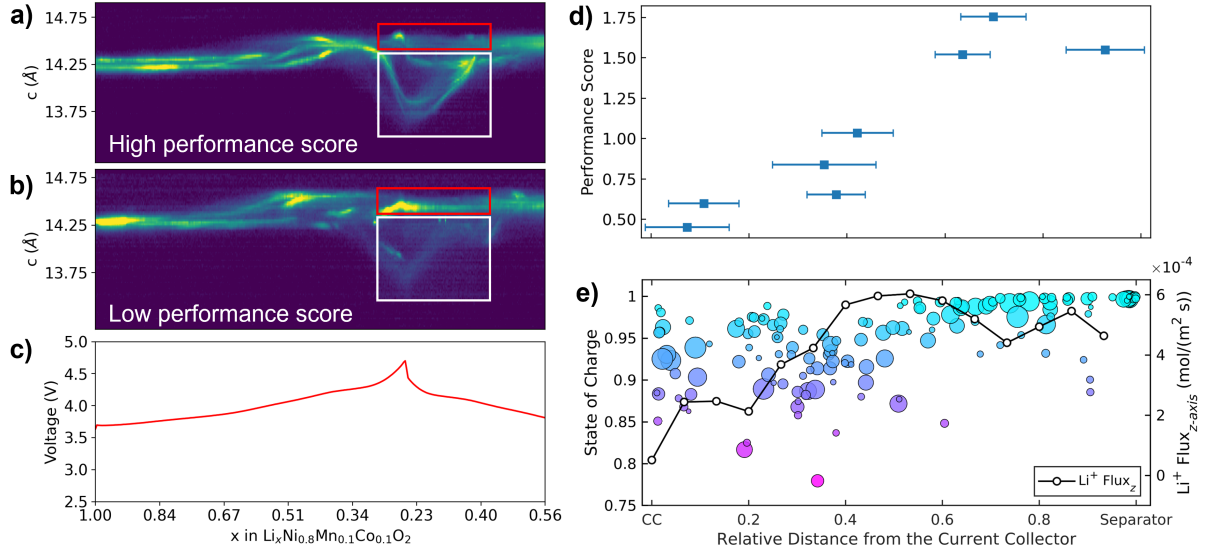


Figure 3.8: Representative examples of intensity maps showing a high-performance score (a) and low-performance score (b) cathode primary particle during C/3 cycling. In these maps, the performance score is defined as the ratio of intensity inside the white box (where the c lattice parameter is expected to decrease and then increase) and the intensity inside the red box, where the intensity is expected to be low. (c) shows the voltage curve for the cycled cell. Single-particle performance score (d), as well as state of charge and Li flux (e) as a function of distance from the current collector.

3.5 Conclusion

In this work, we present a synchrotron X-ray experiment to track the lattice parameter evolution of individual NMC811 cathode nanoparticles during operando cycling. We further demonstrate a novel approach to determine the depth of the measured nanoparticles. We focus our study on understanding the nanoscale causes of performance deterioration when using thicker, 120 μm cathode electrodes, as well as the observed differences between wet and dry cathode processing methods. We first show that the electrochemical performance improvement of the dry cathode at C/10 charge rate can be attributed to a more homogeneous across cathode particles compared to the slurry-based cathode (Fig. 3.7). This result signifies that the dry electrode manufacturing method is not only more cost-effective, mechanically robust, and environmentally friendly, but can also lead to better-performing batteries.

We further find that at C/3 charge rate, dry cathode nanoparticles closer to the separator exhibit better electrochemical performance compared to those closer to the current collector (Fig. 3.8). Using modeling, this trend is attributed to higher Li^+ flux present on the separator side. Our findings can guide future efforts towards more energy-dense, thick-cathode batteries that can sustain consistent performance at high charge/discharge rates demanded by electric vehicles. The two main issues that get in the way of the increased energy density promised by thick-cathode batteries are electrode cracking and limited penetration depth for ion diffusion within the electrode [54, 55]. Dry cathode shows significant promise to overcome the cracking issue, while design optimizations that allow

more uniform Li^+ flux throughout the cathode can address the electrochemical limitations.

3.6 Acknowledgements

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Chapter 3, in full, is currently being prepared for submission for publication of the material “Understanding Nanoscale Cause of Performance Deterioration of Thick-Cathode Batteries Using Coherent X-rays.”, Boyan K. Stoychev, Minghao Zhang, Weiliang Yao, Mehdi Chouchane, Anatoly Shabalin, Devin Cela, Rourav Basak, Mingze Wan, Wonsuk Cha, Ross J. Harder, Oleg G. Shpyrko, Y. Shirley Meng.

Chapter 4

Role of Structure and Nanoscale

Defects in Enhancing Ionic

Conductivity of Na-Y-Zr-Cl Solid

Electrolyte

4.1 Abstract

Despite their promise of increased safety and energy density, all-solid-state batteries are yet to reach the performance capabilities and stability of conventional Li-ion cells. A novel Na-Y-Zr-Cl solid electrolyte is a promising candidate, with a near-liquid ionic conductivity for a 75:25 ratio of Zr to Y. We use Bragg coherent diffractive imaging to study the strain and lattice defects in four Na-Y-Zr-Cl stoichiometries. By reconstructing

multiple nanocrystals in 3D, we find an abundance of anti-phase domains and dislocations in the $P\bar{3}$ phase. An emergent $P2_1/n$ phase with significantly fewer defects was observed for the 75% and 100% Zr-substituted samples. Our results show that lattice spacing, strain, and defect density may play a key role in the ionic conductivity of these materials.

4.2 Introduction

All-solid-state batteries (ASSBs) are a promising alternative to conventional liquid-electrolyte Li-ion systems, with the potential for significantly improved safety, energy density, and cost. These improvements could enable more widespread adoption of electric vehicles and trucks, an important step towards a carbon-neutral future. Na-based ASSBs are a particularly appealing alternative thanks to the global abundance of sodium when compared to lithium [56]. Oxide and sulfide solid electrolytes have exhibited ionic conductivity on par with liquid electrolytes, but are plagued by issues around incompatibility with high-voltage cathode materials [57, 58, 59, 60, 61].

Solid Electrolytes (SEs) require high ionic and low electronic conductivity, as well as electro-chemical and mechanical compatibility with electrodes. While significant progress has been made in the former direction, the stability of interfaces with common electrodes remains a critical bottleneck for practical applications. Recently, it was discovered that substituting Y^{3+} in Na_3YCl_6 with Zr^{4+} to form a $Na_{3-x}Y_{1-x}Zr_xCl_6$ (NYZC) enhances Na^+ conductivity by two orders of magnitude, while simultaneously preventing electrochemical decomposition when paired with a $NaCrO_2$ cathode (Fig. 4.1). A test cell utilizing this

substitution was able to cycle over 1000 times with an 89.3% capacity retention at 40 °C, the highest cycle life for a solid-state sodium-ion battery to date [4].

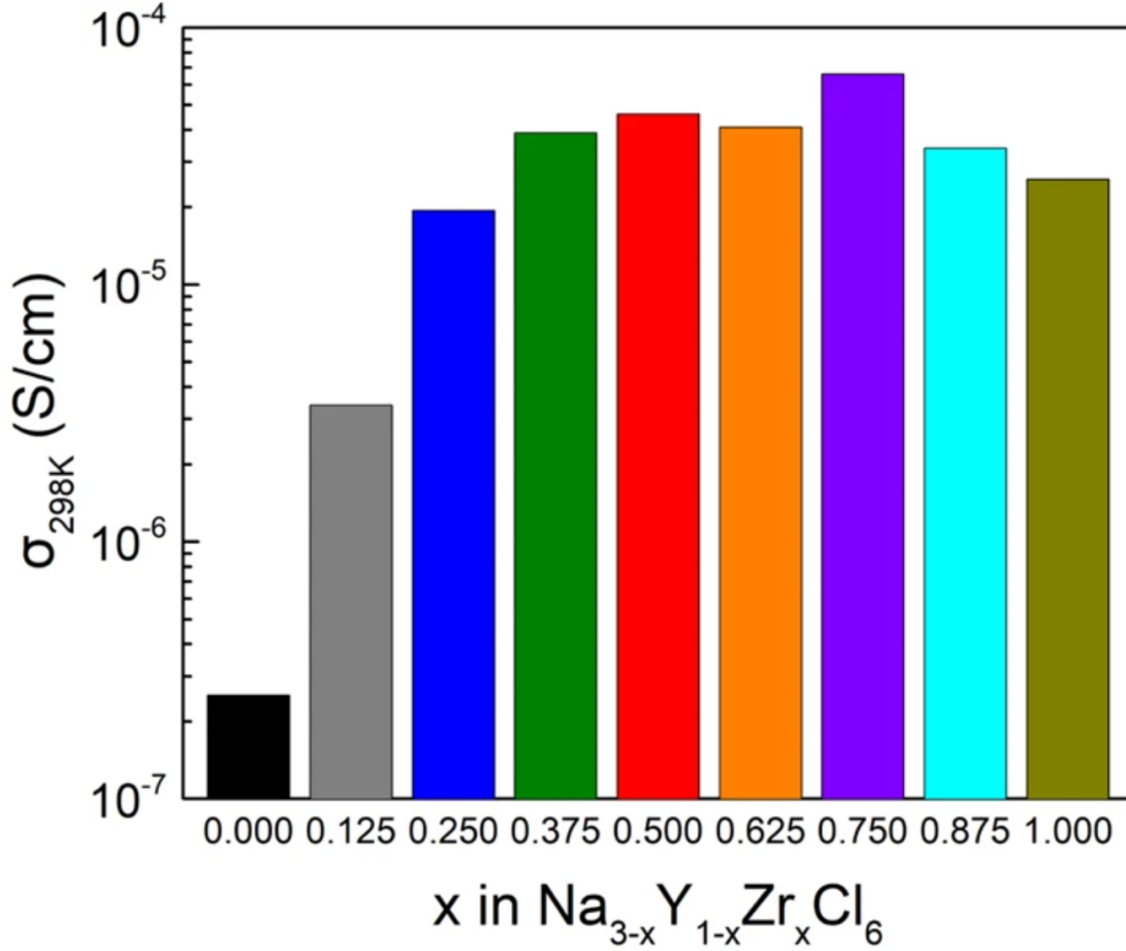


Figure 4.1: Ionic conductivity as a function of Zr doping in NYZC. Adapted from [4].

Given how little is known about the nanoscale structural properties of NYZC, we aimed to study the material on an individual nanoparticle level using Bragg Coherent Diffractive Imaging (BCDI). BCDI is an advanced synchrotron characterization technique that makes use of coherent X-rays to indirectly image the full depth of a nanocrystal in 3D via an iterative phase retrieval algorithm. By solving for the phase of the nanocrystal

in real space, we are able to measure the displacement field in 3D, which contains rich information about the types and abundance of lattice defects present in the material.

BCDI has played an important role in revealing a direct link between the nucleation of dislocations in battery cathode nanoparticles and voltage fade[31, 30]. Furthermore, discovering this link enabled a pathway to voltage recovery. More broadly, BCDI has been used to demonstrate the importance of lattice defects such as dislocations on the performance and longevity of battery materials. This leads us to believe that understanding the role and dynamics of defects in solid electrolytes could be the key to improved interface stability, which has the potential to make ASSBs commercially viable.

4.3 Experiment

The material synthesis precisely followed the approach in [4]. All fabrication processes were carried out within an Ar-filled glovebox (mBraun 200B, with H_2O ppm < 0.5 and O_2 ppm < 1). The precursors NaCl (> 99%, Sigma Aldrich) and YCl_3 (99.9%, Sigma Aldrich) were combined in stoichiometric amounts. They were hand-mixed in a mortar and pestle for 10 minutes. The resulting powder mixture was then placed in a 50 mL ZrO_2 ball mill jar (Retsch Emax) along with eleven 10-mm-diameter Y- ZrO_2 milling balls. The mixture underwent milling for 2 hours at 500 r.p.m. After milling, the material was extracted from the jars inside the glovebox, pelletized under a pressure of 370 MPa using a 13 mm pellet die, and loaded into a quartz tube. The tube was flame-sealed and heated in a box furnace (Lindberg Blue M) at 500 °C for 24 hours. To achieve material homogenization,

the heat-treated material was ball milled again for 4 hours using 88 5-mm-diameter Y-ZrO₂ milling balls. Subsequently, the material was extracted and stored in the glovebox before further testing. For the Zr substituted compounds, the same procedure was followed, but with the additional precursor ZrCl₄ (99.99%, Sigma Aldrich). The reagent ratios were adjusted to ensure stoichiometry.

The BCDI experiment presented here was performed at the 34-ID-C beamline of the Advanced Photon Source of Argonne National Laboratory. NYZC is highly air-sensitive, so the samples were handled inside an Argonne glovebox. NYZC powder was scratched onto double-sided tape, which was taped onto a washer, and that washer was sealed in an aluminum moisture-resistant bag inside the glovebox. This bag was then mounted using a coin-cell holder at the 34-ID-C beamline hutch. A total of 4 stoichiometries of Na_{3-x}Y_{1-x}Zr_xCl₆ were measured for $x = (0, 0.125, 0.75, 1)$. We will refer to these four stoichiometries as NYC, NYZC125, NYZC750, and NZC respectively throughout this work.

Each sample was then scanned across the beam with the CCD detector positioned on the (021) Bragg powder ring until a suitable Bragg peak was located. Once a Bragg peak with clearly visible fringes was seen, it was aligned and expanded on the detector by increasing detector distance (Fig. 4.3). Several rocking curve scans were performed on each measured nanocrystal, in order to map out the Bragg peak in 3D and ensure reproducibility. Each rocking curve scan was carefully optimized to ensure the entire 3D Bragg peak was covered, with a sufficiently small step size to ensure the oversampling of fringes. X-ray energy was set to 11.0 keV - even though beamline 34-ID-C is optimized for highest flux at 9 keV, we were able to obtain a better signal-to-noise ratio at 11 keV due

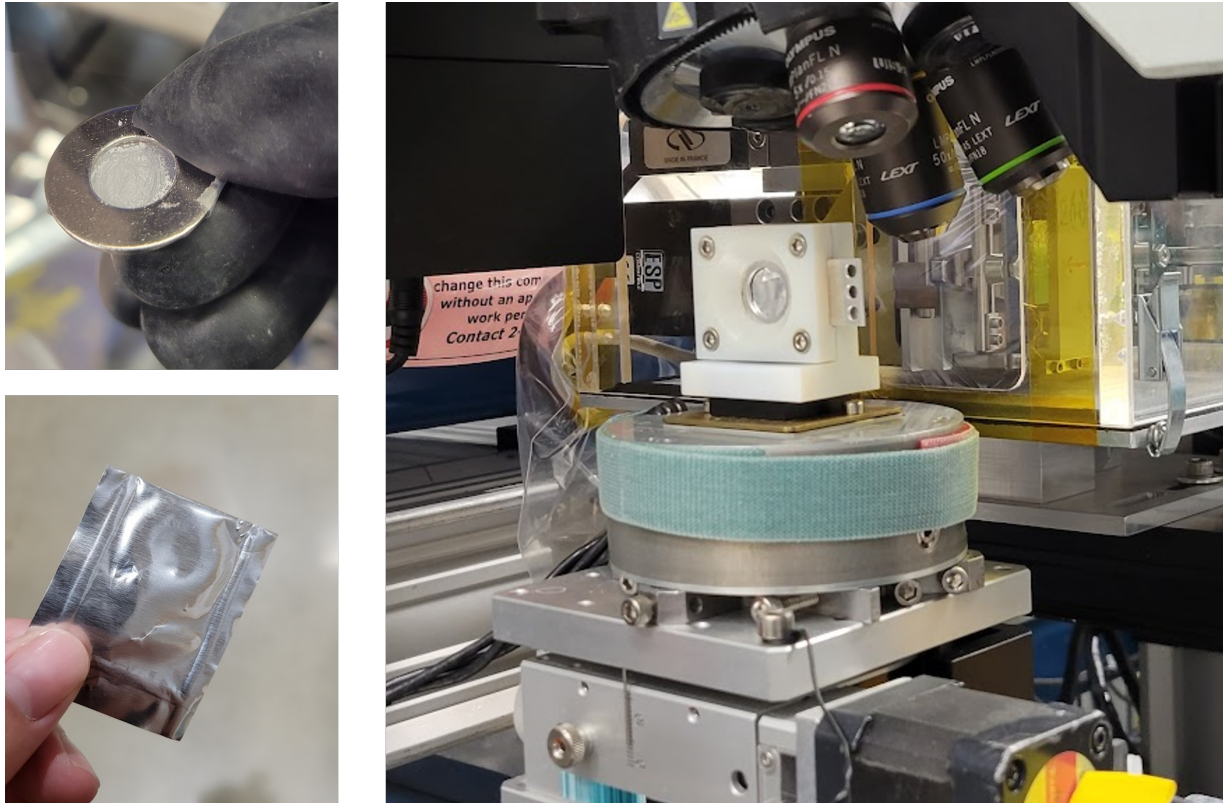


Figure 4.2: Photos of NYZC powder scratched onto tape inside a washer (top left), sealed in an aluminum bag (bottom left), and mounted at the experimental hutch (right).

to higher transmission through the sample and aluminum bag. Each chosen Bragg peak was measured 3 consecutive times, to ensure that the nanoparticle remains stable under X-ray irradiation and confirm the reproducibility of phase retrieval.

Our dataset consists of approximately 5 nanocrystals each for the 4 NYZC stoichiometries measured, for which we were able to produce robust real-space reconstructions via phase retrieval. For each of those, phase retrieval was performed using the Genetic Algorithm (GA) as implemented in the *cohere* Python package developed at Argonne National Lab’s Advanced Photon Source specifically for beamline 34-ID-C. A total of 5 generations of reconstructions were performed. Each generation consisted of the following

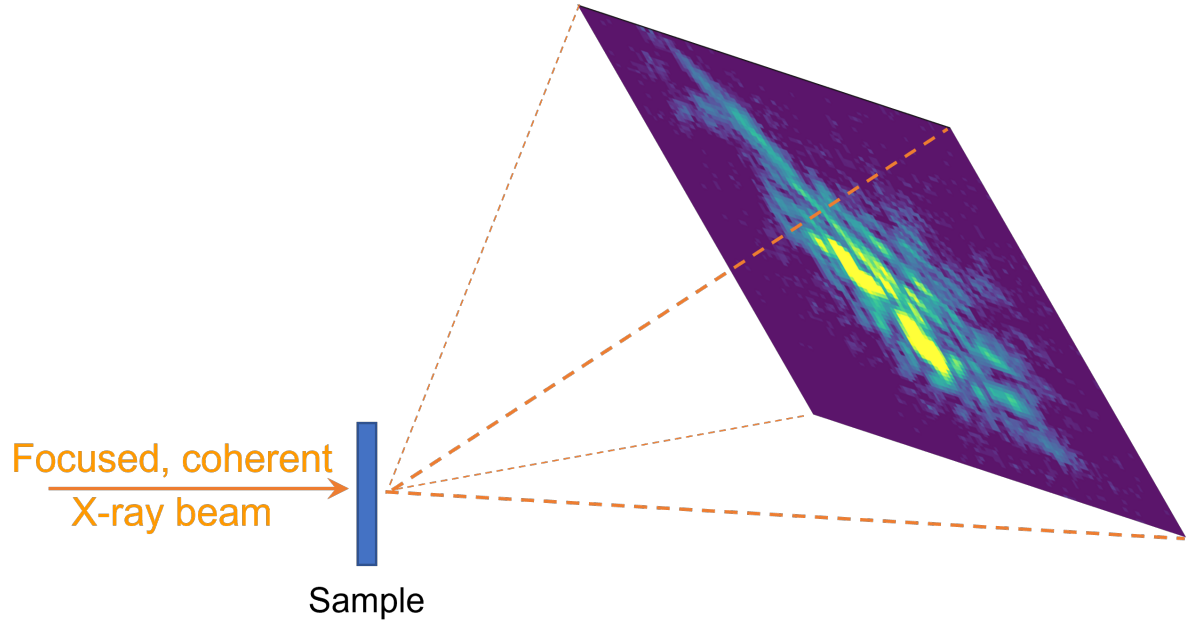


Figure 4.3: A schematic of the experimental setup.

algorithm sequence: 10 x [10 steps of Error Reduction (ER) + 90 steps of Hybrid Input Output (HIO)], with a final 10 steps of ER at the end. At the end of each generation, reconstruction quality was determined based on the pixel-by-pixel χ^2 error between the measured 3D reciprocal space amplitude and the predicted amplitude based on a Fourier Transform of the reconstruction (Fig. 4.4). The GA consisted of 20 initial reconstructions in parallel for the first generation, after which the 10 worst-scoring reconstructions were discarded. The remaining 10 reconstructions were used as a starting point for the next generation. Similarly, (2, 1, 1) of the worst reconstructions were discarded after the second, third, and fourth generation respectively, leaving us with the best 6 reconstructions as the output of the GA.

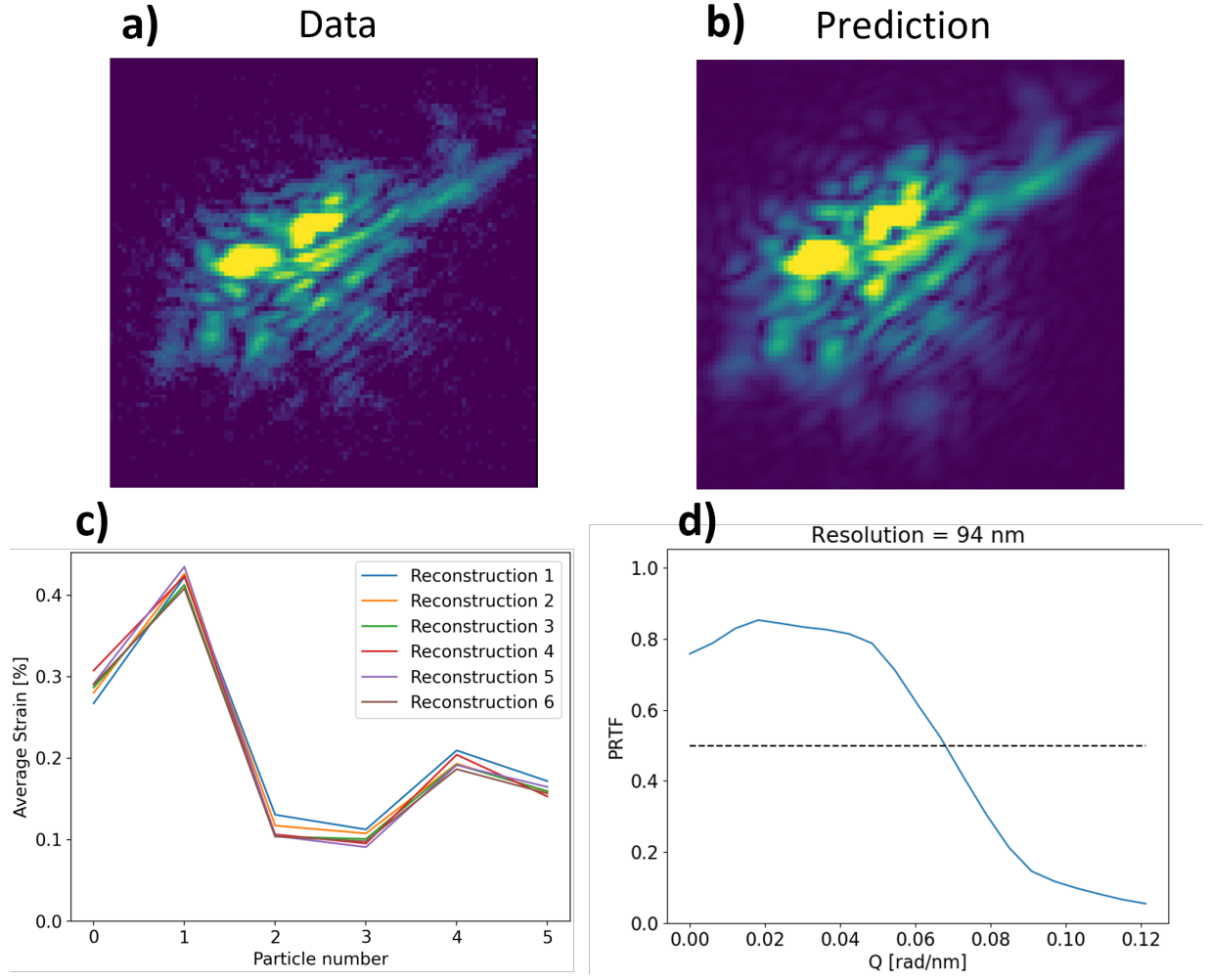


Figure 4.4: a): An example detector image representing a slice across the 3D Bragg peak of an NZC particle. b): Predicted detector image based on a slice of the amplitude of the Fourier Transform of the reconstructed real-space NZC particle. c): Average strain for each of the six final reconstructions of six NZC nanoparticles. d): Phase Retrieval Transfer Function (PRTF) for the same NZC particle.

4.4 Results

Many of our NYZC reconstructions exhibited a significant number of defects. The most obvious of these were anti-phase domains. Fig. 4.5 shows a representative example of

a reconstructed NYZC750 particle. The slices through the phase field show an abundance of anti-phase domains - the green and purple regions differ in phase by π , which corresponds to a displacement by half a unit cell along (021). Note that the value of the phase itself has no physical significance, but phase differences do. Note also that the color map is cyclical, since π and $-\pi$ represent the same displacement.

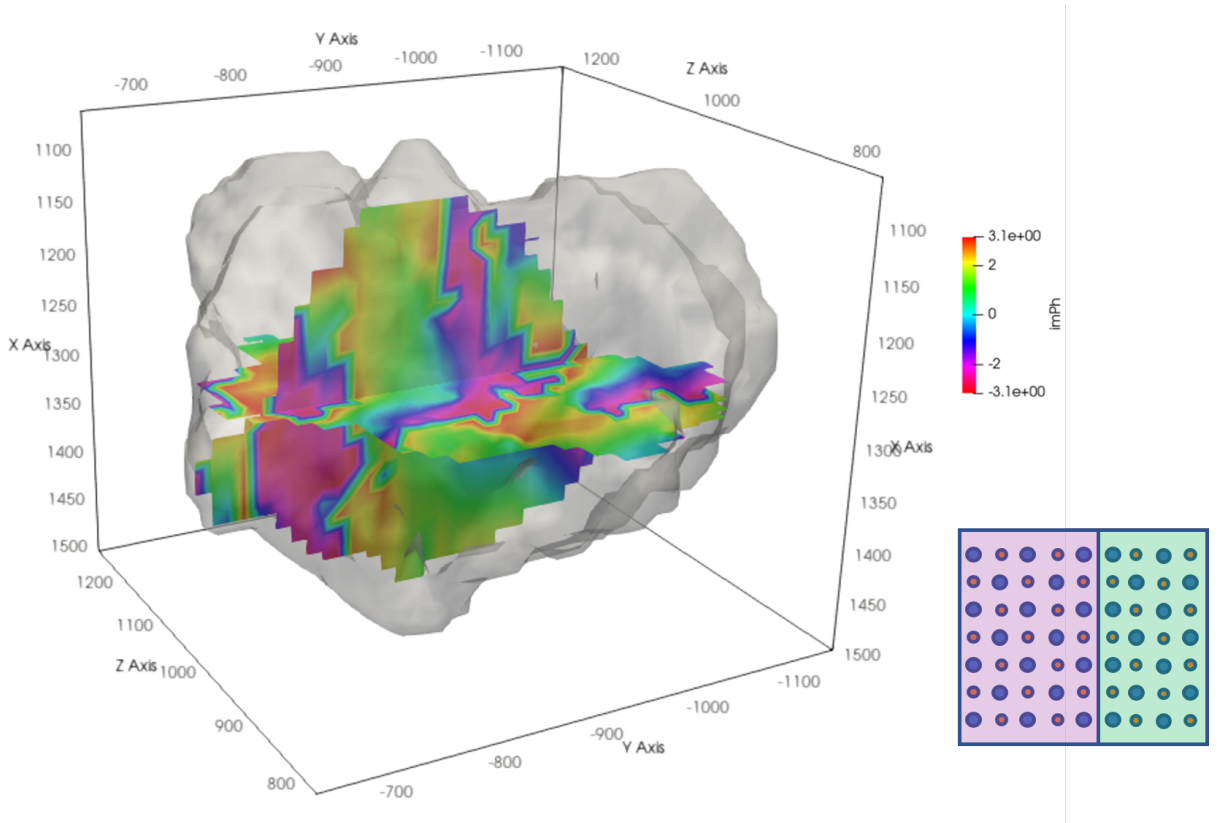


Figure 4.5: A reconstruction of a NYZC750 nanoparticle. The X, Y, and Z axes are in *nm*. The transparent isosurface is generated at 15% of the maximum electron density, and the intersecting planes are color-coded by phase. The green and purple regions differ in phase by π and represent anti-phase domains present in the nanoparticle. The sketch in the corner demonstrates how for a simple 2-site square lattice, skipping an atomic layer would shift the displacement field by half a unit cell, corresponding to a phase difference of π .

To quantify the defects present in the reconstructed NYZC nanocrystals, the first and second derivatives of the displacement field were calculated, adapting the approach from [62]. The gradient of the phase field, which is proportional to strain along (021), was calculated using:

$$F_x(a, b, c) = (1/h) \arg \left[e^{i\phi(a+h/2, b, c)} e^{-i\phi(a-h/2, b, c)} \right] \quad (4.1)$$

where $\phi(a, b, c)$ refers to the phase field at voxel (a,b,c). F_y and F_z were calculated analogously. This somewhat non-intuitive form of a discrete gradient avoids ambiguities that arise due to the periodicity of ϕ . A second set of gradients are then calculated in the same way, which helps to isolate defect locations. This gives a total of 9 components:

$$K_{x,w}(a, b, c) = \nabla F_x(a, b, c) \quad (4.2)$$

$$K_{y,w}(a, b, c) = \nabla F_y(a, b, c) \quad (4.3)$$

$$K_{z,w}(a, b, c) = \nabla F_z(a, b, c) \quad (4.4)$$

where $w = x, y, z$. These 9 components are combined into a single function as follows:

$$N(a, b, c) = \max_{a,b,c} \left[\left| \prod_w K_{x,w}(a, b, c) \right|, \left| \prod_w K_{y,w}(a, b, c) \right|, \left| \prod_w K_{z,w}(a, b, c) \right| \right] \quad (4.5)$$

Here, $\prod$ is the voxel-by-voxel product, and $\max_{a,b,c}$ selects the maximum value from

the 3 sets of K products for each voxel.

There is one final ambiguity related to N , caused by the fact that the phase field is set to 0 outside of the reconstructed crystal. Any abrupt change in phase across the crystal boundary would show up as a false defect in N , which has no physical meaning since the phase outside of the crystal is arbitrary and undefined. To circumvent this issue, a series of 100 phase offsets ranging from 0 to π were added to the phase field outside the crystal, and the N function was calculated for each of those offsets. Finally, the voxel-by-voxel minimum of these 100 N functions was used to quantify defects.

Fig. 4.6 illustrates the rich information that was extracted from our 3D NYZC reconstructions. The arrows point to defects that can be identified across all four fields. In the amplitude, they appear as low-amplitude regions corresponding to lower electron density or crystallinity. In the displacement field, those same locations exhibit a vortex around a singularity, which is a known signature of an edge dislocation [30]. The strain field shows a distinct change in strain across those locations, which would occur when an edge dislocation is present. The N field is effective at isolating the defect network found in the crystal. Single-particle defect density was computed based on the number of voxels where the N field as defined above was above a certain threshold, divided by the volume of each particle.

The computed strain and N fields for each reconstruction were used to calculate the average displacement, average strain, and defect density for each particle. These were

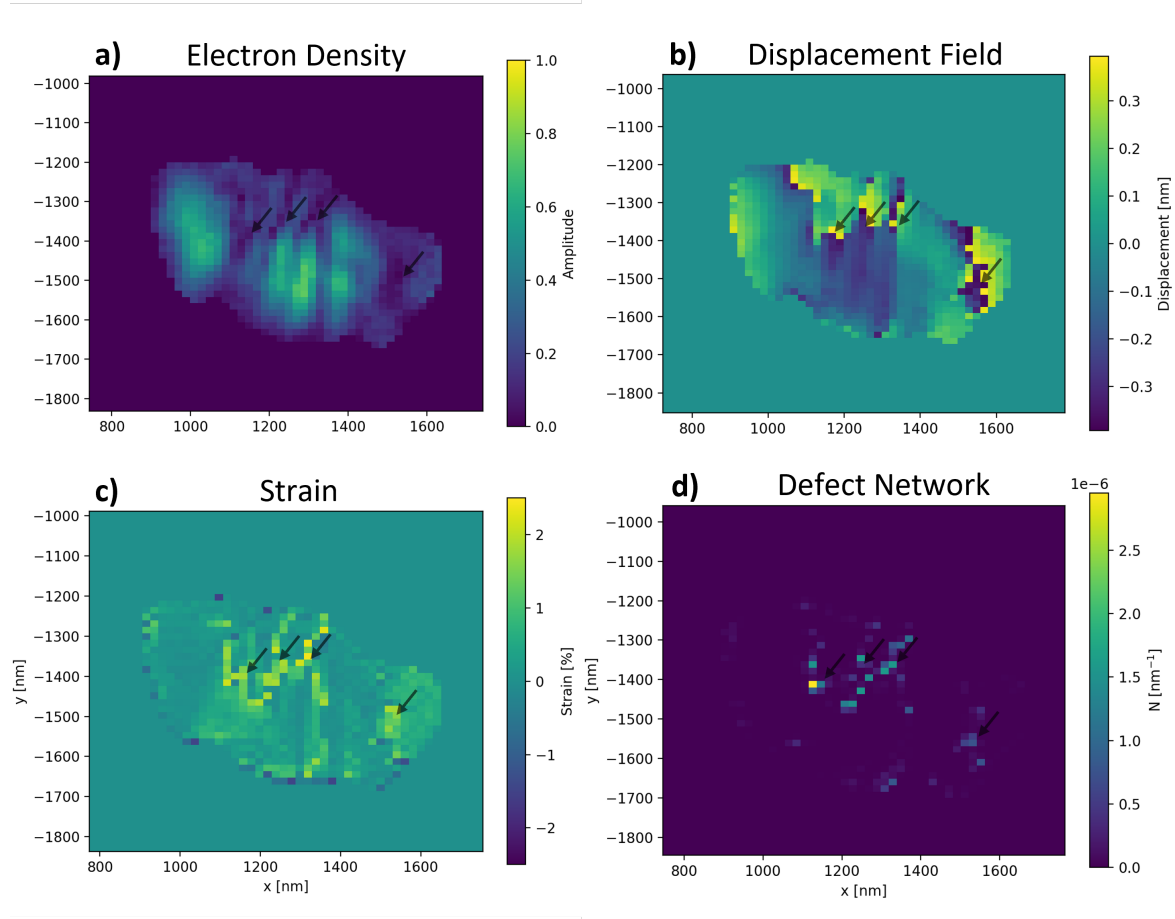


Figure 4.6: Slices shown through the amplitude (a), displacement field along (021) (b), strain (c), and the N function formed from second derivatives of displacement (d). The arrows point to defect networks that can be seen in all four fields.

then averaged for the 6 final reconstructions that the GA outputted for each particle, after ensuring the results for each reconstruction were consistent. For displacement and strain, the absolute value of the respective values was used since they can also be negative. Due to this, average displacement in a reconstruction can be thought of as a measure of anti-phase domain density

While our initial focus was on the (021) Bragg peak of the $P\bar{3}m1$ space group, we observed the emergence of two sets of peaks with slightly offset lattice spacing in our

NYZC750 and NZC samples. Le Bail refinement was used to determine that the peaks we observed are the $P2_1/n$ ($11\bar{2}$) and (111). We found that the particles in the $P2_1/n$ exhibit significantly lower defect density, suggesting that the emergent $P2_1/n$ phase for NYZC750 and NZC is more robust (Fig. 4.7). Excluding the emergent $P2_1/n$ phase, we also found that the (021) lattice spacing of the $P\bar{3}m1$ phase is somewhat correlated with the ionic conductivity for the four NYZC stoichiometries measured, although more data is needed to verify this claim. In particular, the slight lattice expansion of NYZC750 d-spacing increase may explain the enhanced ionic conductivity of that particular stoichiometry reported in [4].

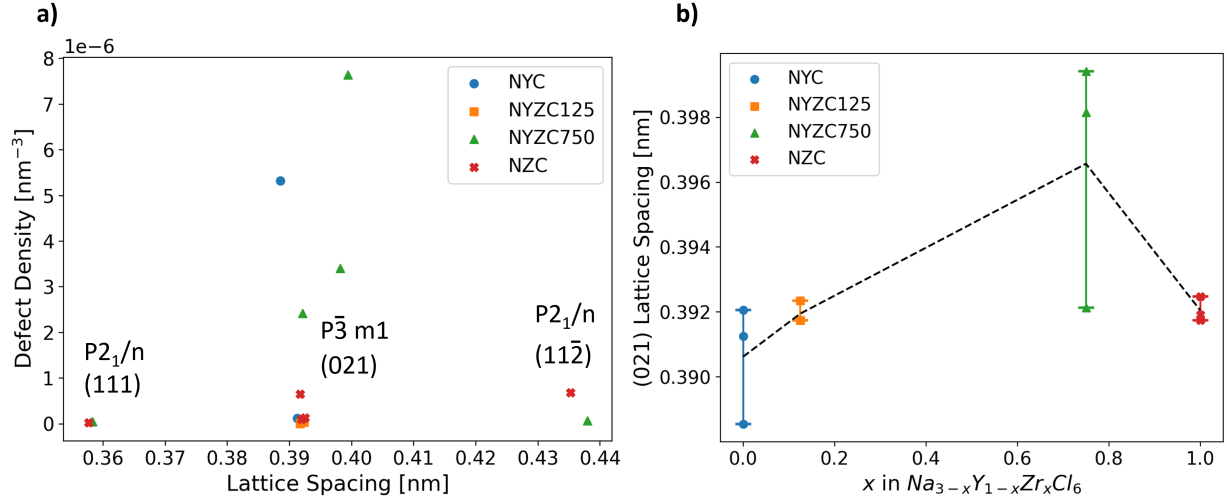


Figure 4.7: a): Defect density as a function of lattice spacing for each NYZC nanoparticle measured. The cluster of spacing values around 0.78nm corresponds to the $P\bar{3}m1$ phase of NYZC, while the other two lattice spacing values correspond to $P2_1/n$. b): Lattice spacing vs. Zr doping for all NYZC particles measured in the $P\bar{3}m1$ phase.

We found high variability in average displacement, strain, and defect density across different nanocrystals for the four NYZC stoichiometries, as shown in Fig. 4.8. Despite

this, it is worth noting that for NYZC125, NYZC750, and NZC, the trend across average displacement, strain, and defect density correlates to the ionic conductivity trend in reported in [4]. This suggests that the increased strain and defect density may play an important role in the observed ionic conductivity increase. NYC shows a departure from this trend, particularly when it comes to average displacement. This may be due to its smaller d-spacing when compared to NYZC750. We hypothesize that the combination of an increase in (021) d-spacing and higher levels of strain/defect density present in the $P\bar{3}m1$ phase of NYZC750 play a key role in its increased ionic conductivity compared to other NYZC stoichiometries.

We also observed that defect density found in a given particle has a strong dependence on its volume across the measured stoichiometries (Fig. 4.9). A fitting function of the form:

$$\rho(V) = \rho_0 + \left(\frac{a}{V}\right)^\beta \quad (4.6)$$

was used to fit the observed trend. The least-square best fit parameters were $\rho_0 = 1.10 \times 10^{-8} \text{ nm}^{-3}$, $a = 3.23 \times 10^6 \text{ nm}^{(3-3/\beta)}$, $\beta = 6.74$. It would be intuitive to think that defect density would scale with volume according to the surface-area-to-volume ratio:

$$A/V \propto 1/r = (1/V)^{1/3} \quad (4.7)$$

β was found to be over 20 times greater than $1/3$, which indicates that the ball-milling

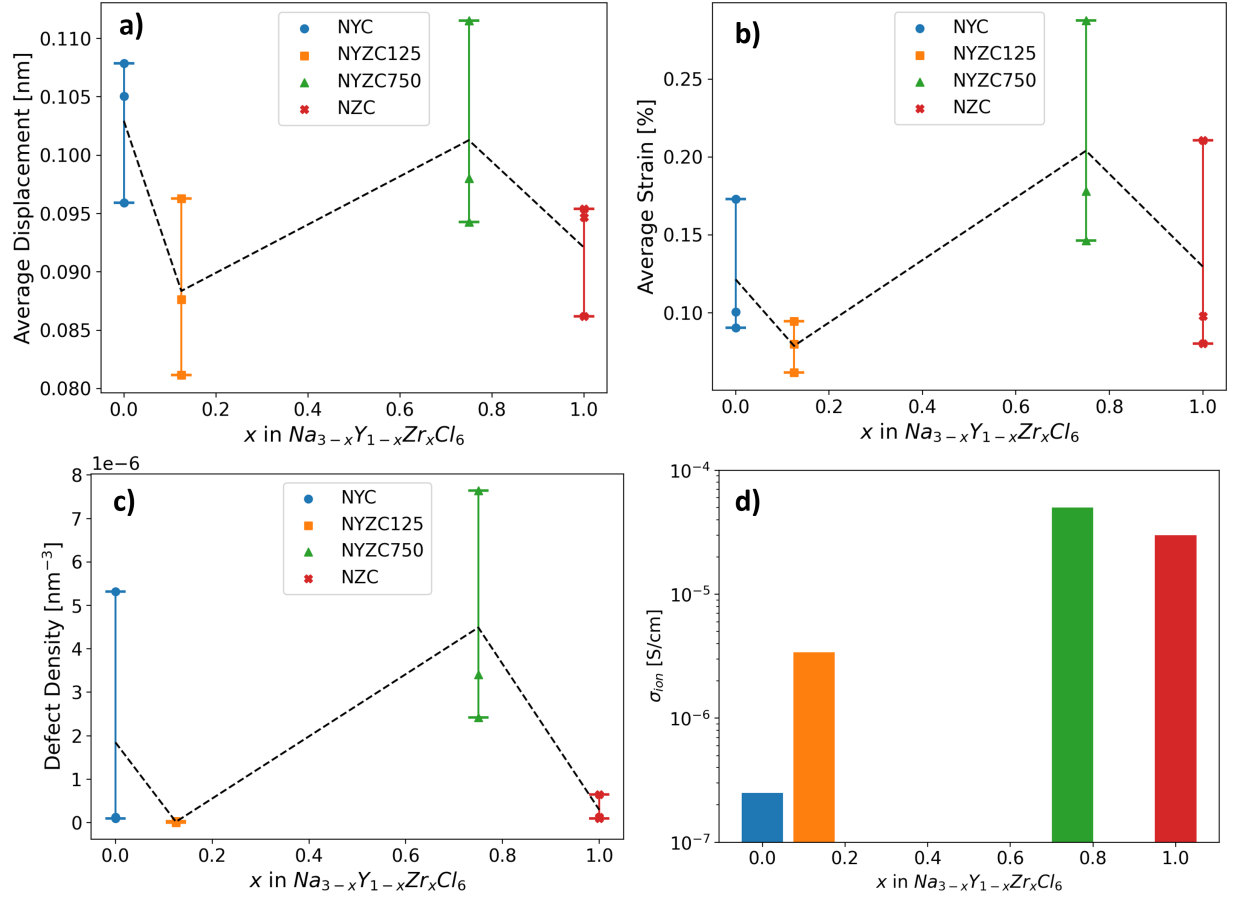


Figure 4.8: Average displacement (a), average strain (b), and defect density (c) as a function of Zr doping. Each point corresponds to an individual reconstructed NYZC nanoparticle. The black line shows the mean for each stoichiometry, while the error bars visualize the spread. d) shows the ionic conductivity reproduced from [4].

process introduces significant defects very quickly as the particle size is reduced.

We note that the NYZC750 and NZC particles we measured in the $\text{P2}_1/\text{n}$ phase (shown as black markers in Fig. 4.9) deviate significantly from the observed defect-density-vs-volume trend. Even at particle sizes below $2.3 \times 10^7 \text{ nm}^3$, the defect density remains near 0, which shows that the $\text{P2}_1/\text{n}$ structure is significantly more robust to ball-milling than the $\text{P}\bar{3} \text{ m1}$ phase for NYZC750 and NZC.

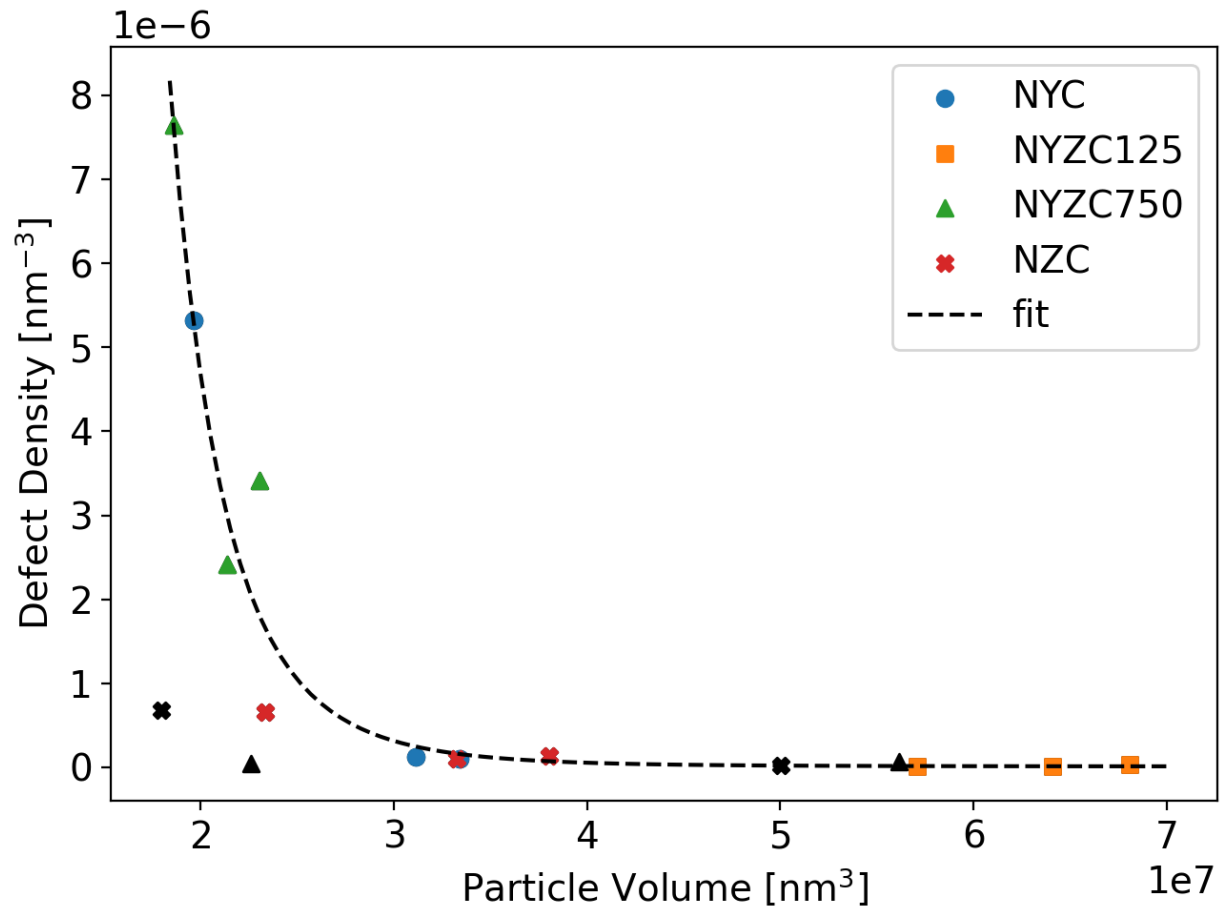


Figure 4.9: Defect density as a function of particle volume. The black data points correspond to NYZC750/NZC particles measured in the $P2_1/n$ phase, while the color points show the $P3\ m1$ phase. Only the $P3\ m1$ data was fitted.

Fig. 4.9 also shows that our limited sample size may bias our defect density results. For example, all of our NYC particles measured are smaller than $3.3 \times 10^7 \text{ nm}^3$, while all of the $x = 0.125$ particles are larger than $5.7 \times 10^7 \text{ nm}^3$. In an attempt to account for the effect of particle size on defect density, we calculated the normalized defect density for each particle by dividing each value by the fitted value for that volume. NYZC125 was excluded from this normalization due to its low measured defect density, making the normalization too sensitive to slight variations in our fitting parameters.

Fig. 4.10 shows how the $P\bar{3}m1$ (021) lattice spacing and the volume-normalized defect density correlate to ionic conductivity in the NYZC stoichiometries. We find evidence that both may play an important role in the ionic conductivity of solid electrolytes. Despite our limited sample size, our results suggest that NYZC750 and NZC exhibit both the highest defect density for a given volume on average, as well as the highest variability in defect density. We hypothesize that individual NYZC750 / NZC particles with an especially high concentration of defects could enable ionic conduction channels that substantially increase the overall conductivity for those NYZC stoichiometries. The observed increase in $P\bar{3}m1$ (021) lattice spacing may make NYZC750 and NZC a lot more prone to defects.

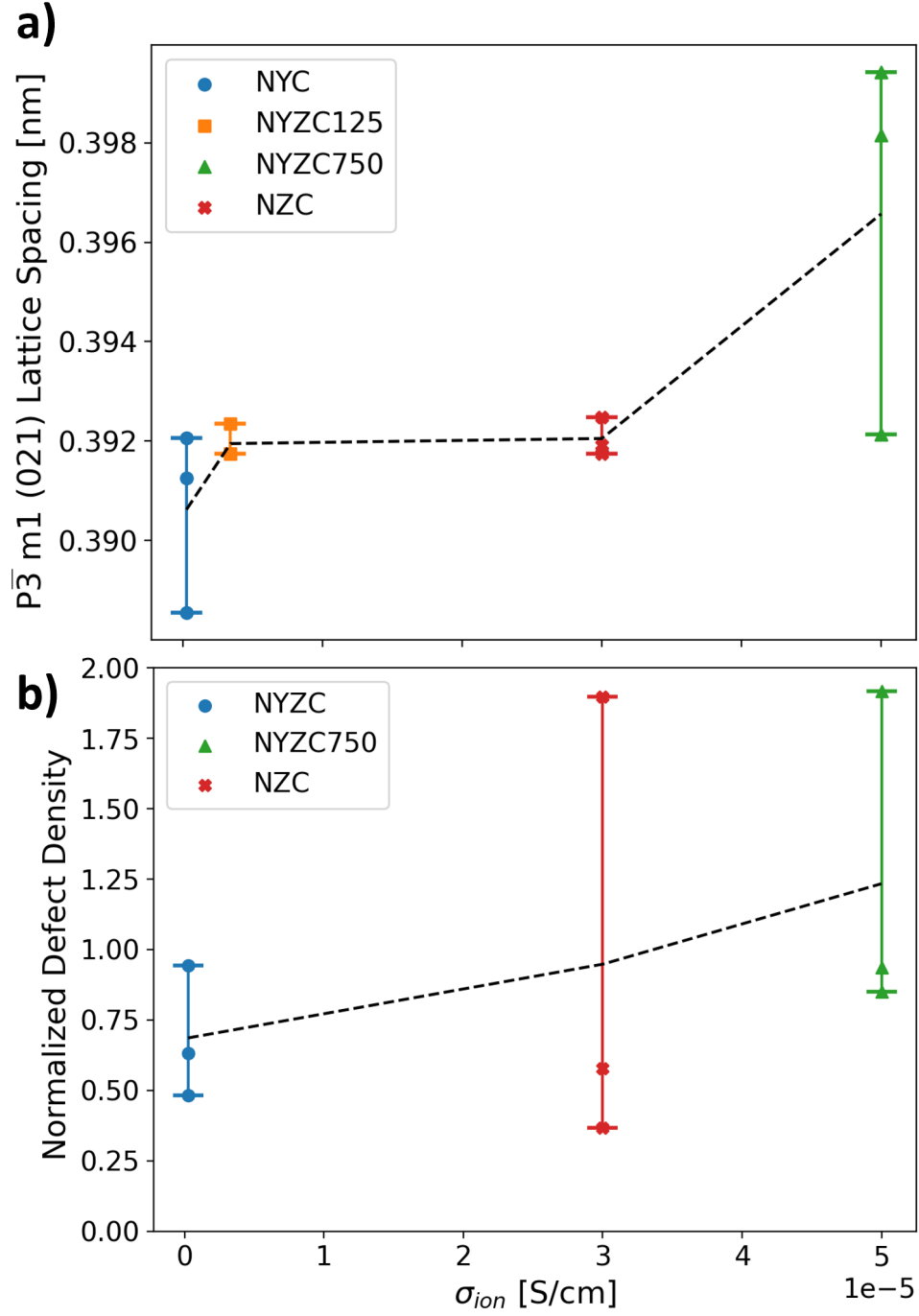


Figure 4.10: $P\bar{3} m1$ (021) lattice spacing (a) and volume-normalized defect density (b) as a function of ionic conductivity. NYZC125 is excluded from (b) due to the very low measured defect density and large particle size, making it unreliable to normalize.

4.5 Conclusion

In summary, we surveyed the nanoscale structure and defects of four stoichiometries of the halide solid-state electrolyte $\text{Na}_{3-x}\text{Y}_{1-x}\text{Zr}_x\text{Cl}_6$ (NYZC), particularly NYC, NYZC125, NYZC750, and NZC. We employed Bragg coherent diffractive imaging, a synchrotron X-ray technique that allows us to indirectly image the electron density and displacement field projection of single NYZC nanocrystals via an iterative phase-retrieval algorithm. The displacement fields measured for each particle were used to calculate average displacement, average strain, and defect density. We found an abundance of defects in these materials, including anti-phase domains and edge dislocations (Fig. 4.5, Fig. 4.6). All four stoichiometries measured were found in the $\text{P}\bar{3} \text{ m1}$ phase, but NYZC750 and NZC also exhibited the $\text{P2}_1/\text{n}$ phase. We found that the $\text{P}\bar{3} \text{ m1}$ structure exhibits significantly higher defect density than $\text{P2}_1/\text{n}$. We further observed that NYZC750 in $\text{P}\bar{3} \text{ m1}$ form has the highest average (021) d-spacing, which could contribute to its enhanced ionic conductivity over other NYZC stoichiometries (Fig. 4.7).

NYZC750 also shows the highest levels of strain and defect density on average, although with high variability across nanocrystals (Fig. 4.8). We further observed a strong dependence of the measured defect density on particle volume for all four stoichiometries. Our findings indicate that ball-milling introduces defects into the $\text{P}\bar{3} \text{ m1}$ phase at a rate 20 times faster than what we would expect based on the surface-area-to-volume ratio. Finally, when accounting for the effect of particle volume on defect density, we find a possible

correlation between normalized defect density and ionic conductivity. Previous studies have shown that ion diffusion within solid electrolytes can be highly inhomogeneous [63]. We hypothesize that it is precisely the higher-strained and more defect-prone crystals for a given stoichiometry that may enable higher ionic conductivity. Defects such as vacancies, edge dislocations, and anti-phase boundaries could play a key role as ion diffusion channels.

Our work suggests that ionic conductivity in these materials may be enhanced by a combination of increased d-spacing and increased defect density for a given particle size. It highlights the importance of studying the role of defects as ion migration channels and opens up new avenues toward developing high-performing halide SEs. Since Na^+ ions are larger (102 pm) than Li^+ ions (72pm), further optimization of fabrication methods aimed at optimizing defect density and d-spacing may be especially important for the further development of Na SEs [64]. We further observed that defect density has a very strong dependence on particle volume. Our experiment confirms that conventional ball-milling strategies produce highly variable particle sizes. Alternative approaches such as wet-milling and dissolution-precipitation would allow for more precise control over particle size [65]. We emphasize that fine-tuning of particle size and defect properties of solid electrolytes could lead to key improvements in Na-ion ASSB performance.

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Chapter 5

Probing Anomalous Magnetic Order in Magnetite Using Resonant X-ray Scattering

5.1 Abstract

We observe an anomalous spin order in thin films of Fe_3O_4 grown epitaxially on MgO, present on both sides of the Verwey transition. Diffuse X-ray scattering in the shape of an inverted pyramid emanating from the reciprocal space origin was measured. The underlying order behind this structure is modeled as a series of domains with a thickness of 0.5 unit cells and a 2.2° degree tilt along all in-plane directions. Finally, X-ray Magnetic Circular Dichroism was used in scattering geometry to determine that the order parameter of the observed ultrathin domains is likely the spin.

5.2 Introduction

Fe_3O_4 , also known as magnetite, is the oldest known magnetic material, as well as the first material discovered to exhibit a metal-insulator transition known as the Verwey transition at $T_V = 124$ K [66, 67, 68, 69]. Upon cooling through T_V , the magnetite crystal lattice changes from an inverse spinel cubic to a monoclinic structure, and its conductivity decreases by 2 orders of magnitude. This structural change is accompanied by charge-orbital ordering in linear chains of 3 Fe sites known as trimerons [70]. Magnetite further undergoes a spin reorientation transition at approximately $T_{SR} = 130$ K, at which point the in-plane easy axis direction switches from $\langle 110 \rangle$ at room temperature to $\langle 100 \rangle$ below the transition [71]. Doping of magnetite was found to affect T_V and T_{SR} in a correlated manner, but a detailed understanding of how these two transitions are connected is still missing [72]. The precise mechanism behind this fascinating and complex phenomenon is still the subject of ongoing research, over 80 years after its discovery. It is a model system to understand the metal-insulator transition in a wide range of materials, such as manganites and nickelates.

5.3 Diffuse Scattering

When X-rays interact with a crystal lattice, the periodic arrangement of atoms leads to constructive interference for certain incident angles, which produces sharp, well-defined diffraction peaks as described by Bragg's law. In contrast, any deviations from an infinite, perfect lattice lead to additional scattering signal around and between the main Bragg peaks. This phenomenon is known as diffuse scattering, and it occurs when correlated

disorder is present within a material

Diffuse scattering arises from a variety of factors, including the presence of lattice defects, chemical disorder, finite crystal effects, and domain boundaries within the structure. Unlike the highly ordered Bragg peaks, which correspond to coherent scattering from well-defined atomic planes, diffuse scattering occurs due to incoherent scattering from multiple atomic planes or regions with imperfect alignment. The variety of effects that result in diffuse scattering makes the data extremely complex to analyze and understand. It often requires developing and refining a model based on intuition between some particular types of defects and their corresponding diffuse scattering signatures.

One illustrative example of the type of intuition required is known as crystal truncation rods, which are elongations of Bragg peaks that can be observed when a crystal lattice is truncated in a particular direction. These elongations appear in reciprocal space, and point in a direction that is perpendicular to the truncated direction of a crystal. This effect can be understood using the well-known Convolution Theorem, which states that the Fourier Transform of the product of two functions equals the convolution of the Fourier Transforms of the two functions, and vice versa:

$$\mathcal{F}\{g(\mathbf{x}) \cdot h(\mathbf{x})\} = \mathcal{F}\{g(\mathbf{x})\} \otimes \mathcal{F}\{h(\mathbf{x})\} \quad (5.1)$$

$$= G(\mathbf{q}) \otimes H(\mathbf{q}) \quad (5.2)$$

In the context of crystals, we can think of $g(x)$ as a periodic lattice of atoms, in

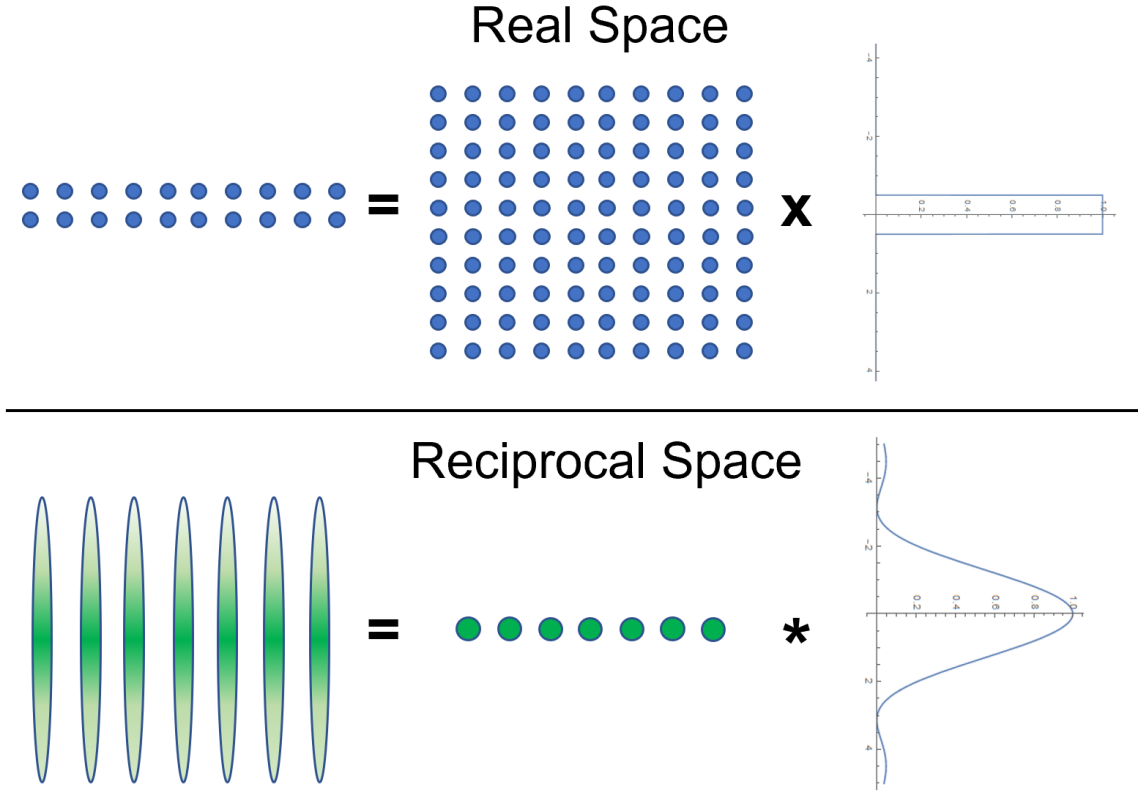


Figure 5.1: Crystal truncation rods as explained by the convolution theorem: In real space, an infinite lattice can be truncated to a few atomic layers along a direction by multiplying with a box function. Therefore, in reciprocal space, the infinitely sharp Bragg peaks will be convolved with a *sinc* function along that direction, elongating them into Bragg rods.

which case $\mathcal{F}\{g(\mathbf{x})\} = G(\mathbf{q})$ is the reciprocal lattice of Bragg peaks. If we were to multiply an infinite real-space lattice with a box function of width x_0 along a given direction, the resulting lattice would be finite along that direction. The convolution theorem tells us that in reciprocal space, the Bragg peaks would be convolved with the Fourier Transform of a rectangular pulse, $\mathcal{F}\{h(\mathbf{x})\} = H(\mathbf{q}) = \text{sinc}(qx_0/2)$. For a small x_0 , the *sinc* function will

be very broad, and therefore each Bragg peak will be significantly elongated in the direction perpendicular to the surface of the thin film, resulting in so-called truncation rods that extend from Bragg peaks and can be observed experimentally. Fig. 5.1 illustrates this example.

5.4 Mapping diffuse scattering in Magnetite

The focus of our study was epitaxial Fe_3O_4 grown on MgO , with (001) in the out-of-plane direction. We first observed a diffuse ring around the $(00\frac{1}{2})$ superlattice peak during an experiment focused on studying the dynamics of the Verwey transition [73]. This ring appeared only when the X-ray energy was tuned to the resonant energy at the $Fe\ L_3$ edge, and remained present on both sides of the transition temperature. This observation prompted us to conduct a follow-up experiment to study this structure. We performed rocking-curve scans to map the three-dimensional reciprocal space structure at the SEXTANTS beamline of the SOLEIL synchrotron. Fig. 5.2 shows our experimental setup with an example detector image.

Our initial experiment revealed that the reciprocal space structure has the shape of an inverted pyramid: hk planes show a diffuse slightly-rounded square around a central peak, and this square expands outwards in size with higher l values. Moving to lower l values suggested that the edges of this inverted pyramid originate from (000) in reciprocal space. Fig. 5.3 shows hk and kl slices through the reconstructed and interpolated reciprocal space map. It is important to note that the same structure was observed in

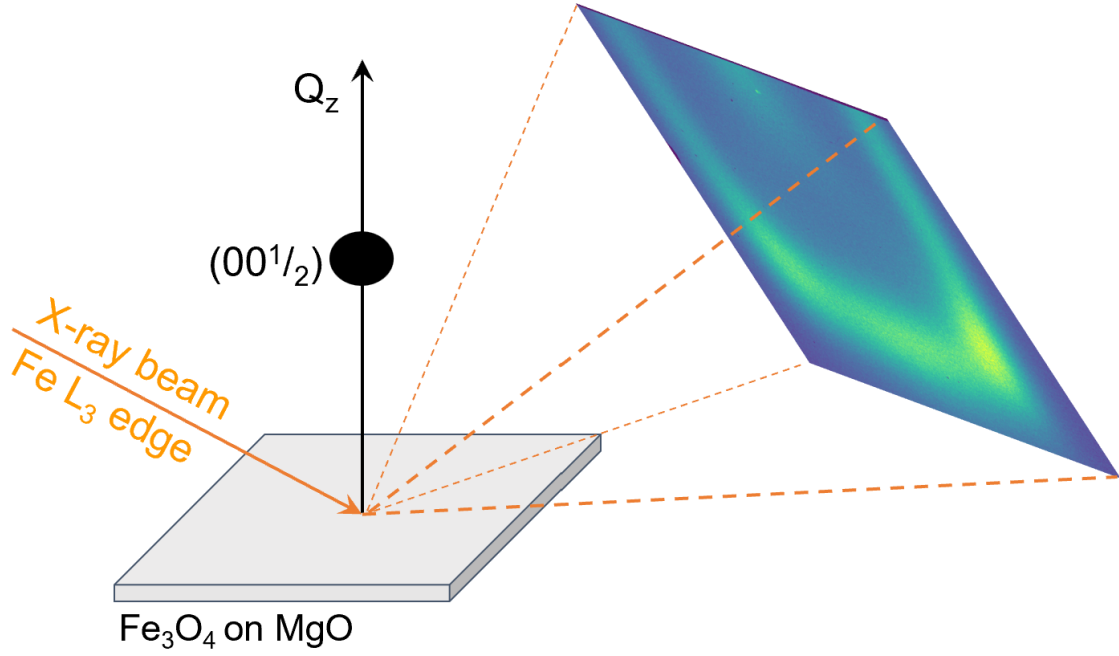


Figure 5.2: A schematic of the experimental setup. A synchrotron X-ray beam with energy near the $Fe\ L_3$ edge is incident on the sample of Fe_3O_4 , and a CCD detector is placed such that it captures the diffuse scattering signal around the $(00\frac{1}{2})$ Bragg peak

a different, 100 nm sample of magnetite, and the fact it only appears at resonance rules out the possibility that we are seeing a purely structural effect. This feature suggests the presence of long-range order of a very particular texture that has never been observed before.

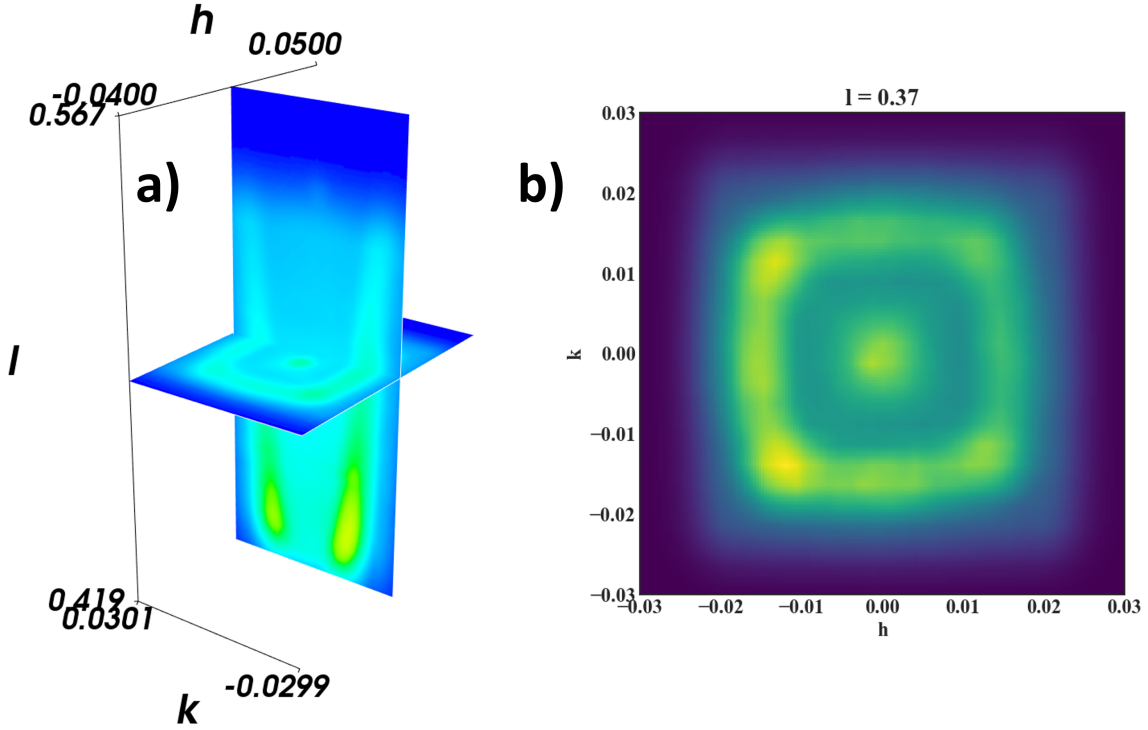


Figure 5.3: Slices through the measured 3-dimensional reciprocal space structure in the region around the $(00\frac{1}{2})$ superlattice peak (a). h , k , and l here represent the reciprocal lattice numbers. b): A better look at a horizontal slice through the diffuse data at $l = 0.37$, showing a square shape with slightly round edges and varying corner brightness.

5.5 2D Modeling of Diffuse Scattering

To understand the real-space structure that would produce the observed pyramid shape in reciprocal space, we first focused on a 2D model that aimed to describe what real-space structure would reproduce the base of the pyramid, which looks like a square with slightly rounded edges as shown in figure 5.3. As a starting point, some fundamentals of how real and reciprocal space are related were used to establish the foundation for the model used. From the width of the pyramid edge in reciprocal space, the correlation length (or domain size) was estimated to be $\Delta x = \frac{2\pi}{\Delta q} = 160nm$ in the in-plane direction. In the

same way, the extended pyramid edges along Q_z suggest that the correlation length along that direction is extremely short - no more than a few unit cells.

All modeling presented below was performed using DISCUS, which is a Fortran-based tool for the analysis and modeling of diffuse scattering data [74, 75]. For the initial 2D model, a simple cubic lattice was used, with each atom representing a unit cell. Two atom types, A and B, were assumed to exist in equal amounts and random locations initially. To generate a random distribution of domains of the appropriate size, Ising energy terms were introduced:

$$E = \sum_{\langle ij \rangle} J_{ij} \sigma_i \sigma_j \quad (5.3)$$

Using a thoughtful selection of J_{ij} values, followed by Markov Chain Monte Carlo energy minimization, random domain distributions were generated. Negative J_{ij} values imply that it is energetically favorable for atoms of the same type to be a vector (i, j) apart, while a positive J_{ij} value makes it more favorable for opposite type of atoms to be (i, j) apart. After careful optimization, the following J_{ij} values were used:

$$J_{\langle 1,0 \rangle} = -1; J_{\langle 0,40 \rangle} = 1 \quad (5.4)$$

where $\langle 1, 0 \rangle$ refers to the four symmetrically equivalent directions $\{(1, 0), (-1, 0), (0, 1), (0, -1)\}$. Fig. 5.4 demonstrates an example of domains formed after Monte Carlo energy minimization with the Ising terms described above, as well as the corresponding calculated diffuse scattering intensity. It is interesting to note that the

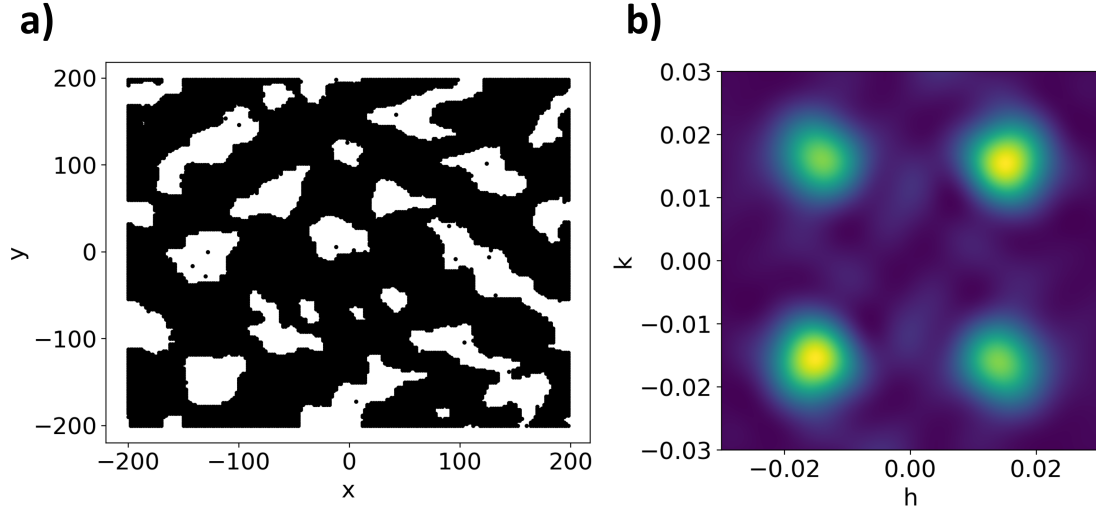


Figure 5.4: (a) Real-space domains formed from a minimized Ising model with non-zero terms $J_{\langle 1,0 \rangle} = -1$; $J_{\langle 0,40 \rangle} = 1$. Note that the axes are in units of the model lattice parameter. As expected, those two families of energy terms result in domains of approximately 40 unit cells in size. (b) Calculated diffuse scattering due to model domain distribution, with the average scattering from 50% of the crystal subtracted to emphasize the diffuse component. The four diffuse peaks appear as a result of long-range correlations between neighboring domains along the 4 diagonals.

resulting long-scale correlations between domains are in the diagonal direction, although the only non-zero J_{ij} terms are along the two axes.

This 2D domain model demonstrated that the corners of the observed square diffuse scattering in hk planes of reciprocal space (Fig. 5.3) can be explained by domains that would form due to a short-range negative energy term and a long-range positive energy term in a 2D Ising Model. A larger such model with domain correlations along a distribution of directions, as opposed to just the four diagonals, would show diffuse scattering along the edges connecting the 4 peaks seen in Fig. 5.4. However, a 2D model is unable to account for the Q_z dependence of the observed 3D diffuse scattering. To fully understand the origin of the measured pyramid structure, we turned our attention to developing a 3D model.

5.6 3D Modeling of Diffuse Pyramid Structure

The Q_z dependence of the diffuse pyramid has two notable properties. Firstly, it extends very far along the Q_z direction - from $l = 0$ to $l = 0.54$ and beyond. Secondly, the observed diffuse elongation is not parallel to the Q_z axis. The first property implies that the real-space domain structure must be extremely short in the Q_z direction, such that it gives rise to crystal truncation rods. The second suggests these thin domains must be slightly tilted away from Q_z to account for the elongation direction. With this in mind, our first model consists of 5 thin planes made of $160 \times 160 \times 0.5$ unit cells, with 4 of them tilted by $(\pm 2.2^\circ, \pm 2.2^\circ)$ along the x and y axes respectively. These planes generated truncation rods in reciprocal space that matched the 4 edges of the pyramid, as well as the central peak, as demonstrated in Fig. 5.5.

In order to model the diffuse sides of the pyramid, we added more families of thin domains with a distribution of tilt angles along x and y . To achieve the slight curvature seen in the data, the tilt angles had the form $\theta_1 = -2.2^\circ + \frac{4.4n}{10}^\circ$, $\theta_2 = -2.4^\circ + \text{abs}\left(\frac{n-5}{20}\right)^\circ$, where n is an integer from 1 to 9. Fig. 5.6 shows the modeled diffuse sides. Our simulations also revealed that the entire observed structure appears as a result of crystal truncation rods emanating from the origin in reciprocal space.

Our modeling efforts also allowed us to determine the thickness of the thin domains that would best match the data. By varying the thickness and comparing how the intensity of the simulated scattering decreases with Q_z compared to our data, we found that a thickness of 0.5 unit cells matches our observations precisely.

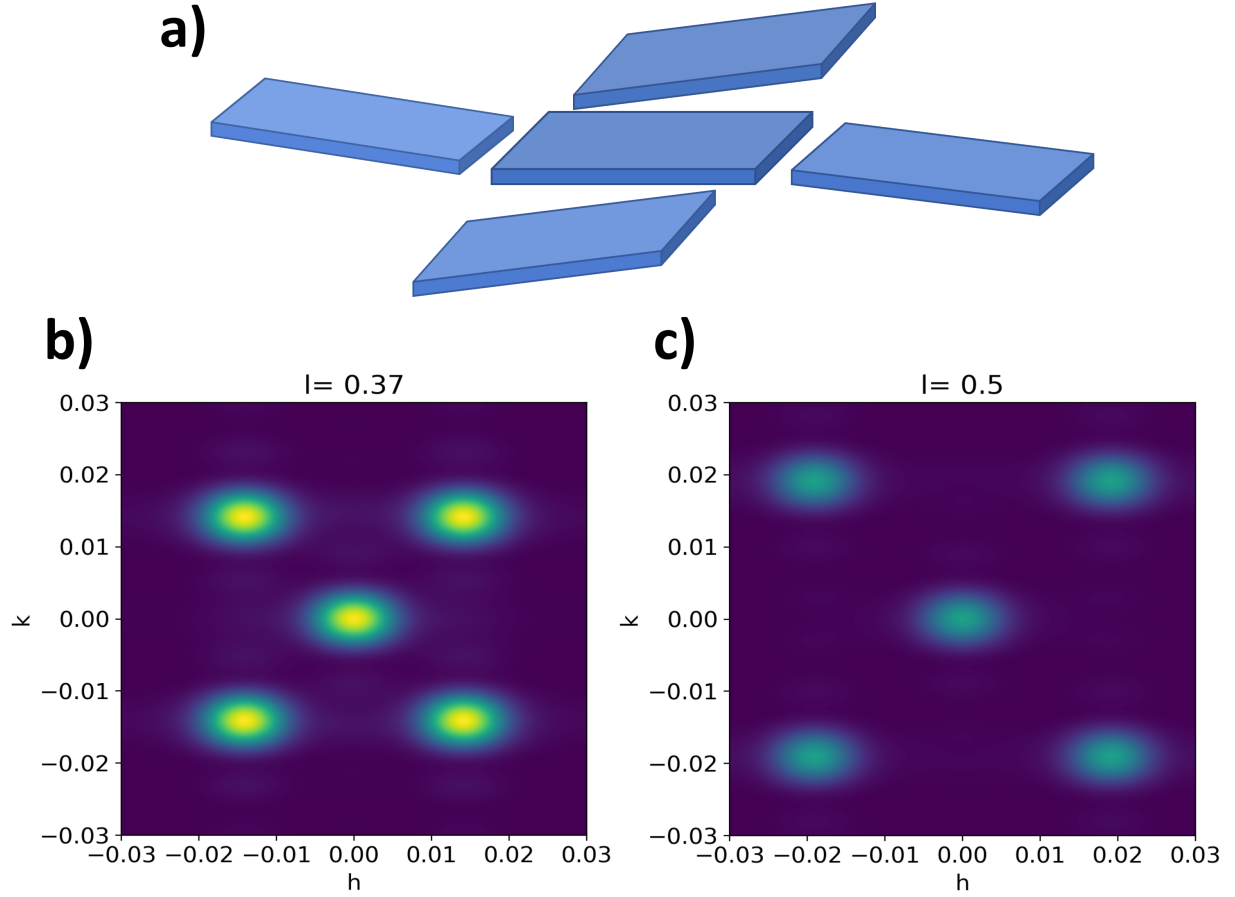


Figure 5.5: (a) Five Model tilted thin domains consisting of $160 \times 160 \times 0.5$ unit cells used to simulate corners of the pyramid. Four of the planes are rotated by $(\pm 2.2^\circ, \pm 2.2^\circ)$ around the x and y axes respectively. Slices through the simulated diffuse scattering for the $l = 0.37$ (b) and $l = 0.50$ (c) planes. The behavior of the corners and central peak matches the data in Fig. 5.3 - namely, the size of the square pattern increases with higher l , while the intensity decreases.

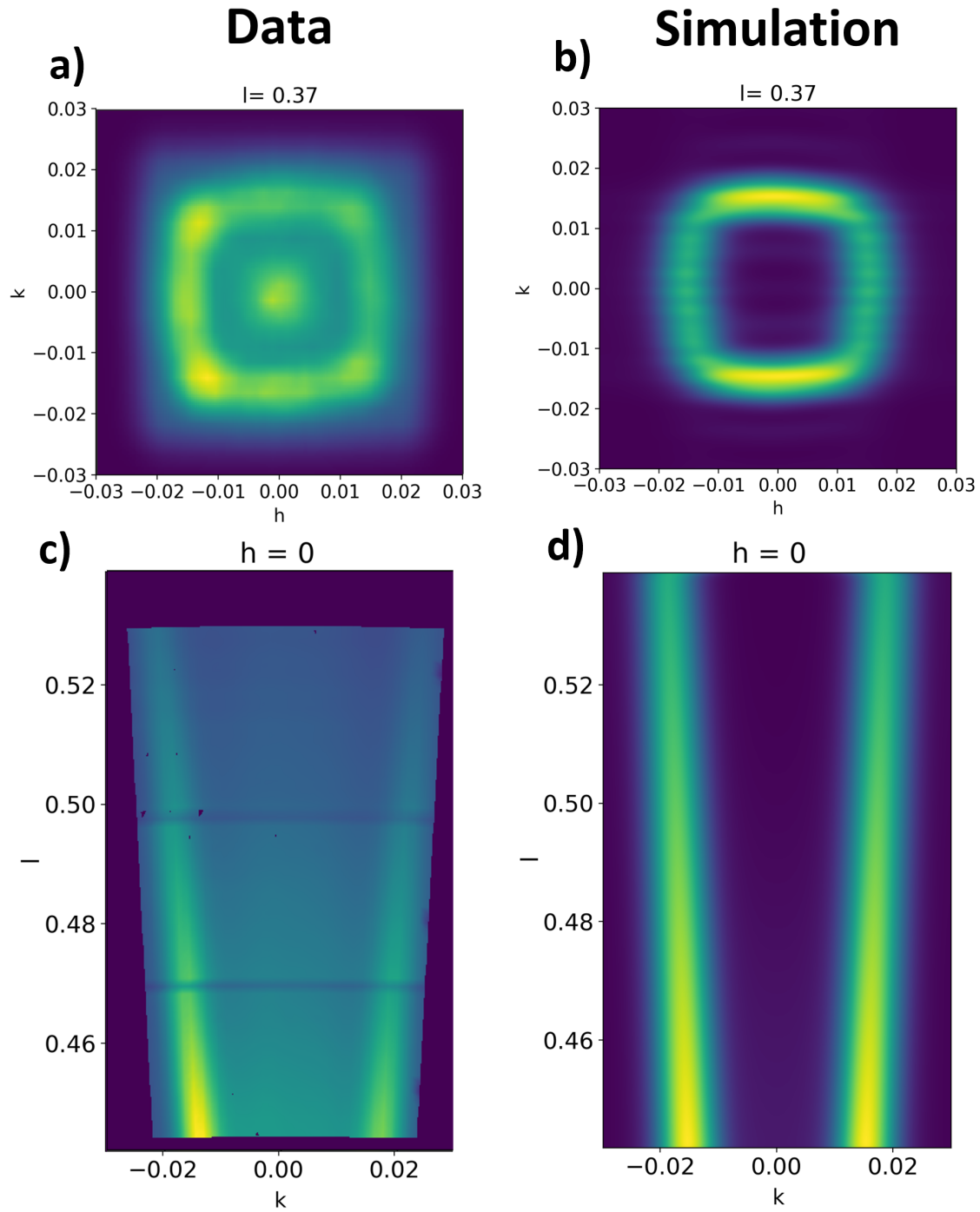


Figure 5.6: $l = 0.37$ slice of the measured (a) and simulated (b) diffuse scattering showing the sides of the pyramid structure connecting the corners, as a result of a distribution of thin domains. (c) and (d) show a slice of the measured and simulated $h = 0$ slice respectively.

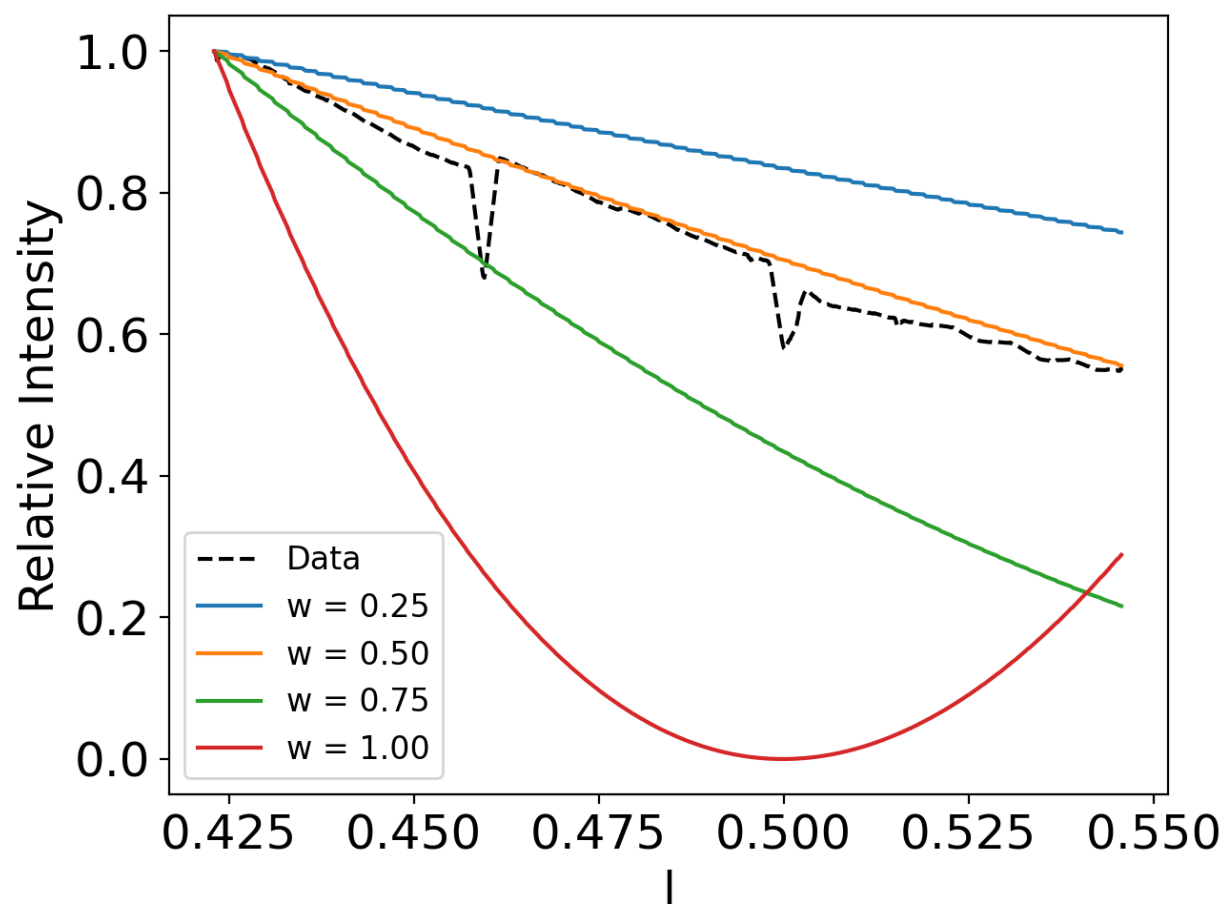


Figure 5.7: Integrated diffuse scattering intensity as a function of l for our data, as well as our model based on 4 domain thickness values. Note that the two dips in intensity occur due to insufficient overlap in our reciprocal space map, and are not a physical effect.

5.7 Probing Magnetic Order in Observed Domains

In a follow-up experiment, we scanned a slice of the pyramid structure across the $Fe\ L_3$ edge using four X-ray polarizations - right and left circular, as well as horizontal and vertical linear. Our goal was to disentangle any potential structural, charge, orbital, and spin components of the thin domains that give rise to the observed pyramid structure. To do this, the X-ray energy was scanned between 705 – 712 eV for each of the four polarizations. This allowed us to use X-ray Magnetic Circular Dichroism (XMCD) to isolate any magnetic contribution to the underlying order. XMCD is a technique that relates the difference in absorption spectra of left and right circular X-rays to atomic magnetic moments [76, 5].

XMCD experiments are typically conducted via X-ray Absorption Spectroscopy (XAS), which provides element-specific information on the overall spin and magnetic moments of atoms in a sample, but without any information about the spatial distribution of these order parameters within the sample. Our experiment takes the XMCD approach a step further by measuring scattering instead, which makes it possible to obtain rich data that contains information about the type of order parameters involved, as well as their spatial distribution. More specifically, we aimed to understand whether the pyramid structure arose due to a purely structural effect, or whether there was charge, orbital, and/or spin order involved.

Integrating the intensity of a region of the diffuse pyramid revealed a very similar

XMCD profile to ones obtained from absorption measurements, particularly for the $Fe\ L_3$ edge. Fig. 5.8 shows this comparison with absorption results from [5]. This suggests that there is a significant magnetic component to the underlying order. Theoretical calculations have been used to assign the three XMCD peaks to octahedral Fe^{2+} , tetrahedral Fe^{3+} and octahedral Fe^{3+} , in order from left to right [5]. The opposite sign of the tetrahedral peak from the other two in the XMCD spectra is a consequence of the ferrimagnetic nature of magnetite, where tetrahedral site spins are known to be opposite to the octahedral ones. This result shows that the observed pyramid structure in reciprocal space has a significant magnetic (spin/orbital) component. Applying an in-plane 1.1T external magnetic field flipped the XMCD spectrum, which implies the magnetic moment direction flipped (Fig. 5.9). Turning the field off led to a very slight decrease in XMCD contrast, showing that this order is highly persistent.

We further investigated the temperature dependence of the observed thin-domain order. The diffuse pyramid was found to increase in intensity with increasing temperature beyond T_V . This suggests that this emergent order is unrelated to both $(00\frac{1}{2})$ orbital order, and the trimeron charge order, both of which disappear above T_V (Fig. 5.10). The $(00\frac{1}{2})$ data was adapted from [73]. However, we observe a kink in the intensity profile at T_V , which still suggests that this order is indirectly related to the Verwey transition.

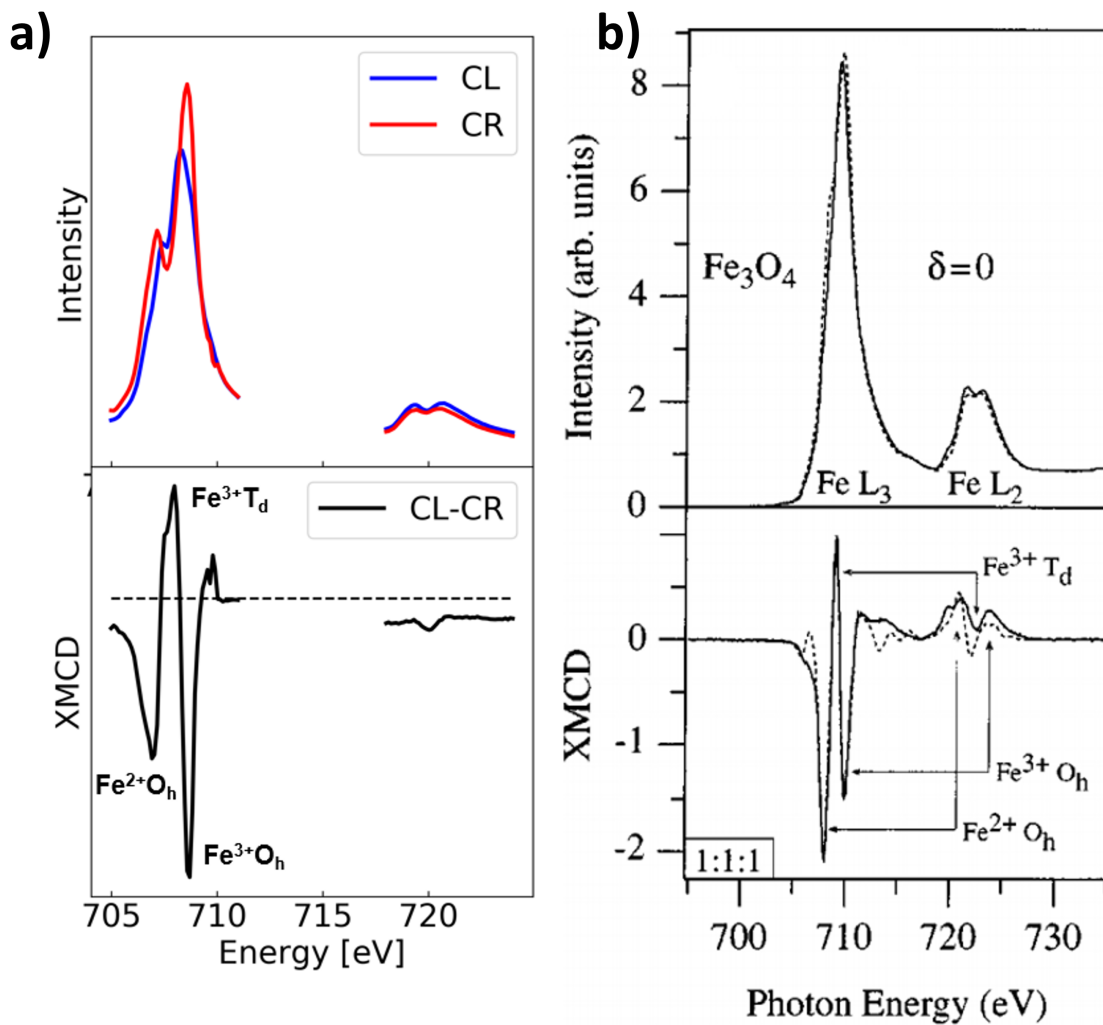


Figure 5.8: Intensity and XMCD spectra for a region of the pyramid in our diffraction data (a), and XAS measurements (b) adapted from [5]. The XMCD profiles are generated by subtracting the Circular Right (CR) intensity from the Circular Left (CL). The strong agreement between these spectra suggests that the thin domains that give rise to the pyramid structure have significant magnetic order.

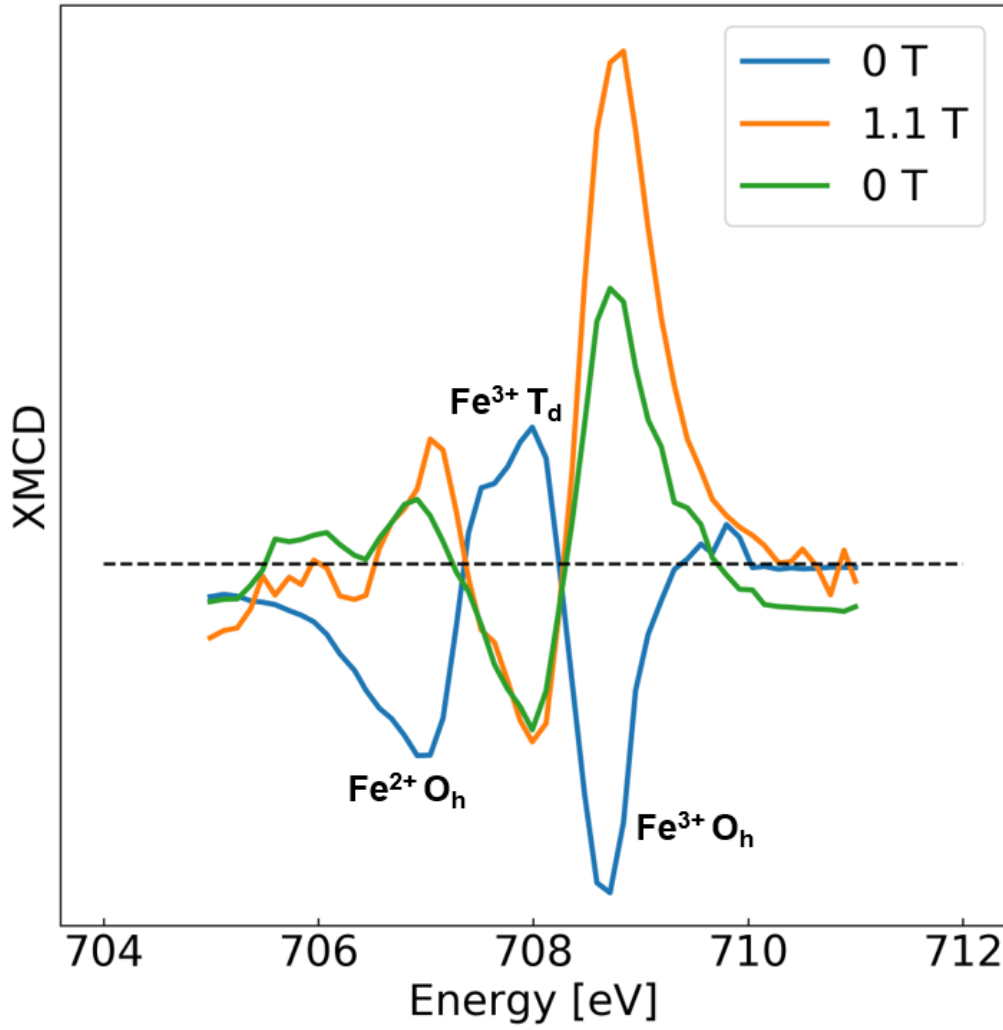


Figure 5.9: XMCD spectra of pyramid structure before (blue), during (orange), and after (green) a 1.1 T in-plane magnetic field was applied, measured at 300K.

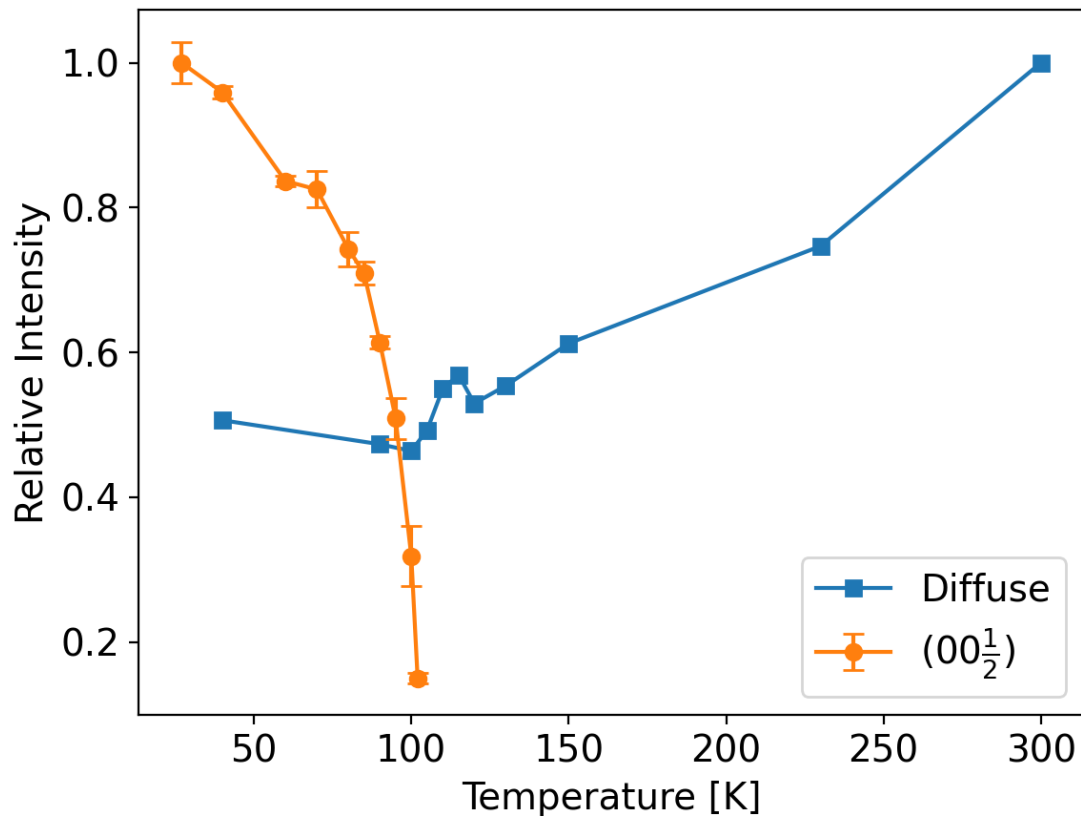


Figure 5.10: Temperature dependence of the intensity of observed pyramid order (blue) compared to the $(00\frac{1}{2})$ peak.

5.8 Conclusion

In summary, we observed an anomalous order in Fe_3O_4 thin films grown on MgO in the form of a diffuse inverted pyramid with a square base and slightly rounded corners. Mapping out this reciprocal space structure revealed that it gets less intense at higher Q_z , and its tip points towards the origin (Fig. 5.3.) We created a model that consisted of $160 \times 160 \times 0.5$ unit cell thin domains, tilted by approximately 2.2° in x and/or y , which successfully reproduced the main features of the data in 3D reciprocal space (Fig. 5.5, 5.6, 5.7). We emphasize that the agreement of our model with the data is highly sensitive to the domain thickness of 0.5 unit cells. However, the square shape and exact size in the other two dimensions are not strictly required to reproduce the observed data.

We observed a strong resonant response at the Fe L_3 edge, as well as XMCD contrast which suggested the anomalous order is magnetic in nature (Fig. 5.8). The XMCD spectrum could be flipped using an external in-plane magnetic field and exhibited memory properties upon removing the external field. Finally, this anomalous order was found to increase with temperature and exhibit a distinct kink around the Verwey transition (Fig. 5.10). Since the Verwey transition involves an orbital order that disappears at T_V while this pyramid structure persists above T_V , we believe the main order parameter involved in the observed domains is the spin. Furthermore, the kink in the domain intensity appears slightly above the Verwey transition. This suggests it could be related to the spin reorientation transition that occurs in magnetite at temperatures around 10K higher than the Verwey transition [77].

In principle, there exist sum rules that relate the energy integrals of the sums and differences of right- and left-circular polarized signals to the spin and magnetic moments [78, 79, 80]. These determinations are usually done in absorption, where a better signal-to-noise ratio is possible at the cost of spatial modulation information present in a scattering experiment. Furthermore, they require a continuous spectrum across the L_2 and L_3 edges, which we were unable to measure due to time constraints. However, we note that we observe a significant XMCD profile at the L_3 edge, while the L_2 edge displayed a flat XMCD profile (Fig. 5.8). Since the spin sum rule has a stronger dependence on the integral along the L_3 edge alone, we can qualitatively claim that the domains we observed are primarily an ordering of spin.

The thin domains were detected in two separate Fe_3O_4 thin films with a thickness of 40 nm and 100 nm respectively, but were not observed in single-crystal Fe_3O_4 . Epitaxially grown Fe_3O_4 films have been shown to contain anti-phase domains (APDs) with comparable size to our model domains [81]. In some cases, these APDs have distinctly square shapes and lead to detectable satellite Bragg peaks [82]. We hypothesize that APDs may give rise to the observed domain structure. The reasons behind their 0.5 unit cell thickness, as well as their $\approx 2.2^\circ$ tilt, remain an open question. Finally, our work also demonstrates a novel approach to studying the magnetic properties of a particular order of interest using XMCD in scattering geometry.

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