

Local Structural Insights into Exotic Electronic States in d - and f -Electron Oxides with
Joint Neutron and X-ray Pair Distribution Function Analysis

Long Yang

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ABSTRACT

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Quantum materials have strong electron correlation effects. According to the “structure-property” relationship, it is crucial to study the structure of quantum materials to better understand and manipulate the physical properties. The quantum effects are significant at the atomic microscopic length scale, which is not feasible to be studied by the average long-range structure measurement from conventional diffraction methods. Instead the local structure probe, pair distribution function (PDF) analysis, can effectively reveal the mystery of local structure, which is sensitive to the local behavior rather than the bulk average properties. In this thesis, the joint neutron and x-ray PDF (NXPDF) method is implemented. Because of their different interactions with matters, a combination of neutron and x-ray scattering can help comprehensively understand the atomic structures of some strongly correlated d - and f -electron systems that are difficult to be studied alone.

Though powerful for understanding the structure of complex materials, performing the PDF modeling and structure refinement usually requires a lot of work on model selection for candidate structures. To address this problem, a new approach is developed to obtain candidate atomic structures from NXPDF, called structure-mining, in a highly automated way. It fetches, from open structural databases, all the structures meeting the experimenter’s search criteria and performs structure refinements on them without human intervention.

Tests on various material systems show the effectiveness and robustness of the algorithm in finding the correct atomic crystal structure. It works on crystalline and nanocrystalline materials including complex oxide nanoparticles and nanowires, low-symmetry and locally distorted structures, and complicated doped and magnetic materials. The examples of applying structure-mining method to identify the local structures of Pr_6O_{11} , $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$, and MgTi_2O_4 materials, which have strongly correlated d - and f -orbital electronic states under study in the thesis, are shown as well. This approach could greatly reduce the traditional structure searching work for quantum materials as well as other systems.

The NXPDF method is first applied to the praseodymium oxide semiconductor nanoparticles to investigate the local structure behavior accompanied by the loss of electrical conductivity when temperature changes. The Pr and O sublattices can be determined precisely by x-ray and neutron PDF, respectively, because of their distinct x-ray atomic form factors and neutron scattering lengths. A combination of a highly ordered structure motif and a locally distorted oxygen deficient structure environment can describe the measured NXPDFs reasonably well. The iron doped barium titanate $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ system is also investigated using PDF methods for studying the multiferroic behavior in the nanocrystals, which are synthesized near room temperature. The perovskite structure is established to be non-centrosymmetric, consistent with predictions of the pseudo-Jahn-Teller effect being the underlying cause of off-center displacements of B-site (Ti and doped Fe) atom, lowering the symmetry in order to make additional overlap between the $3d$ orbital of Ti and neighboring O atoms to create π molecular orbitals. This triggers the spontaneous polarization of the crystal. The PDF results establish that Fe is successfully doped into the ferroelectric BaTiO_3 phase, and the measured dielectric and magnetic properties also validate the multiferroic behavior of the synthesized $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ nanocrystals. In addition, the NXPDF analysis is also conducted on the MgTi_2O_4 system to track the evolution of the local atomic structure

across the temperature-dependent metal-insulator transition, and the results reveal that local tetragonality is persistent, preformed with reduced magnitude, deep in the metallic and on average cubic regime. Significantly, the high temperature local state revealed by PDF is not continuously connected to the orbitally ordered band insulator ground state and the transition cannot be characterized as a trivial order-disorder type. The shortest Ti-Ti bond lengths corresponding to spin singlet dimers shift to longer distances on warming but are still shorter than those seen in the cubic average structure. These seemingly conflicting observations could be reconciled within the model of a local fluctuating t_{2g} orbital-degeneracy-lifted (ODL) precursor state. These results undoubtedly establish the effectiveness of the joint neutron and x-ray PDF analysis to investigate the structure-property relationship on the sub-nanometer length scale of strongly correlated electron materials, utilizing the complementary structure information obtained from neutron and x-ray scattering.

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To my family

Chapter 1

Strongly electron correlated quantum materials

1.1 Introduction

Atoms make up everything. There are not many selections on the atom types in nature, merely around a hundred elements as recorded in the periodic table. However various combinations of atoms in certain spatial arrangements can result in countless colorful materials with different functionalities in the world.

This is the topic of condensed matter physics, as the largest research field in physics nowadays [1], which is for studying how the interactions between atoms give the macroscopic and microscopic physical properties of condensed phases, such as solids and liquids. The study of systems in the condensed phases can help understand a series of frontier physical problems, such as superconductivity [2; 3], superfluidity [4; 5], and colossal magnetoresistance [6; 7].

Quantum mechanics is a theory for describing the physical properties of nature at the

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atomic and subatomic length-scale fundamental level. Though in many cases, the physical properties can be approximated by a classical description at the macroscopic level, there are increasing number of advanced material systems where the quantum effects remain manifest over a wide range of energy and length scales [8]. Quantum materials stand for the compounds and phenomena where the consequence of quantum mechanics is significantly real [9], such as transition metal oxides, Fe and Cu based high-temperature superconductors, topological insulators, quantum spin liquids, graphene, and Weyl semimetals. Moreover, the microscopic quantum effects in these quantum materials are not subtle, instead they usually control the macroscopic behavior of materials. In quantum materials, electrons cannot be considered as independent from each other anymore, but interact strongly and give rise to collective excitations, which result in altering the properties of the material [8].

The strongly correlated electrons often result in complex behavior at the atomic scale. However, most of the experimental techniques that have been developed to study condensed matter are mainly bulk probes that measure the average properties, such as the conventional x-ray or neutron diffraction method for determining the average long-range crystal structure of material and the magnetic or electric susceptibility measurements for probing the average response to an applied magnetic or electric field. These bulk probes are not suitable for revealing the local behaviors in the quantum materials. Thus, we need some local probe techniques for understanding the strongly correlated electron systems, and investigating the local and microscopic behavior instead of measuring the average response.

In this thesis, I will report experiments performed on some quantum materials using a powerful local structure probe, i.e., pair distribution function (PDF) analysis, which is a highly effective technique measuring the local atomic structure of materials at the atomic length scale. The PDF analysis is based on the joint neutron and x-ray total scattering data in order to take the advantage of the complementary aspects of neutron and x-ray scattering.

1.2 Mott insulator

The theory on non-interacting or weakly interacting electron systems was established in the early years of quantum mechanics, which is called non-interacting band theory [10; 11; 12]. It is the first successful theoretical description, based on the electron filling of energy bands, on how to distinguish metals and insulators at zero temperature. Unlike free electrons, the periodic lattice structure of atoms in crystals restrict the movement of electrons, which results in the formation of band structure of materials [12]. The Fermi level (or the chemical potential, μ) determines up to which energy level that electrons are filled. For insulators, the Fermi level lies between two bands, i.e., in the gap of bands, such that the highest filled band is completely filled and electrons cannot be easily moved anymore, so the electrical conductivity is small. For metals, on the other hand, the Fermi level is located inside a band, consequently, the band is partially filled, which results in high electrical conductivity. By the early 1930s, people realized that some insulators can be further classified into the condition when the energy band gap between the highest filled and lowest empty bands is small, which may not trap electrons due to the thermal excitation at finite temperature [13; 14]. This category of materials is named as semiconductor, which is the foundation of inventing transistors [15] and the laptop I am using to write my thesis.

This classification based on the band structure has been successful in many materials, however it does not always work, especially that it fails on a series of transition-metal oxides with a partially filled d -electron band such as NiO, as de Boer and Verwey first pointed out [16]. These “strange” materials were predicted to be metals according to the non-interacting band theory but were experimentally found to be insulators.

Mott and Peierls suggested that the strong electron-electron correlations would explain this mismatch that the strong Coulomb repulsion between electrons could be the origin of

the insulating behavior [17]. The first theoretical treatment of this problem was provided by Mott in 1949 [18]. Thus this type of materials is named as Mott insulators. He considered a simple lattice model with only one single electronic orbital on each site. In the non-interacting picture, a single band would be formed from the overlap of the atomic orbitals in this system, such that the band is completely full if two electrons (one spins up and one spins down) occupy the site according to the Pauli exclusion principle [19]. Considering the fact that the Coulomb repulsion between two electrons would be large if sitting at the same site, the single band could split into two bands that the lower energy band is formed from electrons that occupy an empty site and the higher energy band is from electrons which occupy a site already taken by another electron. In this way, only one electron is allowed at one site, thus the lower band would be full, and the system would be insulating state.

Since then, the topic on the strong electron correlations has become a major focus of the condensed matter physics. The observations on more Mott insulators launched the long and continuing history of quantum materials, especially the efforts to understand how partially filled bands could result in insulating state. While a lot of progress has been made for this subject, there are still a series of open questions, an example relevant to this thesis is the metal-insulator transition (MIT) that occurs between a Mott insulating phase and a metallic phase through changing the external control parameter such as temperature.

Inspired by the basic idea from Mott, more theories were proposed to better understand the strong electron-electron interactions. Slater provided an explanation for antiferromagnetic insulators that, since most Mott insulators have magnetic ordering near zero temperature, a superlattice structure of the magnetic periodicity may generate a band gap due to the folding of the Brillouin zone, which could explain the insulating behavior [20].

A more challenging problem besides the Mott insulating phase is how to understand the metallic phase near the insulating state. The fluctuations of spin, charge, and orbital

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correlations are strong in this regime. If the phase transition is first-order, the metallic phase with the strong fluctuation near MIT is called the anomalous metallic phase.

Hubbard proposed a simplified many-body theory, the so called Hubbard model [21] to describe two opposing tendencies in the system, that a kinetic term (t) allows for hopping of particles between sites of the lattice, and an on-site repulsion potential term (U) represents the energy cost for having two electrons on the same site. So larger t in the system means favoring free motion of the electrons through the lattice, while larger U in the system stands for a strong localization of the electrons so that they cannot freely move. This theory is based on the tight-binding approximation, and it includes many simplifications such as considering only a single non-degenerate orbital, which is rarely the case of transition-metal oxides with degenerate d -orbitals, but it serves as a very useful starting point for understanding the phenomena behind strong electron correlation. The Hubbard model was further developed by Brinkmann and Rice afterwards [22]. Importantly, the Hubbard model provides us a way to interpret how a transition might occur between the Mott insulator and the nearby metallic phase given the strong fluctuation near MIT. The key is about the electron correlation strength U/t ratio, or equivalently U/W where t is proportional to the bandwidth W of the single electron band. When $U/t \ll 1$, the hopping term dominates the system such that a half-filled band would be metallic, as expected in the non-interacting band theory. But if $U/t \gtrsim 1$, the electron-electron interaction originated from the Coulomb repulsion becomes increasingly dominant, which results in the fully localized electrons, i.e., the insulating state. The transition from a metal with $U/t \ll 1$ to an insulator with $U/t \gtrsim 1$ is called the bandwidth-controlled Mott transition, because the bandwidth W (or t) is changed during the transition. Another way to achieve the transition is by doping electrons or holes to change the band filling, increasing or lowering the chemical potential μ , respectively, which is referred as the filling-controlled Mott transition [23].

The transition-metal oxides, are indeed more complicated than what the Hubbard model describes. Since the degenerate d -orbitals in the transition-metal oxides raise the complexity of energy bands near the Fermi level. Zaanen, Sawatzky, and Allen developed a theory to investigate the relevant energy bands and Coulomb repulsion energies for transition-metal compounds [24], that the Mott insulators can be divided into two groups, i.e., Mott-Hubbard insulators and charge-transfer insulators. For Mott-Hubbard insulators, only one band, or one degenerate band, is near the Fermi level thus the on-site repulsion U splits the d band into a lower band with singly occupied states and an upper band with doubly occupied states. For charge-transfer insulators, the $2p_\sigma$ level from ligand oxygen atoms located between transition-metal atoms could overlap with the d band from heavier transition-metal near the Fermi level, such as Ni and Cu, forming a strong pd hybridization, resulting in a charge excitation gap between the singly occupied d band with a fully occupied p band and a singly occupied d band with a p_σ hole.

The achievements in the field of strongly correlated electrons, especially in the d -electron systems, provide people a deeper understanding on more complicated situations when there are degrees of freedom in orbitals, spins, and lattices. Although much of the research work for the strongly correlated system centers on the d -electron systems, other systems also provide many interesting phenomena due to the strong-correlation effects. For example, in f -electron systems, non-Fermi-liquid properties were observed due to orbital degeneracy effects [23].

1.3 Structure-property relationship

Structure determines properties. This is a powerful concept in the material-related fields including condensed matter physics, chemistry, and biology. An illustrative example is diamond and graphite. They both have the same composition (carbon), however the distinct

atomic spatial arrangements result in significantly different mechanical, chemical, and electronic properties.

The development of science and technology is built on advanced materials, and new materials lie at the heart of technological solutions to major global problems such as sustainable energy [25]. The study of material structure plays a key role in the development of novel materials, including quantum materials. Because in order to design the material with desired properties, it is important to understand its structure as the first step. For example, the shapes and sizes of semiconductor quantum dots can be tuned to control the wavelength of emitted lights because of the quantum confinement effects. When the particle size gets larger, the band gap would decrease and resulting in a red shifted (lower energy) fluorescence spectrum, and *vice versa* [26; 27; 28].

In the following, a few attractive physical properties of advanced materials would be introduced individually.

1.3.1 Metal-insulator transition

As described earlier, metals and insulators have dramatically different electrical properties. It is of essential interest to study the materials that can be either metallic or insulating depending on the external environment. The materials with metal-insulator transition (MIT) have a large potential application in the electronic devices, such as switching [29; 30; 31; 32; 33] and sensing [34; 35; 36; 37].

The MIT is accompanied by a phase transition between the metallic phase and the insulating phase [23]. For example, the vanadium oxide VO_2 has historically been one of the most important MIT materials from both technological and scientific research perspectives [38]. Its MIT behavior was first reported by Morin in 1959 [39], undergoing a monoclinic crystal structure as insulator phase to a tetragonal structure as metallic phase on warming. A

structure-driven Peierls transition mechanism, or electron correlation mechanism could help explain the narrowing of the band gap and collapse of lattice symmetry [40]. From the aspect of crystal structure, the low-temperature monoclinic structure was found to have short V-V dimers, thus the $3d^1$ electrons of each V atom are bonded in the dimer, forming the localization that leads VO_2 to show the insulative property. Thus the V-V dimer formation has a direct impact on the change from the high-temperature delocalized state to the low-temperature localized state [38].

The phase transition can be quantitatively described by an order parameter, which is defined in a way where it equals zero at disordered phase, and nonzero at ordered phase. Typically in thermal phase transition, i.e., the materials undergo the phase transition when temperature changes, ordered phase is the low-temperature phase whereas the disordered phase is at high temperature. When temperature increases, more thermal fluctuations are incorporated into the system, such that the order parameter increases, until the long-range average order is completely lost and the order parameter becomes zero. This thermal fluctuation driven phase transition is also called classical phase transition [41].

During the phase transition, the order parameter may jump discontinuously or change continuously with respect to external control parameters. The former situation corresponds to the first-order transition, and the latter one is named as the second-order transition. Landau first used the Gibbs free energy G term to explain how the system undergoes different processes in two types of phase transitions [42]. In the first-order phase transition, the first derivative of Gibbs free energy, G' , changes discontinuously with respect to the external control parameter (such as temperature). While in the second-order phase transition, the first-order derivative, G' , changes continuously, but the second-order derivative, G'' , changes discontinuously. This may be the reason why people name it as first- or second-order.

In thermodynamics, when temperature is the only changing control parameter, the change

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of G' is equal to the change of entropy, and the change of G'' is equal to the change of specific heat c_p (at constant pressure). Thus, people can measure how c_p changes with temperature to determine whether it is first-order (continuous c_p) or second-order (discontinuous c_p) across the phase transition temperature [42].

There are a few other important features of first-order transition. At the first-order transition, two different phases coexist, since two relative minima of the Gibbs free energy G exist, i.e., they are both at equilibrium at that point, such that the system discontinuously jumps from one value of order parameter to another. On the other hand, no such phase coexistence occurs for the second-order transition, because the ordered and disordered phases are identical at the transition point.

As mentioned above, many quantum materials have a thermal MIT when temperature is changed. In Mott MIT, nearly all systems have a high-temperature metallic phase, and it undergoes a transition to an insulating phase when lowering the temperature. The transition is usually first-order, as suggested by Mott that the MIT is usually discontinuous due to the long-range nature of the Coulomb interaction, i.e., the effects of electron-electron interactions beyond just the on-site repulsion potential term U in the Hubbard model [18]. This is also called the Mott-Hubbard phase transition. In many cases, there is an accompanying phase transition in one or more of the lattice, orbital, or spin degrees of freedom [23], which immediately increases the complexity of the phase transition mechanism.

People have proposed various theories trying to interpret the phase transition in MIT. One important theory to be introduced here is the Peierls phase transition. Peierls proposed a simple 1D physical model that the 1D lattice conductor is composed of atoms of equal spacing, each with a conducting electron. This 1D system is unstable due to the interaction between electrons and lattices such that the lattice distortion occurs at pairs of atoms at low temperatures. When the modulation wavevector equals to the twice of Fermi wavevector,

the Fermi surface and the Brillouin zone boundary would be fixed. As a result, when the energy dissipated by the opening of the band gap is greater than the elasticity of the lattice distortion, the energy of the system would decrease, resulting in the transition from metallic to insulative property [43].

1.3.2 Semiconductor

Besides metal and insulator, the third type of material is the semiconductor. Semiconductors are undoubtedly the foundation of the information age, or the silicon age, which brings the rapid economic growth and technological development [44; 45] since the semiconductor based field-effect transistor was invented in 1959 [46].

In the non-interacting band theory, semiconductors have the band gap, whilst the gap between conduction and valence bands is not as large as insulators. As a result, the thermal effects at finite temperature can produce excitation for electrons to exhibit conducting. In another word, the electrical conductivity of semiconductors falls between conductors and insulators. The conducting properties can be modified by introducing doping atoms into the semiconductors. Depending on the type of doping atoms, it can be classified into p -type or n -type semiconductors. When the doped atoms bring extra electrons into the crystal lattice, the effective charge carrier would be electron, known as n -type, and if the dopant contains mostly free holes to act as the charge carrier, it would be p -type.

When the charge carrier, electron or hole, freely moves through the crystal lattice, it may interact with the atoms in the material. The polaron theory was established to describe the interactions between charge carrier and the crystal lattice, which was first proposed by Landau in 1933 [47]. When the charge carrier (electron for n -type and hole for p -type) is inside the lattice, the surrounding ions can interact with it due to the Coulomb interaction, thus the ions would slightly deviate from their equilibrium average atomic positions, known

as a phonon cloud, to balance the Coulomb repulsive or attractive force. The adjustment of ion positions results in the polarization locally centered on the charge carrier. The interaction between the electron and the surrounding ion displacements due to the Coulomb interaction is known as electron-phonon coupling, as first proposed in 1933 by Landau [47]. This was further developed by Pekar to investigate the electron motion with lattice polarization. The charge carrier together with the induced lattice polarization can be considered as one entity, which is called a polaron [48; 49]. Depending on the size of the polarization phonon cloud, the polarons can be classified into small or large polarons, which refer to the situation when the polarization length scale is within similar size as or larger than the atomic spacing in the material, respectively.

The conduction mechanism in rare-earth oxides can be described by the polaron model, since the corresponding f -electron band widths are usually very small [50; 51; 52]. In addition, the polaron theory pointed out that the effective mass of polaron would be larger than that of the sole charge carrier (electron or hole) [48], therefore, the electron conductivity in semiconductors can be greatly decreased by the formation of polarons. Thus studying the local structure distortions would help understand the conductivity mechanism of semiconductors.

1.3.3 Multiferroicity

A ferroic is when a material has a spontaneous and switchable alignment internally. The commonly seen ferroic orderings are ferroelectric, ferromagnetic, and ferroelastic. For example, ferromagnetic materials have the spontaneous magnetization that is switchable by an applied magnetic field. In analogy, ferroelectricity stand for the materials that have a spontaneous electric polarization that can be reversed by applying an external electric field, and ferroelastic materials have a deformation that is switchable by an applied stress [53].

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The term “multiferroics” stands for the materials that exhibit two or more of the ferroic properties, which was first introduced by Schmid in 1994 [54]. Depending on which of the two order parameters are coupled, the multiferroics can be divided into magnetoelectric (ME), piezoelectric, and piezomagnetic couplings.

Among these multiferroics, the materials that exhibit both the ferroelectric and ferromagnetic properties have attracted a lot of attentions and interests in both scientific research and industrial applications, especially in the subjects of information storage in recent years [55; 56; 57; 58; 59]. Though the pioneering work on the possibility of coupling ferromagnetic and ferroelectric orderings, i.e., ME effects, in solids was carried out much earlier, which was first predicted by Curie in 1894 [60] and Dzyaloshinskii and Astrov first reported the study on the ME effects on Cr_2O_3 [61; 62].

The magnetoelectricity enables the possibility to exploit the functionality of both orders. For example, due to the ME coupling, the magnetic properties of the material can be controlled by an external electric field, and *vice versa*. In the memory storage devices, the magnetic bit can then be complemented by an electric bit to establish a four-state memory element, which would double the storage of traditional two-state memory [63; 64]. In addition, if the electric voltage pulse can be used directly for reading and writing the magnetic bit, other than by the electric current generated by magnetic fields, the waste heat can be avoided and the response time would be much shorter as well. So studying the multiferroics, especially the ME coupling, would lead to revolution of information storage for faster, smaller, and more energy-efficient memory devices [65; 53].

The multiferroics can be single-phase or made up with composites. One of the most popular single-phase multiferroic material is BiFeO_3 . The multiferroic properties of bulk BiFeO_3 are quite weak, but can be enhanced if made into thin films, as first successfully fabricated by the Ramesh group in 2003 [66]. Many other single-phase multiferroics were

also reported, such as Fe doped PbTiO_3 [67], TbMnO_3 [68], and YMnO_3 [69].

On the other hand, multiferroic composites, that have heterogeneous structures, can be designed to have quite large ME coupling. For instance, one can layer alternating ferroelectric and ferromagnetic materials to achieve enhanced ME coupling effect [70; 71; 72; 73; 74; 75; 76]. But the shortcome is obviously the fabrication and device integration would be complicated compared with single-phase multiferroics, which remains one of the biggest challenges for the industrial application of heterogeneous multiferroic materials.

A simpler structure, and preferably a single-phase multiferroic material would greatly ease the synthesis procedure, but are rare in nature or synthesis in the laboratory [77] because of the following requirements. We would expect the ferroelectric property that exhibits a switchable electric polarization with large atomic displacements to manifest the electric dipole moment, and meanwhile the ferromagnetic property that exhibits a switchable magnetization originated from the quantum mechanical phenomenon of exchange [71]. For conventional ferroelectric materials, it is the non-magnetic cation moving away from the center of the surrounding anions that gives the electric dipole moment, which is proportional to the atomic displacement. But for ferromagnetism, the magnetic cations usually sit at the center of the surrounding anions. The different behaviors between magnetic and non-magnetic cations can be understood by the competition between energy-lowering covalent bond formation and energy-raising electronic Coulomb repulsion [58].

As a result, the multiferroic single-phase materials would have some strict requirements on the structure symmetry. The ferroelectricity requires the time-reversal symmetry and the ferromagnetism requires the spatial-inversion symmetry [65]. Among all the possible crystallographic point groups, Shuvalov and Velov showed that only 13 point groups are possible for the coexistence of electric and magnetic ordering in the same phase [78]. Thus it is important to study the structure-property relationship while searching for multiferroic

single-phase candidate materials.

1.3.4 Local structure

With the development of diffraction technique over 100 years, the structural determination on well-ordered crystalline materials, conventionally by analyzing Bragg peaks, is mostly a solved problem. In many cases, the average crystal structure from diffraction patterns can be determined at the push of a button nowadays [79]. In reality, however, the atoms in a crystalline material could never sit at the ideal lattice site obeying the translational symmetry, due to the effects from thermal vibrations, defects, and local distortions, which results in the fact that atoms usually deviate from their average structure.

The study of strongly correlated electron systems requires the knowledge on short-range structural correlations and phase fluctuations on the nanoscale [23; 80; 81; 82; 83; 84]. On the other hand, investigating the local structures of many advanced quantum materials was not feasible if using bulk structure probes. For example, the conventional powder diffraction technique or electric/magnetic susceptibility characterization only measure the volume-integrated average quantities, which do not have the sensitivity to the local structure information especially at the quantum effect regime.

Thus, an experimental local structure probe is required, such as the pair distribution function (PDF) analysis, which is a highly effective technique measuring the local atomic arrangement of materials at the sub-nanometer length scale. The PDF method has been established as a powerful probe of local structure features that cannot be easily studied by conventional diffraction techniques. Because the short-range ordering results in diffuse scattering signals, which are usually broad and weak in the reciprocal space, as the case of conventional diffraction technique, however, these features would be sharp and strong after Fourier transforming into the real space, where we analyze the PDF data [79; 85]. So

PDF is an ideal tool for easily and effectively understanding the local structure of quantum materials as well as many other systems. As will be introduced in Chapter 2, the PDF analysis does not presume periodicity so goes well beyond bulk crystalline materials [86; 87], especially suitable for nanostructured materials [88; 89; 90; 91].

1.4 Symmetry breaking

Symmetry breaking is a common physical phenomenon in nature. For condensed matters, a few symmetric states can exhibit the symmetry breaking and become asymmetric. Take the ferromagnetism as an example, when the temperature is above the Curie temperature, the order parameter of the material, i.e., magnetization, is zero, and the magnetic dipoles would be spatially invariant as a symmetric state. However, when the temperature is below the Curie temperature, there is a spontaneous symmetry breaking and all the magnetic moments would align with the neighbors.

The local structures of materials often exhibit the symmetry breaking. The Jahn-Teller effect (JTE), or Jahn-Teller distortion, is an important mechanism of the spontaneous symmetry breaking for many materials. In 1937, Jahn and Teller first formulated the JTE [92] to explain why the break in degeneracy can stabilize the molecular system. The first experimental evidence of the JTE was carried out by Bleaney in 1950 when measuring the paramagnetic resonance in copper fluosilicate [93].

Roughly speaking, JTE refers to the phenomenon that a spatially degenerate electron orbital has a spontaneous geometrical distortion to remove the degeneracy, so as to lower the overall energy of the system and become more stable. Even for the electronic structures that do not have precisely degenerate electron orbitals, a similar tendency of JTE distortion can still be observed in the system, which is called the pseudo-Jahn-Teller effect (PJTE) [94;

95], or sometimes referred as second-order JTE. The JT-related symmetry breaking has been established to explain well for a broad range of experimental structural observations in many different molecular and solid-state systems [96; 97; 98; 99; 100; 101; 102; 103; 104], as well as supported by a series of theoretical calculations [105; 106; 107; 108; 109; 104].

The orbitals of a material represent the shape of the electron cloud. The d -orbital electrons in transition-metal oxides are important for understanding some novel properties, such as superconductivity and colossal magnetoresistance [110; 111; 112]. Here we use an octahedral complex as an example here to explain how the JTE would result in a spontaneous symmetry breaking, as depicted in Fig. 1.1 adapted from [113], in which the transition metal sits in the center and the anions or ligands, such as O^{2-} , are located at the six vertices of an octahedron. The surrounding six O^{2-} ions gives rise to the crystal field potential, which disables the rotation symmetry of electrons and brings effects on the orbital angular momentum by introducing the crystal field splitting of the d -orbital. The electrons at the d -orbitals along the x , y , and z axes, where ligands approach the metal cation, would experience greater Coulomb repulsion with the ligands than along the orbitals between anions (xy , yz , and zx directions). Thus it requires more energy to have an electron in these orbitals. This causes a splitting in the energy levels of the d -orbitals, known as crystal field splitting. The d -orbitals can therefore be classified into two types, the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals pointing toward O^{2-} ions are called e_g orbitals having higher energy, and the d_{xy} , d_{yz} , d_{zx} orbitals pointing between ions are called t_{2g} orbitals having lower energy, as shown in the left of Fig. 1.1. The splitting energy Δ_o (or Δ_{oct}) between these two orbitals would determine the order for electrons to fill these orbitals in the octahedral complex. When Δ_o is large and is larger than the energy cost for pairing electrons (spin pairing energy), electrons would pair in t_{2g} before occupying e_g . On the other hand, when Δ_o is small and is smaller than the spin pairing energy, electrons would occupy e_g before pairing in t_{2g} . The electron configuration with more

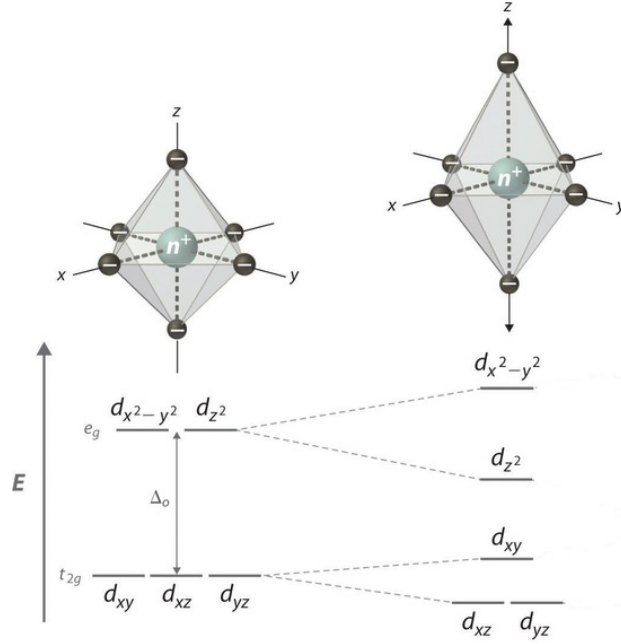


Figure 1.1: The d orbitals in an undistorted regular octahedral complex (left) and a distorted octahedron, showing the elongation Jahn-Teller distortion as an example here that the distortion can lower the energy of the system.

paired electrons is called low spin state, since the spin angular momentum S would be small, and the opposite case is called high spin state with large S .

According to the JTE theory, to further lowering the energy of the octahedral complex, the structure would be distorted to break the degeneracy. Take the elongation as an example, i.e., $c > a$ in the case of cubic to tetragonal phase transition, the d -orbitals with a z component would have lower energy, because the Coulomb interaction gets weaker when distance increases, whereas the d orbitals without a z component would be higher in energy, i.e., destabilized, and *vice versa* for the compression distortion ($c < a$). So the degenerate t_{2g} and e_g orbitals would be non-degenerate due to the symmetry breaking. In another word, for JTE to occur in transition metal oxides, there must be degeneracy in either the t_{2g} or e_g orbitals.

The local structure distortions, such as lowering the symmetry from cubic to tetragonal,

are widely observed in materials, which would help understand the mechanism behind phase transition between the low and high symmetric phases [114; 115; 116]. A local structure probe such as PDF technique, can enable the possibility for a direct observation on the local JT distortions [97; 117; 118; 119; 112; 120; 121]. This would provide the structure-property relationship insights for some novel properties, such as the colossal magnetoresistance in the manganese-based perovskite compounds [105; 122; 117; 123; 99; 112; 120; 124].

1.5 Material systems studied in this thesis

The strongly correlated d - and f -electron oxides studied in this thesis are Pr_6O_{11} , $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$, and MgTi_2O_4 , which have aroused continuous research interests accordingly in decades. In this section, the necessary basic background information on these systems will be introduced, and more detailed experimental results will be discussed in later chapters.

1.5.1 Pr_6O_{11}

The rare-earth (lanthanide) oxides with f -orbital electronic states are well known for their refractory nature and chemical stability and are of great interest for applications in electronic, magnetic, and optical devices [125]. They have also attracted considerable attentions for the potential application in catalysis [126; 127; 128].

The praseodymium oxides are particularly intriguing among the rare-earth oxides, because a series of homogeneous PrO_x compositions have been synthesized successfully, ranging from $x = 1.5$ to 2.0 , showing a wide range of stoichiometry choices. However, the choices on x is not continuous, some commonly seen compositions and corresponding average oxidation states of Pr ion for each stoichiometry are listed in Table 1.1. The phase diagram of this system, projected onto the temperature-composition plane, is shown in

Table 1.1: The stoichiometry of the homologous PrO_x series. The average oxidation state of Pr ion is also listed.

x in PrO_x	Formula	Pr oxidation
1.500	Pr_2O_3	3.000
1.714	Pr_7O_{12}	3.428
1.778	Pr_9O_{16}	3.556
1.800	Pr_5O_9	3.600
1.818	$\text{Pr}_{11}\text{O}_{20}$	3.636
1.833	Pr_6O_{11}	3.667
2.000	PrO_2	4.000

Fig. 1.2, adapted from [129]. The structures of different stoichiometry materials in this binary system were studied before [129; 130]. Their corresponding bulk average crystal structures are closely related with each other, and to a parent cubic fluorite structure, PrO_2 [131]. Transitions between these phases can be achieved by heating and cooling [129; 132].

The PrO_2 material has a fluorite structure and is usually described in terms of a face-centered-cubic unit cell which contains four units of PrO_2 , as shown in Fig. 1.3.

The Pr_6O_{11} (or $\text{PrO}_{1.833}$) is a unique composition because the phase of Pr_6O_{11} , rather than the parent phase PrO_2 , is stable at ambient temperature in air. The material under study in this thesis is Pr_6O_{11} nanoparticles. They are semiconductor nanoparticles, which have many emerging applications as modern electronic [133; 134; 135], catalytic [136; 137; 138], sensing [139], and electrochemical [140; 141; 142] materials. Pr is the second most naturally abundant rare-earth element and has the electronic configuration of $4f^35d^06s^2$. The switchable oxidation state of Pr ion between Pr^{3+} and Pr^{4+} makes Pr_6O_{11} (average oxidation state $\text{Pr}^{3.667+}$) an exceptional redox active electrode material for electrochemical supercapacitors [140].

The electrical resistivity of the Pr_6O_{11} nanoparticles spans several orders of magnitude

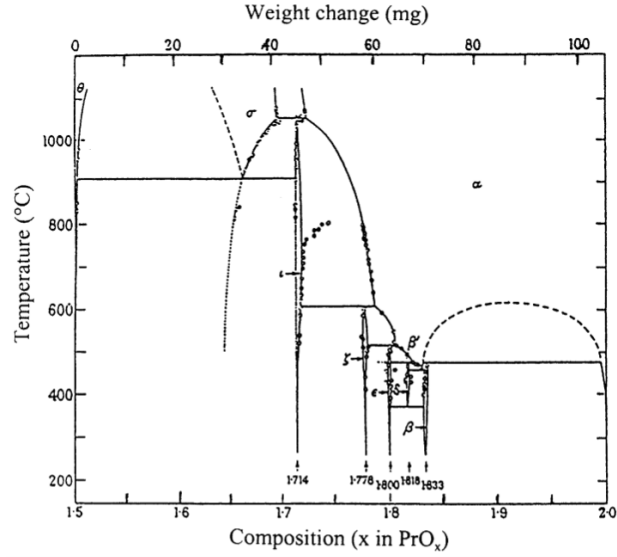


Figure 1.2: The projected phase diagram of PrO_x on the temperature-composition plane.

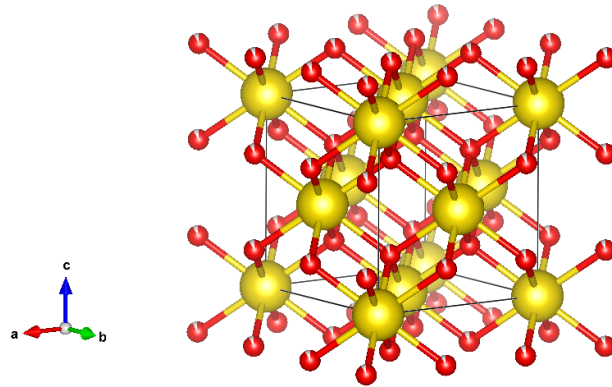


Figure 1.3: The crystal structure of cubic Pr_6O_{11} fluorite structure. The Pr and O atoms are shown in yellow and red, respectively. The occupancy of oxygen site is set as 0.917 to match the Pr_6O_{11} composition.

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within a very narrow temperature range, decreasing from $10^8 \Omega$ to $10^4 \Omega$ when heating from RT to 350°C . A hard x-ray photon-in photon-out spectroscopy study demonstrated that the delocalization of f -electrons would be the key to explain the changes in the electrical conductivity [143].

Numerous experiments have been carried out on the Pr_6O_{11} systems for the investigation on how the fluorite structure motif gives rise to its unique electrical properties. For example, the x-ray conventional diffraction experiments were performed and reported in many references [144; 145; 146; 147; 148], but with only limited number of neutron diffraction measurements on its PrO_x members [149; 150; 151], which were mostly centered on the magnetic structure, not atomic structure.

By analogy with the d -electrons in many transition-metal oxides, the f -electrons play an important role for the electrical properties in rare-earth oxides. Thus, we would like to extend the combined neutron and x-ray PDF (NXPDF) analysis on Pr_6O_{11} nanoparticles to investigate how the local structure changes in response to the delocalization of f -electrons when temperature changes. Considering that Pr was a strong scatterer for x-rays (Pr $Z = 59$) and O has a large neutron coherent scattering length ($b = 5.803 \text{ fm}$ for O, where $1 \text{ fm} = 1 \times 10^{-15} \text{ m}$), we combined the neutron and x-ray scattering information to accurately determine both Pr and O sublattices so as to understand the full picture of the structure. The simulated x-ray and neutron PDFs for Pr_6O_{11} cubic fluorite model are shown in blue and red curves in Fig. 1.4, respectively. Clearly, the Pr-Pr bonds and O-O bonds are evident in x-ray and neutron PDF, separately, which illustrated that a combination of neutron and x-ray signals would be an effective tool to investigate Pr_6O_{11} system, especially on how the local atomic structure of Pr and O sublattice changes when temperature changes.

In this thesis, we applied the NXPDF analysis, as will be described in Chapter 2 and 3, to study the local structure changing of the Pr_6O_{11} semiconductor nanoparticles from room

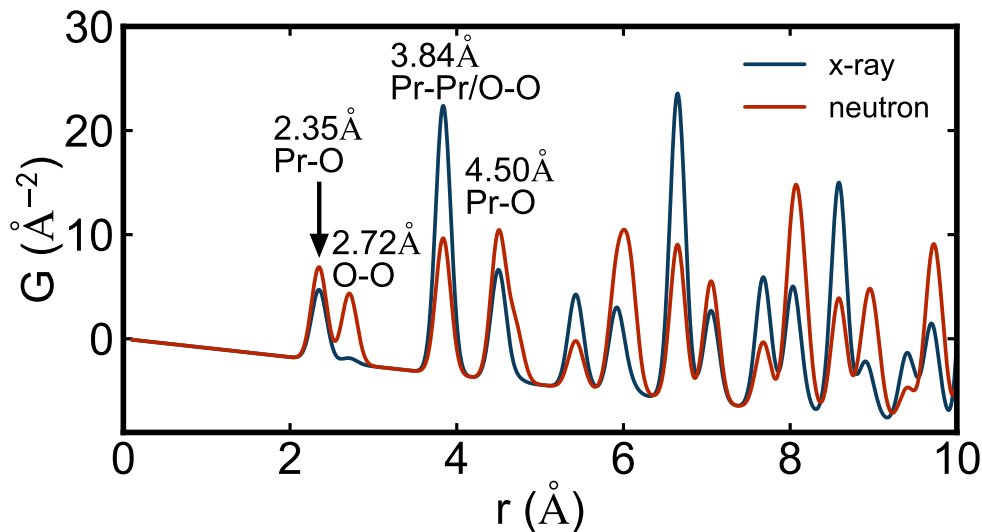


Figure 1.4: The simulated x-ray (blue) and neutron (red) PDFs for Pr_6O_{11} cubic fluorite model.

temperature to high temperature.

1.5.2 $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$

Barium titanate (BaTiO_3) is one of the most extensively studied perovskite materials. The general chemical formula for perovskite compounds is ABX_3 , where A and B are two cations that A is usually an alkaline-earth or rare-earth element while B is usually a transition-metal element, and X is an anion such as oxygen ion that forms the A-O and B-O bondings to both cations. The crystallographic unit cell of cubic BaTiO_3 structure is shown in Fig. 1.5, that B-site (Ti) cation sits in the center of unit cell, forming the BO_6 octahedron, and the A-site cations occupy the corners of unit cell.

The origin of perovskites can be traced back to 1839. A calcium titanate mineral was found in the Ural Mountains by Gustav Rose. This class of compounds having the same type of crystal structure as CaTiO_3 , which was named as “perovskite” in honor of the Russian mineralogist Lev von Perovski [152; 153]. The first crystal structure of perovskite studied by

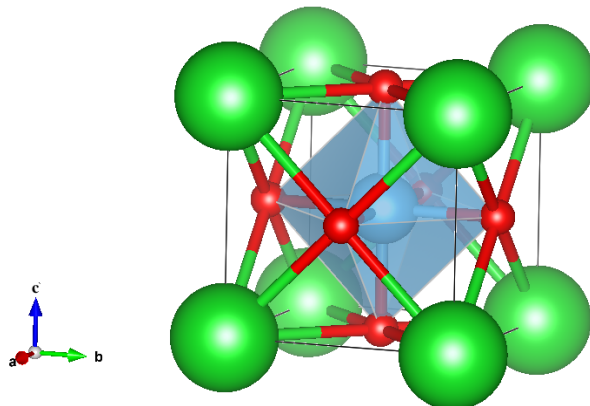


Figure 1.5: The crystallographic unit cell of BaTiO_3 perovskite centrosymmetric cubic structure. The Ba, Ti, and O atoms are shown in green, blue, and red, respectively. The blue polyhedra represents the TiO_6 octahedra.

x-ray diffraction is barium titanate (BaTiO_3), by Megaw in 1945 [154]. It is also the first discovered ferroelectric perovskite [155]. Its highly symmetric cubic crystal system, space group (s.g.) $Pm\bar{3}m$, can have the symmetry breaking which results in the non-centrosymmetric structures, such as tetragonal (s.g. $P4mm$), rhombohedral (s.g. $R3m$), and orthorhombic (s.g. $Amm2$) [156]. Without the centrosymmetric constrain, the B site ion (Ti atom) would not be fixed at the center of unit cell anymore, instead, it can form a polarization along different directions, i.e., $\langle 001 \rangle$ axes for tetragonal phase, face diagonal $\langle 011 \rangle$ for orthorhombic phase, and body diagonal $\langle 111 \rangle$ for rhombohedral phase. In this way, the distorted TiO_6 octahedron will form an electric dipole moment and its magnitude is proportional to the displacement of Ti atom away from the unit cell center. As a result, the non-centrosymmetric structure itself would have the ferroelectric property whereas the centrosymmetric cubic structure is paraelectric. It has phase transitions among these structures when temperature changes, the bulk BaTiO_3 material can change from rhombohedral (below -90°C), orthorhombic (-90 to 5°C), tetragonal (5 to 120°C), to cubic (above 120°C) on warming [156; 157]. The nanocrystalline BaTiO_3 have the similar phase transition behavior, though the

transition temperatures would be different from the bulk form [158].

This unique structure-property relationship attracts a lot of research interests in BaTiO_3 due to its room temperature ferroelectricity [159; 156] and high dielectric constant [160], which is ideal for industrial applications in piezoelectric devices [161; 162], capacitors [163; 164; 165], and thermistors [166; 167]. Even seventy years after its discovery, barium titanate is still the most important ceramic dielectric material.

In the recent decade, there is a growing interest in exploring the materials that exhibit both ferroelectric and ferromagnetic properties, i.e., multiferroics [58; 65]. The coupling between these two order parameters can potentially enable the control of ferromagnetic behavior by an electric or magnetic field and a magnetic bit may be complemented by an electric bit to establish a four-state memory element instead of two states [63; 64] as well as the applications for quantum computing [168; 169].

To obtain single-phase multiferroic materials, one possible solution is by doping a magnetic species into a known ferroelectric material [53]. Barium titanate is a promising candidate material because of its versatility in electronic applications. The nanocrystalline BaTiO_3 was found to have a strong ferroelectric polarization down to 5 nm crystallite size [170; 171]. As a result, it is of great interest to pursue the development of multiferroic compounds based on the nanoscale BaTiO_3 .

Iron can be doped into BaTiO_3 for achieving multiferroics, as supported by a series of theoretical calculations [172; 173; 174; 175; 176]. Extra care is needed for monitoring whether the perovskite BaTiO_3 still keeps the ferroelectric phase when Fe is doped into the system, plus validating the existence of the ME coupling effects of the material. However, most of the published experimental work on the Fe-doped BaTiO_3 [177; 178; 179; 180] only reported the long-range ordering structure information from conventional x-ray powder diffraction or the qualitative structural morphology based on spectroscopic characterizations such as

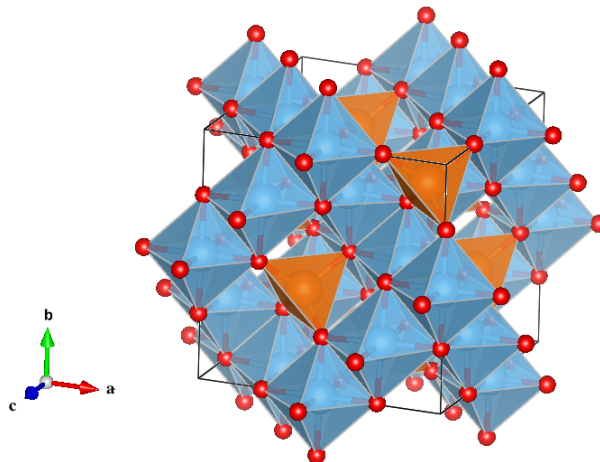


Figure 1.6: The crystal structure of cubic MgTi_2O_4 spinel structure. The orange polyhedra are the MgO_4 tetrahedra and the blue polyhedra represent the TiO_6 octahedra.

transmission electron microscopy (TEM). A quantitative local structure probe, such as PDF technique, is required to understand the full picture of the structure-property relationship in iron-doped barium titanate.

In this thesis, the full series of $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ nanocrystals ($x = 0, 0.1-0.3, 0.5, 0.75, 1.0$), ranging from undoped, low-doped, to high-doped conditions were synthesized using the uniform and aggregate-free gel collection method [181]. The PDF analysis was applied to investigate the detailed local structure distortions of the synthesized nanocrystals, and to determine the existence of multiferroics.

1.5.3 MgTi_2O_4

MgTi_2O_4 is a transition-metal compound. It is a spinel material with the AB_2X_4 formula, where A and B are cations and X is an anion such as O or S. Its crystal structure is complicated, as visualized in Fig. 1.6, that B cations form a pyrochlore lattice, the geometrically frustrated network of corner-sharing tetrahedra.

The crystal structure of spinel material was first determined by William Henry Bragg [182]

and Nishikawa [183] independently in 1915. This polyhedral arrangement is consistent with several space groups ranging from the high-symmetry cubic crystal system, space group (s.g.) $Fd\bar{3}m$, to lower symmetry systems such as the cubic crystal system with s.g. $P4_132$, the tetragonal crystal system (s.g.: $P4_12_12$, $I41/amd$, $I41/a$, $P\bar{4}m2$), and the rhombohedral crystal system (s.g.: $R3$) [184]. In many research work, if the spinel material has a phase transition between high- and low-symmetries, conventionally, the high-symmetry spinel structure is referred as the disordered phase, and the low-symmetry one is the ordered phase.

The structures of mineral species belonging to the spinel family can be described in terms of a heteropolyhedral framework. The AX_4 tetrahedra is isolated from each other and sharing corners with the neighboring BX_6 octahedra, as depicted by the orange and blue polyhedra in Fig. 1.6, respectively. The BX_6 octahedron shares six of its twelve X-X edges with the nearest BX_6 octahedra.

Such unique and complicated structure motif makes spinels exhibit remarkable electrical, optical, and magnetic properties [185]. The spinel family is also one of the most extensive series of related chemical compounds found in nature, with more than 200 of different combinations for the A, B, and X elements. Many of the naturally formed oxide spinels, such as $MgAl_2O_4$ and $ZnAl_2O_4$, are transparent materials with high optical refractive index and with a high hardness just below diamond and corundum. but are much cheaper, they are important in the traditional jewelry trade and other decorative purposes in the past 100 years [186]. Nowadays, their application in the electronic devices attracts more of people's attentions to make use of the promising high-frequency magneto-dielectric property of some spinel materials [187; 188; 189]. Besides, the luminescent properties of some spinels serve as the basis to search for advanced optical host materials, such as the Cr^{3+} , Mn^{2+} , and Eu^{3+} doped $MgGa_2O_4$ that has strong luminescence over the visible light wavelength range [190; 191; 192]. In addition, many of the transition oxide spinels play an important role in chem-

ical catalysts [193; 194; 195; 196; 197] and superconductors [198; 199]. Overall, the spinel family has shown rich functionalities in different fields.

For instance, the CuIr_2S_4 spinel system has many exotic properties, such as a transition from paramagnetic metal to diamagnetic insulator on cooling [200; 201; 202], the formation of structural isomorphic octamers [203; 204], and anomalous electrical properties [205; 206]. In particular, CuIr_2S_4 has broken symmetries in its ground state accompanied by formation of charge order, orbital order, and the creation of magnetic spin singlets on dimerized Ir^{4+} - Ir^{4+} pairs [204].

CuIr_2S_4 and MgTi_2O_4 were found to be quite similar in the structure motif, as well as physical properties [207].

One of the most interesting phenomena of these two systems is that they both exhibit a temperature-induced MIT [208; 209]. They both have a global symmetry lowering, from cubic to tetragonal phase on cooling through MIT. The heat capacity and magnetic susceptibility measurements on the CuIr_2S_4 and MgTi_2O_4 establish that it is likely to be a first-order phase transition [208; 210] though some disagreements exist [209].

A series of earlier experiments have been carried out on these two systems using different techniques to understand their electrical and magnetic properties related with the structures. For example, the neutron and x-ray conventional diffraction methods were used to determine the cubic and tetragonal average structures [211; 209]. In addition, a series of theoretical studies were also applied to understand their structure-property relationship more in detail [211; 212; 213; 214].

However, there is an unsolved problem about the anomalous electrical resistivity behavior in the high-temperature metallic phase. The measured temperature-dependent electrical resistivity $\rho(T)$ curve of MgTi_2O_4 was found to have a negative slope above MIT [210], and that of CuIr_2S_4 has an unusual exponential-type temperature dependence [205], suggesting

an anomalous metallic behavior in the high- T metallic state for MgTi_2O_4 and CuIr_2S_4 . This phenomenon is related with the mechanism underlying the MIT, the origin of which has been attributed to an orbital-selective Peierls mechanism [207].

In this thesis, we applied a combined neutron and x-ray PDF (NXPDF) analysis to understand the full picture of the mechanism behind MIT. By analogy with CuIr_2S_4 [215], partially filled t_{2g} transition-metal orbital manifolds of MgTi_2O_4 , which are triply degenerate in the average cubic symmetry, utilize their favorable overlaps fostered by the pyrochlore sublattice topology to form an orbital-degeneracy-lifted (ODL) state, which would help understand the mechanism of MIT in this system.

1.6 Thesis outline

This thesis will focus on the combination of neutron and x-ray PDF (NXPDF) analysis for different d - and f -electron oxides. The following chapters will be structured as follows.

In Chapter 2, a basic scattering and PDF theory and an overview of NXPDF experimental methods are introduced. The complementary nature of neutron and x-ray scattering are highlighted to establish the importance of NXPDF technique for a comprehensive understanding of material structures. In Chapter 3, I will introduce a new approach to obtain candidate atomic structures designed for NXPDF, called structure-mining, which can automatically find the best-fit candidate atomic structures for the given neutron and x-ray PDF data. Some testing examples will be shown to illustrate its robust structure searching work for quantum materials and many other different systems. In Chapter 4, the semiconductor Pr_6O_{11} nanoparticles are investigated by the NXPDF method, monitoring how the Pr and O atomic sublattices change with temperature, which induces the change of electrical resistivity. In Chapter 5, the multiferroic behavior in the iron doped barium ti-

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tanate $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ nanocrystals is also studied by the PDF analysis. The coexistence of ferroelectric and ferromagnetic properties of the system is established from the PDF modeling based on the structure-property relationship, which is further validated by sample characterizations. Lastly in Chapter 6, the NXPDF experimental study on MgTi_2O_4 , which has a temperature-induced metal-insulator transition. The orbital-degeneracy-lifting (ODL) theory is presented to explain the anomalous electrical resistivity behavior in the high-temperature metallic phase.

Chapter 2

The neutron and x-ray pair distribution function (PDF) technique

2.1 Overview of the PDF technique

The pair distribution function (PDF) is a local structure probe based on diffraction experiments. It exploits the scattering of particles (x-rays, neutrons, or electrons) from a material to obtain detailed information about the local atomic arrangements. It gives the scaled probability of finding two atoms in a material a distance r apart and is related to the density of atom pairs in the material. It does not presume periodicity and so goes well beyond just well-ordered crystals [79; 85].

The advantage of the PDF technique over the conventional diffraction method is its sensitivity to short-range structural correlations, which may deviate largely from the average long-range structure probed by the traditional diffraction technique. This sensitivity to the local atomic arrangements is because, different from the conventional diffraction, PDF is based on the total scattering data, which include both the strong Bragg peaks and weak dif-

CHAPTER 2. THE NEUTRON AND X-RAY PAIR DISTRIBUTION FUNCTION (PDF) TECHNIQUE

fuse scattering [79; 85]. The Bragg peaks gives the long-range average structure information, and the diffuse scattering, which is the key for PDF technique, provides the insights on how the local structure deviates from the average structure.

In the absence of long-range periodicity, such as for nanomaterials, glasses, liquids, and amorphous materials, the strong Bragg peaks may be weaker and even disappear, whereas the diffuse scattering signals containing local structure information would be evident and important. This gives rise to the nanostructure problem [84], and PDF is an ideal technique to analyze it.

As discussed in Section 1.3, since the properties of materials have close relationship with the local atomic structure, the PDF technique can provide unique insights into the structure-property relationship for a variety of complex materials. PDF analysis of x-ray and neutron powder diffraction datasets has been demonstrated to be an excellent tool for studying local structures of many advanced materials, especially nanostructured materials [88; 216; 89; 90; 217; 218; 219; 91], but also bulk crystalline materials [86; 87; 220; 221].

The PDF analysis is mostly used for analyzing powder samples, i.e., taking the isotropic averaging on material properties. It also works well for other types of samples, such as thin films [222; 223], liquids [224], and single crystals [225], and the corresponding PDF concepts and analysis methods are under active development, for instance, 2-dimensional texture PDF for thin films [226] and 3-dimensional (or 3D- Δ) PDF for single crystals [227; 228].

During a PDF experiment, the phase ordering of materials can be investigated when the external environment parameters are controlled, such as temperature, pressure, and magnetic fields. Most PDF beamlines can control the sample temperature ranging from low (a few K using cryostat), intermediate (100 K to 500 K using cryostream), to high temperature (up to around 1000 K using furnace). This allows us to explore how the local structure changes as

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a function of temperature, so as to investigate the physics behind thermal phase transitions.

The PDF can also be applied to study materials under real conditions, for example *in situ* and *operando* diffraction experiments such as *in situ* synthesis to monitor how the structure changes with the real-time ongoing synthesis process [229; 230; 231; 232; 233; 234; 235; 236; 237].

The atomic PDF analysis of x-ray and neutron diffraction data is getting popular and more widely used for studying material structures in the recent decade [84; 79; 85]. However, PDF is not a new member of the scattering technique family, instead it is more than 90 years old. The ideas behind the PDF methods can be tracked back to the work by Zernike and Prins in 1927, who first derived the formalism for the correlation functions of atomic pair density [238]. It gives a histogram of atom pair distances, and this is why we call it “pair distribution function”.

This approach was applied as early as in 1930 by Debye and Menke to study liquid mercury [239]. In the late 1930s, Warren and his colleagues performed a series of significant structure studies based on radial distribution function analysis, which is closely related with PDF [240; 241; 242; 243]. Since then, the early PDF studies were almost exclusively focusing on the study of liquids, glass, and amorphous materials [244; 245; 246; 247].

In the 1980s when pulsed spallation neutron sources became available, such as the Intense Pulsed Neutron Source (INPS) at Argonne National Laboratory, which was the world’s first pulsed neutron scattering instrument open to public scientific researchers [248], the PDF technique was tried to study the local disordering in quasicrystalline and crystalline materials by the group of Egami [249; 250]. More recently, with the development of modern synchrotron x-ray sources and more powerful spallation neutron sources, studying the nanostructured and complex materials become a new focus in the PDF community [251; 88; 216; 252; 89; 253; 217; 218; 254; 255; 256]. A more detailed history of PDF technique can be found in the

references [257; 79].

2.2 Basic scattering theory

Before deriving the PDF equations, a basic introduction on the scattering theory is provided here as foundations. A detailed description of x-ray or neutron diffraction can be found in many references and textbooks [258; 259; 260], and it is not the purpose of this section.

The Bragg's law was established by William Henry Bragg and his son William Lawrence Bragg in 1913 [261], who won the Nobel Prize in Physics together in 1915. The Bragg equation,

$$2d_{hkl} \sin \theta = \lambda, \quad (2.1)$$

opens the door of the whole crystallography arena. The d_{hkl} represents the interplanar distance of the (hkl) atomic plane, denoted by Miller indices, θ refers to the half angle between incident and scattered wave vector, k_i and k_f , and λ stands for the wavelength of the incident x-ray or neutron beam.

Thus, the momentum transfer Q , representing the difference between incoming k_i and scattered beam k_s , where $|k_i| = |k_s| = \frac{2\pi}{\lambda}$ for an elastic scattering process, can be expressed as

$$\vec{Q} = \vec{k}_s - \vec{k}_i, \quad (2.2)$$

and from the geometry, it is clear that

$$|\vec{Q}| = 2|\vec{k}| \sin \theta = \frac{4\pi \sin \theta}{\lambda}, \quad (2.3)$$

The $\vec{Q}$ is also called scattering vector in convention.

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The scattering information can be analyzed to determine the atomic structure of materials. Within a material structure, there is a set of i atoms at points r_i , and r_i is the vector from the origin to the i -th atom. In the assumption of kinematical limit, the scattering amplitude from one atom can be written as

$$\Psi_i(\vec{Q}) = f_i(\vec{Q}) \exp(i\vec{Q} \cdot \vec{r}_i), \quad (2.4)$$

where $\vec{Q}$ is the scattering vector, or momentum transfer, and $f_i(\vec{Q})$ is the atomic form factor of the i -th atom which describes the scattering ability of an isolated atom, defined as

$$f_i(\vec{Q}) = \int_V \rho(\vec{r}_i) \exp(i\vec{Q} \cdot \vec{r}_i) d^3r_i, \quad (2.5)$$

where $\rho(\vec{r}_i)$ is the spatial density of the scatterer about its center of mass. Due to the Fourier transform relationship, when the distribution of the scatterer $\rho(\vec{r}_i)$ gets broader in real space r , the distribution of the form factor $f_i(\vec{Q})$ would be narrower in reciprocal space Q , i.e., faster decaying in higher Q .

Thus the scattering amplitude from a set of i atoms at points $\vec{r}_i$ is simply summing over all the $\Psi_i(\vec{Q})$,

$$\begin{aligned} \Psi(\vec{Q}) &= \sum_i \Psi_i(\vec{Q}) \\ &= \sum_i f_i(\vec{Q}) \exp(i\vec{Q} \cdot \vec{r}_i) \end{aligned} \quad (2.6)$$

The full coherent scattering intensity is given by

$$\begin{aligned} I_c &= |\Psi(\vec{Q})|^2 \\ &= \Psi^*(\vec{Q}) \Psi(\vec{Q}) \\ &= \sum_i \sum_i f_j^* f_i \exp[i\vec{Q} \cdot (\vec{r}_i - \vec{r}_j)] \\ &= \sum_{i,j} f_j^* f_i \exp(i\vec{Q} \cdot \vec{r}_{ij}). \end{aligned} \quad (2.7)$$

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Here we dropped the Q -dependence of the atomic form factors to simplify the notation in the following derivation, but the f 's are understood to retain the Q -dependence as defined in Eq. 2.5. The interatomic distance vector $\vec{r}_{ij} = |\vec{r}_i - \vec{r}_j|$ represents the distance between atoms i and j .

We can further separate out the self-scattering contribution, i.e., $i = j$ and $\vec{r}_{ij} = 0$, from I_c :

$$\begin{aligned} I_c &= \sum_{i=j} f_i^* f_i \exp(i\vec{Q} \cdot 0) + \sum_{i \neq j} f_j^* f_i \exp(i\vec{Q} \cdot \vec{r}_{ij}) \\ &= N\langle f^2 \rangle + \sum_{i \neq j} f_j^* f_i \exp(i\vec{Q} \cdot \vec{r}_{ij}), \end{aligned} \quad (2.8)$$

where N is the total number of atoms in the material.

In another word, the distinct scattering intensity for $i \neq j$ can be written as

$$\begin{aligned} I_d &= I_c - N\langle f^2 \rangle \\ &= \sum_{i \neq j} f_j^* f_i \exp(i\vec{Q} \cdot \vec{r}_{ij}), \end{aligned} \quad (2.9)$$

and the totally incoherent scattering, i.e., self-scattering for $i = j$, from each atom i itself, would be

$$\begin{aligned} I_{inc} &= \sum_i \Psi_i^*(\vec{Q}) \Psi_i(\vec{Q}) \\ &= \sum_i f_i^*(\vec{Q}) f_i(\vec{Q}) \\ &= \sum_{\alpha} N_{\alpha} f_{\alpha}^*(\vec{Q}) f_{\alpha}(\vec{Q}) \\ &= N \sum_{\alpha} c_{\alpha} f_{\alpha}^*(\vec{Q}) f_{\alpha}(\vec{Q}) \\ &= N\langle f^2 \rangle, \end{aligned} \quad (2.10)$$

where α represents the different species of atoms in the sample and N_{α} is the number of atoms of type α . The concentration of species α can be defined as $c_{\alpha} = N_{\alpha}/N$. The asterisk

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indicates the complex conjugate and the angle brackets indicate a sample average as defined in the equation.

Now we have defined all the necessary quantities for deriving the PDF equations in the Section 2.3.

As a side note, in the traditional diffraction theory for a well crystalline material, with the help of periodicity (translational symmetry along three dimensions), it is not necessary to sum over all atoms in the material to calculate the scattered intensity. Instead, only the atoms in the unit cell need to be summed over. The intensity of a Bragg reflection hkl is proportional to the squared absolute value of crystallographic structure factor F_{hkl} , as given by

$$F_{hkl} = \sum_{i=1}^{N_{uc}} f_i \exp[-2\pi i (hx_i + ky_i + lz_i)], \quad (2.11)$$

where the sum is only over the totally N_{uc} atoms in the unit cell, x_i, y_i, z_i are the positional coordinates of the i -th atom. It is obvious that the square of absolute value, $|F_{hkl}|^2$, is exactly in the form of the coherent scattering intensity, Eq. 2.7, though the latter has no presumption of the translational symmetry of unit cell.

An alternative view using the Fourier transform concept may help understand the scattering process. In crystallography, the lattice and basis can be treated separately and they get convoluted together to form the crystal structure, i.e., (structure) = (lattice) * (basis), where the symbol * denotes the convolution operation. The scattering process is mathematically equivalent to the Fourier transform, $\mathcal{F}(\text{structure}) = \mathcal{F}(\text{lattice}) \cdot \mathcal{F}(\text{basis})$, i.e., (scattering) = (reciprocal lattice) · (structure factor). Thus, the lattice determines the positions of diffracted beams, and the basis gives the crystallographic structure factor F_{hkl} which gives the amplitude and phase of the diffracted beams. Now, let us go back to the real space via the (inverse) Fourier transform again to get the PDF in Section 2.3.

2.3 Deriving the PDF equations

The PDF, $G(r)$, can be defined in real-space quantities, as a function of the atomic pair density, $\rho(r)$ [238],

$$G(r) = 4\pi r [\rho(r) - \rho_0], \quad (2.12)$$

where ρ_0 is the number density of material, given by the number of atoms per unit volume.

It can be defined in reciprocal space quantities as well, as a function of the reciprocal-space scattering intensity, $F(Q) = Q[S(Q) - 1]$ as follows [262; 79]:

$$G(r) = \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} F(Q) \sin(Qr) dQ, \quad (2.13)$$

where Q is the magnitude of the scattering momentum transfer, $Q_{\min}$ and $Q_{\max}$ are the minimum and maximum accessible Q range in the diffraction experimental setup, respectively. Their effects on PDF will be discussed in detail later. The total scattering structure function, $S(Q)$, is extracted from the Bragg and diffuse components of x-ray, neutron, or electron powder diffraction pattern.

It is noteworthy to mention here that different definition of correlation functions were used in numerous different definitions of PDF in the history, which is summarized in the reference [263]. The PDF $G(r)$ and its definition in Eq. 2.13 is used throughout the thesis to keep the same notations as in [79; 85].

Now let us start deriving the formalism for atomic pair distribution function (PDF) to achieve its definition in Eq. 2.13 in the following steps [85].

The only quantity in Eq. 2.13 we do not know yet is the total scattering structure function, $S(Q)$. From the Faber-Ziman formalism [264], the structure function $S(Q)$ is defined as

$$S(Q) = \frac{I_c(Q)}{N\langle f \rangle^2} - \frac{\langle (f - \langle f \rangle)^2 \rangle}{\langle f \rangle^2}. \quad (2.14)$$

Since the atomic form factor f is Q -dependent for x-rays, it has been customary to introduce

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the total structure factor (or interference function), defined in such a way that it will modulate about a constant, usually chosen to be unity. The second term in this definition is the Laue monotonic diffuse scattering, which is from the imperfect cancellation of intensity at the destructive interference condition when atomic sites are occupied by atoms of different scattering length, that results in a monotonically decreasing background. The Laue diffuse scattering term can be further expanded as follows:

$$\begin{aligned}\frac{\langle (f - \langle f \rangle)^2 \rangle}{\langle f \rangle^2} &= \frac{\langle f^2 - 2f\langle f \rangle + \langle f \rangle^2 \rangle}{\langle f \rangle^2} \\ &= \frac{\langle f^2 \rangle - \langle f \rangle^2}{\langle f \rangle^2} \\ &= \frac{\langle f^2 \rangle}{\langle f \rangle^2} - 1.\end{aligned}\tag{2.15}$$

Thus, substituting Eq. 2.15 into Eq. 2.14, we have

$$S(Q) = \frac{I_c}{N\langle f \rangle^2} - \frac{\langle f^2 \rangle}{\langle f \rangle^2} + 1.\tag{2.16}$$

So the first step to derive the PDF equation is about normalizing the coherent scattering intensity I_c in Eq. 2.8, and removing the incoherent scattering contribution to get $S(Q)$. We therefore normalize I_c by the total number of scatterers in the material, N ,

$$\frac{I_c}{N} = \langle f^2 \rangle + \frac{\sum_{i \neq j} f_j^* f_i \exp(i\vec{Q} \cdot \vec{r}_{ij})}{N}.\tag{2.17}$$

Subtracting the normalized self-scattering term,

$$\frac{I_c}{N} - \langle f^2 \rangle = \frac{\sum_{i \neq j} f_j^* f_i \exp(i\vec{Q} \cdot \vec{r}_{ij})}{N},\tag{2.18}$$

and then normalizing by the square of form factor, $\langle f \rangle^2$, to match the definition of $S(Q)$, we can have

$$\frac{I_c}{N\langle f \rangle^2} - \frac{\langle f^2 \rangle}{\langle f \rangle^2} = \frac{\sum_{i \neq j} f_j^* f_i \exp(i\vec{Q} \cdot \vec{r}_{ij})}{N\langle f \rangle^2}.\tag{2.19}$$

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Now inserting Eq. 2.19 into Eq. 2.16, we obtain

$$\begin{aligned}
 S(Q) - 1 &= \frac{I_c}{N\langle f \rangle^2} - \frac{\langle f^2 \rangle}{\langle f \rangle^2} \\
 &= \frac{I_d}{N\langle f \rangle^2} \\
 &= \frac{\sum_{i \neq j} f_j^* f_i \exp(i\vec{Q} \cdot \vec{r}_{ij})}{N\langle f \rangle^2}.
 \end{aligned} \tag{2.20}$$

This $S(Q) - 1$ term represents the distinct scattering intensity normalized by the total number and the mean scattering of scatterers.

The second step is taking the orientational averaging to calculate the $S(Q) - 1$ term in Eq. 2.20. The PDF method is typically applied for studying the structure of powdered samples, i.e., isotropic samples, assuming the crystallites having every orientation are in equal probability. Thus we can take an orientational averaging to simplify the calculation of Eq. 2.20. We can define θ as the angle between $\vec{Q}$ and $\vec{r}_{ij}$, such that $\vec{Q} \cdot \vec{r}_{ij} = Qr_{ij} \cos \theta$. The orientational averaging implies that θ has an equal probability to appear in every direction in space. Therefore, the averaged complex exponential factor would be

$$\begin{aligned}
 \overline{\exp(i\vec{Q} \cdot \vec{r}_{ij})} &= \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi \exp(iQr_{ij} \cos \theta) \sin \theta d\theta \\
 &= \frac{\sin(Qr_{ij})}{Qr_{ij}}.
 \end{aligned} \tag{2.21}$$

Meanwhile, as a side note, using this useful isotropic approximation for Eq. 2.7, we can have the average coherent scattering intensity, i.e., the famous Debye equation [265],

$$I_c = \sum_{i,j} f_j^* f_i \frac{\sin(Qr_{ij})}{Qr_{ij}}. \tag{2.22}$$

Now using the isotropic approximation for $S(Q) - 1$ in Eq. 2.20, we get the total scattering structure function for an isotropic sample as,

$$S(Q) - 1 = \frac{\sum_{i \neq j} f_j^* f_i \frac{\sin(Qr_{ij})}{Qr_{ij}}}{N\langle f \rangle^2}. \tag{2.23}$$

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Thus, the reduced total scattering structure function, $F(Q) = Q[S(Q) - 1]$, is

$$F(Q) = \frac{\sum_{i \neq j} f_j^* f_i \frac{\sin(Qr_{ij})}{r_{ij}}}{N\langle f \rangle^2}. \quad (2.24)$$

At this point we have everything ready for the PDF expression in Eq. 2.13, but before performing the final Fourier transform step, it is worthwhile to describe the atomic form factor issue. The Q dependence of the x-ray atomic form factor f is problematic in the Fourier transform when the material is made up of more than one atomic species, because we can never know the different Q dependencies of contributions from various atomic species to the scattering intensity in reality. This Q -dependent behavior of x-ray atomic form factor needs to be approximated in some way to simplify the calculation. First, the f is assumed to be isotropic such that it only depend on the scalar Q , not vector $\vec{Q}$, considering that x-ray scattering signal is mainly from the core electrons of the material. Second, we can separate out the $Q = 0$ from Q dependence, $f(Q) = f(0)\tilde{f}(Q)$, where $f(0)$ is equal to the number of the scattering electrons in the atom type, which is generally taken to be the atomic number Z (though it is indeed more accurate to use the number of electrons on the ion rather than Z if scattering from ions), $\tilde{f}(Q)$ contains the Q -dependence of the form factor, with a value of 1 at $Q = 0$. Third, we can apply the Warren-Krutter-Morningstar approximation [240] to calculate the $\tilde{f}(Q)$ term, assuming that the Q -dependent part can be well approximated by an average Q dependence,

$$\overline{\tilde{f}(Q)} = \frac{\sum_{\alpha} c_{\alpha} \tilde{f}_{\alpha}(Q)}{N_{species}}, \quad (2.25)$$

where $N_{species}$ is the number of different atomic species in the material and α represents the different species of atoms in the sample. In this case, the Q -dependent part, $\tilde{f}(Q)$ can be moved out of the double sums in Eq. 2.24 and get canceled out in the denominator and numerator. Thus, the f terms left would be Q -independent, and the value is approximated to be $f(0)$ and is replaced by the atomic number Z . But for neutron scattering, f is a

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constant (f is conventionally denoted as the coherent neutron scattering length b), i.e., Q -independent, because neutrons interact with the nuclei of materials during the scattering process, which is much smaller in physical size (about 10^{-5} Å) than the incident neutron beam wavelength (about 1 Å), thus no orbital momentum is involved in the neutron scattering process. So no approximation is needed here for neutron scattering. The errors introduced by the Warren-Krutter-Morningstar approximation to the processed PDF is similar to the thermal factor effects and it can be recognized as a temperature-independent contribution to the atomic displacement factors when performing PDF fit to the data [266]. The detailed description on the neutron coherent scattering length b and x-ray atomic form factor f will be explained in Section 2.4. Some attempts have been made to take this Q -dependence into consideration or expand the approximation to higher order for a more accurate treatment for atomic PDF calculations [267; 268; 269], but in many cases the Warren–Krutter–Morningstar approximation still performs rather good, and is not the factor limiting the accuracy of PDF modeling.

Now we are able to take the final Fourier transform step to get the PDF equation. We take the (inverse) Fourier transform of the reduced total scattering structure function $F(Q)$. The sine Fourier transform is applied since $F(Q)$ is an odd function of Q ,

$$\begin{aligned}\mathcal{F}(r) &= \frac{2}{\pi} \int_0^\infty F(Q) \sin(Qr) \, dQ \\ &= \frac{2}{\pi N \langle f \rangle^2} \int_0^\infty \sum_{i \neq j} f_j^* f_i \frac{\sin(Qr_{ij})}{r_{ij}} \sin(Qr) \, dQ \\ &= \frac{2}{\pi N \langle f \rangle^2} \sum_{i \neq j} \frac{f_j^* f_i}{r_{ij}} \int_0^\infty \sin(Qr_{ij}) \sin(Qr) \, dQ.\end{aligned}\tag{2.26}$$

Notice that $\mathcal{F}$ is used to indicate the Fourier transform operation. In mathematical notations, f is the conventional notation for a real space function in the Fourier transform, however, since f has been already used to denote the atomic form factor in convention as above, we use $\mathcal{F}$ instead to avoid confusion here. The prefactor $\frac{2}{\pi}$ is used here so that the

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direct sine transform has a prefactor of 1.

Considering that sine functions form an orthogonal basis, the integration part in Eq. 2.26 results in δ functions,

$$\int_0^\infty \sin(Qr_{ij}) \sin(Qr) dQ = \frac{\pi}{2} [\delta(r - r_{ij}) - \delta(r + r_{ij})]. \quad (2.27)$$

If considering the positive r -axis only, substituting Eq. 2.27 into Eq. 2.26, we have

$$\begin{aligned} \mathcal{F}(r) &= \frac{1}{N\langle f \rangle^2} \sum_{i \neq j} \frac{f_j^* f_i}{r_{ij}} [\delta(r - r_{ij}) - \delta(r + r_{ij})] \\ &= \frac{1}{rN\langle f \rangle^2} \sum_{i \neq j} f_j^* f_i \delta(r - r_{ij}). \end{aligned} \quad (2.28)$$

This $\mathcal{F}(r)$ term can be interpreted by the radial distribution function (RDF), $R(r)$. Its physical description can be understood that the $R_i(r)dr$ gives the number of atoms in a shell of thickness dr at a distance r from the atom i as the origin. Inspection on Eq. 2.28, we can found that multiplying $\mathcal{F}(r)$ by r can give the same physical meaning, thus we have [262]

$$\begin{aligned} \mathcal{F}(r) &= \frac{R(r)}{r} \\ &= 4\pi r \rho(r), \end{aligned} \quad (2.29)$$

where $\rho(r)$ is the atomic pair density function. Rearranging Eq. 2.29, we find

$$\begin{aligned} \rho(r) &= \frac{\mathcal{F}(r)}{4\pi r} \\ &= \frac{1}{4\pi r^2 N\langle f \rangle^2} \sum_{i \neq j} f_j^* f_i \delta(r - r_{ij}). \end{aligned} \quad (2.30)$$

A series of other physical quantities can be defined based on RDF, as summarized in [263].

It is important to point out that $\mathcal{F}(r)$ is not equivalent to the PDF, $G(r)$ in Eq. 2.13, because $\mathcal{F}(r)$ is integrated from 0 to ∞ , but $G(r)$ is from $Q_{\min}$ to $Q_{\max}$ [262]. In reality, performing scattering experiment has some limitations on the accessible Q range. First, the scattering intensity at the Q value close to 0 is not accessible, since it is too close to the

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direct incident beam and it would be blocked by a beam stop instead of collected by the detector (see Fig. 2.2). Thus the forward-scattering contributions are lost. On the other hand, because the detector has a finite size, obviously the upper limit of Q range cannot be ∞ . So the integration range from 0 to ∞ in Eq. 2.26 should be separated as

$$\mathcal{F}(r) = \frac{2}{\pi} \left\{ \int_0^{Q_{\min}} + \int_{Q_{\min}}^{Q_{\max}} + \int_{Q_{\max}}^{\infty} \right\} F(Q) \sin(Qr) dQ \quad (2.31)$$

Since only the scattering intensities from $Q_{\min}$ to $Q_{\max}$ is experimental accessible, we can define the measured PDF $G(r)$ as

$$\begin{aligned} G(r) &= \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} F(Q) \sin(Qr) dQ \\ &= \mathcal{F}(r) - \frac{2}{\pi} \left\{ \int_0^{Q_{\min}} + \int_{Q_{\max}}^{\infty} \right\} F(Q) \sin(Qr) dQ \\ &\approx \mathcal{F}(r) - \frac{2}{\pi} \int_0^{Q_{\min}} F(Q) \sin(Qr) dQ. \end{aligned} \quad (2.32)$$

The integral of $[Q_{\max}, \infty]$ is disregarded as the errors introduced by the high Q signal is minimal and can be safely omitted in PDF measurements as the effects are well understood [270]. The integral of $[0, Q_{\min}]$ part is originated from the small-angle scattering signal. In the case of bulk crystals, it yields a straight baseline whose negative slope in the $G(r)$ is proportional to the number density of material ρ_0 . We have [262]

$$\frac{2}{\pi} \int_0^{Q_{\min}} F(Q) \sin(Qr) dQ = 4\pi r \rho_0, \quad (2.33)$$

where ρ_0 is the average number density of atoms in the material. For nanomaterials, the small-angle scattering part is related with the morphology and shape of nanomaterials, usually described by a characteristic function $\gamma_0(r)$ [271]. Notice that both small-angle and large-angle scattering contain information about the shape and size of nanoparticles, but this information is decoupled from the internal nanoparticle structure in the small-angle scattering [262].

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Finally, we can achieve

$$\begin{aligned} G(r) &= \mathcal{F}(r; Q_{\min}) \\ &= \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} F(Q) \sin(Qr) \, dQ \\ &= 4\pi r [\rho(r) - \rho_0], \end{aligned} \tag{2.34}$$

as we gave in the beginning of this Section, Eq. 2.12 and Eq. 2.13.

The PDF equations derived here establish a straightforward connection between the atomic structure of a material and the measured scattering intensity. The theoretical PDF from a structural model can be calculated directly from Eq. 2.34, which depends on the real-space quantities related with the atomic positions. In order to have a better real-space resolution, $\pi/Q_{\max}$, PDF experiments can also be understood as high- $Q_{\max}$ scattering experiments, and as a trade-off, we would lose the reciprocal-space resolution, which is usually for the conventional diffraction methods.

The PDF can provide an intuitive histogram of the atomic correlations on the length scale of Å to tens of nanometers, without any assumptions about the structure symmetry, so it is applicable to non-crystalline materials such as amorphous materials, liquids, glasses, nanomaterials, and of course, highly crystalline materials.

2.4 Neutron and x-ray

Neutron and x-ray PDF methods are commonly used for studying the structure of materials. We will first overview the history of these two techniques, as well as the development of the equipment to review how it grows to meet the demands of PDF experiments sequentially. Finally these two methods are compared for their complementary characteristics for a joint analysis.

2.4.1 History of x-ray source

An x-ray, or x-radiation, is a penetrating form of high-energy electromagnetic radiation. It behaves in the same way as visible light rays, but at much shorter wavelengths, in the range of 0.01 nm to 10 nm. It was first discovered by Wilhelm Röntgen in 1895 while experimenting with the Lenard and Crookes tubes, which are electrical discharge tubes. He referred to the radiation as “X”, which stands for “unknown” [272]. Because of his discovery, he was the first recipient of the Nobel Prize in Physics. Since Röntgen took the very first x-ray picture of his wife Anna Bertha’s hand, x-rays have been widely applied for the medical imaging due to their high penetration.

In 1912, Friedrich, Knipping, and Laue reported the first observation of x-ray diffraction patterns in crystals [273]. The Braggs used the x-rays to determine the structure of single crystals, and yielded the Bragg equation (Eq. 2.1) in 1913 [261]. They showed the world how the observed diffraction pattern could be used to determine the positions of atoms in the rock salt (NaCl) crystal. This is the birth of x-ray crystallography [274]. So far more than twenty Nobel prizes have been awarded to the work related with x-ray crystallography. The Bragg’s method of structure determination is still the foundation of the modern crystallography.

The Braggs built the first single-crystal diffractometer in 1913, which allowed a crystal to be oriented in the primary beam into a reflection condition, and then the diffracted beam was measured in an ionization chamber. Debye and Scherrer [275] and Hull [276] independently invented the method for powdered polycrystalline samples. At that time, Moseley studied x-ray absorption and emission spectra, which are essential for x-ray application [277; 278].

Now let us review how the x-ray equipment develops. In the early 1920s, Coolidge invented the first sealed x-ray tube, which can generate x-rays with different types of anode materials [279]. It is a vacuum tube that has a cathode, which emits electrons into the vacuum and an anode to collect the electrons, resulting in a flow of electrical current through

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the tube. A high voltage power source is connected across cathode and anode to accelerate the electrons. Electrons from the cathode then collide with the anode material, such as Cu and Mo, and accelerate other electrons, ions and nuclei with the anode material. Only about 1% of the generated energy is emitted as x-rays, perpendicular to the path of the electrical current path, and the rest energy is released as heat [280]. Until the late 1980s, x-rays were generated solely by utilizing high-voltage x-ray tubes in this mechanism. The wavelength or the spectrum of x-rays is determined by the types of anode materials. For example, Cu emits 1.54 Å ($K_{\alpha 1}$ emission line), and Ag can provide 0.559 Å x-rays ($K_{\alpha 1}$ emission line). However, these lab source x-ray tubes are not able to generate high energy x-rays, i.e., short wavelength, which are crucial for obtaining high- Q signal for PDF experiments. Mo or Ag sources could give a $Q_{\max}$ in the range of 10-15 Å⁻¹, but still not favorable.

Things started to change when synchrotron radiation was discovered [281]. A synchrotron light source is an extremely powerful source of x-rays. It accelerates electrons to almost the speed of light in a cyclic storage ring. When the electrons are deflected through magnetic fields, the electromagnetic radiation at extremely high energies (GeV) is emitted along the tangent direction of the orbit.

In 1947 the first observation of synchrotron radiation was recorded when the radiation was emitted by electrons as they moved circularly in the magnetic field of the chamber of a particle accelerator [282]. The radiation was called synchrotron radiation since it was observed for the first time in a synchrotron [283]. Though the physics behind it was already recognized by physicists 50 years earlier when Lienard [284] and Heaviside [285] extended the Larmor formula for a nonrelativistic electron, pointing out that an electric charge moving in a circular path should radiate energy [286]. The theory was extended subsequently by Schott for calculating the amount and the angular distribution of radiation from relativistic electrons [287].

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In the 1950s and 1960s, particle accelerators originally designed for studying nuclear physics were modified to allow scientific studies with synchrotron radiation, such as the DESY ((Deutsches Elektronen Synchrotron or German Electron Synchrotron) in Germany. However, for nuclear physics, the storage ring is built for controlling how the accelerated particles will collide, not designed exclusively for the production of synchrotron light. This type of parasitic operation was marked as the first generation of synchrotron light sources [283; 281]. Over the decades of technology development, the synchrotron light source has been improved into the forth generation, in the energy level of GeV [288]. Brighter and more stable x-ray beams are available nowadays with impressive progress in the accelerator physics, electronics, and computing, which benefits the field of research in biology, medical research, material science, and many others [289].

As mentioned earlier, it is crucial to obtain the high- Q scattering information to achieve high real-space resolution PDF data. The high energy synchrotron radiation has significantly smaller wavelength than the lab source x-rays. With the help of high brightness and high flux from synchrotron radiation, people are able to collect high signal-to-noise total scattering diffraction pattern up to high- Q region for PDF experiments and shorten the PDF data acquisition time.

2.4.2 History of neutron source

The neuron was first discovered by James Chadwick in 1932 [290] and the first neutron diffraction experiment was tried in 1936 [291; 292]. However, these early-stage diffraction experiments were aimed for demonstrating the wave-particle duality property of the neutron, other than applying the neutron diffraction to study the structure of materials. Enrico Fermi had been studied the neutron systemically since 1934, and he found that if there are hydrogenous materials around the neutron source, the radioactivity produced by neutrons

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would be greatly enhanced. This process is known as neutron thermalization that neutrons were being moderated, which means slowed down in the moderating substance until neutrons are in approximate thermal equilibrium with the atoms making up the moderator via colliding with protons, which are generally abundant in hydrogenous materials, such that the neutrons can be more susceptible than fast ones to propagate a nuclear chain reaction [293]. Neutron moderator materials usually have low neutron absorption, high neutron scattering cross section, and low mass such that neutrons can be greatly slowed down after being scattered but not be consumed much. The commonly used neutron moderator materials nowadays are light water (H_2O), heavy water (D_2O) which has smaller neutron absorption than H_2O but costly, and graphite (C). He also started the term “thermal neutrons” since the energy falls in the order of $k_B T$ thermal energy (k_B is the Boltzmann constant), referring to the neutrons after being modulated, with wavelengths comparable with interatomic spacing that are applicable for diffraction experiments [294]. However, the low flux of the neutron source prevented people from further investigating its application for diffraction experiment in the 1930s.

The subsequent development of neutron experiments was closely related with the Manhattan Project, which was aimed to develop atomic weapons during the World War II, and it enables the dramatic increase in neutron flux realized with the nuclear chain reacting piles [295]. The early experiments for this project was started at the Pupin Physics Laboratory at Columbia University in 1939, for the fission of uranium by the bombardment of neutrons [296]. The first nuclear reactor, CP-1 (Chicago Pile 1) started being built up in November 1942, under the supervision of Fermi, who moved his Columbia University group to the Metallurgical Laboratory at the University of Chicago in April 1942. CP-1 was a key milestone in the Manhattan Project and it was also marked as an important step for developing neutron scattering. The high-purity graphite (later heavy water) was used for

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the moderation of neutrons, so as to sustain the nuclear chain reaction, and meanwhile it produces sufficient numbers of thermal neutrons needed for performing the diffraction experiments on materials. The Fermi-type choppers were used for selecting monoenergetic beams of neutrons in the CP-1, CP-2, CP-3, and X-10 piles built subsequently.

These neutron sources were exploited for studying the interactions of neutrons with matter even during the Manhattan Project war time. Wollan and Borst installed a neutron diffraction instrument in the X-10 pile at Oak Ridge National Laboratory (ORNL) in 1944. They succeeded in collecting the first neutron diffraction patterns on materials, a gypsum crystal and a sodium chloride crystal in 1944 [297]. Meanwhile, Zinn and Sturm reported the Bragg reflection of thermal neutrons by a single crystal [298] in the CP-3 reactor at Argonne National Laboratory in 1944.

More scientific papers were released to the public after the World War II. For instance, Goldberger and Seitz also provided the theory of Laue-Bragg scattering of neutrons by single crystals, analog of x-ray diffraction [299]. Fermi and Marshall investigated the phase of neutron scattering and systematically measured the values and signs of neutron scattering lengths for a series of elements [300].

The first neutron powder diffraction patterns of polycrystalline samples, such as NaCl and LiF powders, were collected by Wollan and Shull, who joined Wollan's group at Oak Ridge in 1946 [301]. Their pioneering contributions to the neutron diffraction technique were recognized in 1994, when the Nobel Prize in Physics was awarded to Shull, but unfortunately his colleague Wollan died in 1984, who should have shared the honor together [302].

These reactor source generated neutrons are hardly capable of generating neutrons with short wavelength, which is the key for high- $Q_{\max}$ PDF experiments. In addition, the fairly low neutron flux from the fission process and moderator is also a barrier for collecting PDF data. Although for some reactor sources, they could produce reasonably high- $Q_{\max}$ PDFs,

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especially the diffractometers that using a hot moderator, such as D4 beamline [303] at the Institut Laue-Langevin (ILL) in Grenoble, France. It has a standard wavelength of $0.5 \text{ \AA}$ and detector banks covering a range from 2 to 140° that yields PDFs with about $Q_{\max} = 23.6 \text{ \AA}^{-1}$. But overall, reactor neutron sources are not favored by PDF experiments.

By analogy with the synchrotron in x-ray source history, a completely new type of neutron source became available in the late 1980s, i.e., the spallation neutron source. In contrast to the previously available reactor neutrons, the intense pulsed bunches of neutrons are generated by accelerating protons to high energy and get directed onto heavy-metal targets, such as mercury, where spallation occurs. The spalled neutrons are then slowed in the moderator, but not fully slowed down to the thermal equilibrium as in the reactor source. Instead, spallation neutrons are under-moderated and significant quantities of higher energy neutrons are still in the source spectrum. As a result, we can have both short and long wavelength neutrons in the same neutron pulse. These under-moderated epithermal neutrons are exactly what we need for collecting the high- $Q_{\max}$ diffraction signal [257].

So spallation neutron source facilitates the PDF technique, and for some certain beam-lines, the real-space resolution could be extremely high that $Q_{\max}$ can reach almost $50 \text{ \AA}^{-1}$ [304].

2.4.3 Neutron vs. x-ray

Neutrons and x-rays have many different properties from each other. Their selected intrinsic properties are listed in the Table 2.1. For instance, neutron has $1/2$ spin thus it is an effective probe to measure the magnetic signals of materials. But neutron has no net charge, this means that neutron is not an elementary particle, which is made up of quarks, whereas x-rays are intrinsically elementary.

First and foremost, the biggest difference between them regarding the applications in diffraction experiments, which is also the key motivation of the joint neutron and x-ray

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Table 2.1: Selected properties of x-ray and neutron.

Type	Principal scatter	Mass	Charge	Spin	Lifetime	Composition
X-ray	Electron	0	0	0	∞	-
Neutron	Nucleus	1.67×10^{-27} kg	0	$1/2 \hbar$	881.5 s	Quarks

PDF method, is that the nature of the interaction of x-rays and neutrons with matters are significantly different [305]. Briefly speaking, x-rays and neutrons have different principal scatters during the diffraction experiment, that x-rays mostly interact with the electrons of atoms whereas neutrons interact with nucleus only.

X-rays, or in another word, electromagnetic waves, interact with charged matters via the electromagnetic force, such that interacting with both the positive charged atomic nuclei and the surrounding negative charged electron cloud. The atomic nuclei and electrons start oscillating and emit electromagnetic radiations to the outside, which is the scattered waves detected in a diffraction experiment. However, since the mass of x-ray is significantly smaller than that of nucleus, even when comparing with lightest element, hydrogen atom (one proton), after scattered by x-rays, the electromagnetic radiation emitted from the nuclei would be much weaker than that from the electron cloud surrounding the atoms. Thus, considering only the interaction between x-rays and electrons of materials under study is a sufficient approximation. As a result, the scattering of x-rays by atoms take place almost entirely from the electron cloud surrounding the atomic nuclei, such that the scattering ability for x-rays increases with the number of electrons of the atom type, which is often treated as the atomic number Z .

Neutrons interact with the atomic nuclei of matters via the nuclear force, and the interaction varies for different isotopes (the same number of protons, but different number of neutrons in the atomic nuclei) of an element. Neutron is neutral but consists of charged quarks, and Fermi and Marshall proposed that neutron can be treated as a spherical model

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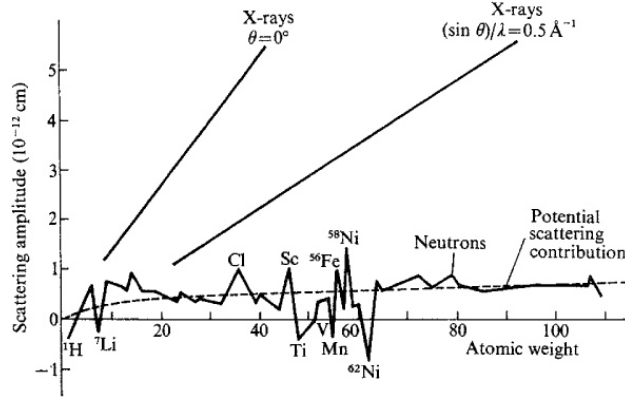


Figure 2.1: The coherent scattering lengths for x-rays ($r_e f$, where r_e is the radius of electron) and thermal neutron (b) as a function of atomic number. Note that the Q -dependence relationship is for the x-ray atomic factor, not for neutrons.

with positive core and negative skin [306], thus the interaction with matters is rather complicated. The Fermi pseudopotential can be used to simplify the scattering of a free neutron by a nucleus. For instance, the appropriate scattering potential for the i -th nucleus, located at position $\vec{r}_i$ in the matter, can be written as [300]:

$$\hat{V}(\vec{r}) = \frac{2\pi\hbar^2}{m_n} b_i \delta(\vec{r} - \vec{r}_i), \quad (2.35)$$

where m_n is the neutron mass and b_i is the coherent neutron scattering length of the i -th nucleus.

Overall, x-ray interacts strongly with heavy elements, but weakly with light elements (low atomic number), such as hydrogen, carbon, and oxygen. On the contrary, these elements can be easily detected by neutrons. This is illustrated in Fig. 2.1, adapted from [307; 308]. This is also the essential reason why the joint neutron and x-ray pair distribution function (NXPDF) technique is important for studying the materials that will be introduced in this thesis work.

Second, x-rays and neutrons have completely different scattering form factors. The scattering length, b for neutrons, and atomic form factor, f for x-rays conventionally, is used

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to quantitatively describe the strength of the interaction of the scatterer with individual atom type. The x-ray scattering lengths (or atomic form factors) decrease at larger angles, usually with respect to $\sin(\theta)/\lambda$ or the scattering vector Q . This is because the electrons are distributed over the atomic volume, which is in the order of 1 Å, and this is within the similar magnitude as the x-ray wavelength, resulting in an enhanced interference effects in the scattering [305]. The reduction relationship is described by the x-ray form factor. As discussed in the Section 2.3, people usually use the atomic form factor where Q is close to 0 to simplify the Q -dependent behavior, which is known as the Warren-Krutter-Morningstar approximation as introduced earlier [240].

Contrary to x-ray, neutron scattering is found to be isotropic. This is because neutron scattering is caused by the interaction with the atomic nuclei, and the scattering is isotropic for such cases because the neutron wavelength, around 1 Å, is significantly larger than the range of interaction, i.e., the size of the nuclei, which is in the order of 10^{-5} Å [305]. This is equivalent to the fact that no orbital momentum is involved in the neutron scattering process ($l = 0$). This can also be explained in Eq. 2.5 straightforwardly, that when the scatterer $\rho(\vec{r}_i)$ has narrow distribution in real space r , which is the case for nuclei, the form factor $f_i(\vec{Q})$ would be quite broad in Q , and can be treated as constant. So the scattering length of neutron does not vary with scattering angle, i.e., Q -independent.

As a side note, high real-space resolution PDF experiments were originally performed by neutrons in the history, since high- Q signal does not decay in neutron scattering. People initially thought x-rays were not feasible for PDF because of the high- Q decaying originated from the Q -dependent atomic form factor issue. However, luckily, with the advent of high-energy synchrotron sources that produce high energy x-rays, it has been established that high-quality PDF could be obtained because of the high flux counting rate. Furthermore, obtaining PDFs from x-rays has become straightforward and much more accessible

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nowadays [85].

For x-ray, the phase difference between scattered and incident wave is typically $\lambda/2$ (180°), because x-ray energies are larger than most electronic resonance energies, but neutrons can be scattered in 0° or 180° which results in a negative or positive scattering length, respectively. The probability of having positive scattering length is much higher than negative one in nature, especially for heavy elements [300]. Some commonly studied elements with negative neutron scattering length include H, Li, Ti, and Mn, though their isotopes may be positive [309]. Conclusively, a negative scattering length of a nucleus indicates that its Fermi pseudopotential is attractive when neutron approaches the nucleus, whereas a positive scattering length means repulsive pseudopotential [300].

Last but not least, extra cares are needed for neutron PDF experiments if samples contain hydrogen. The hydrogen atoms (^1H) would largely raise the complexity for neutron diffraction data processing due to its strong inelastic incoherent neutron scattering. The strong inelastic neutron scattering is because hydrogen is the lightest atom species and recoils when the neutron interacts with it. An intuitive explanation for the large incoherent neutron scattering length of hydrogen (25.274 fm) [309] is as follows [310]. When scattering from a single element, the difference in the scattering lengths arises from the different total spin states of the nucleus-neutron system. ^1H has only one proton in the nucleus, with a nuclear spin of $1/2$. Thus the system can be either singlet ($S^- = 0$) or triplet ($S^+ = 1$) state with the multiplicities of 1 and 3, respectively. These two spin states would have opposite signs of neutron scattering lengths. So the coherent scattering length $b_c = \langle b \rangle$ for ^1H is small and negative, calculated by the weighted average for the two states with their multiplicities. However, the neutron incoherent scattering length is the root mean squared deviation of

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scattering lengths,

$$b_{inc} = \sqrt{\langle b^2 \rangle - \langle b \rangle^2}. \quad (2.36)$$

For ^1H , the $\langle b^2 \rangle$ term is positive and large, and the $\langle b \rangle^2$ term is quite small since $\langle b \rangle$ is already a small quantity. So the resulting incoherent neutron scattering length for ^1H is very large.

Part of the intensity of inelastic incoherent scattering is proportional to the space and time Fourier transforms of the self-correlation function, which represents the probability of finding a scatterer particle at position r at a time t when the same particle was at $r = 0$ and $t = 0$. The inelastic incoherent scattering signal can dominate the measured scattering intensity in systems where the incoherent scattering cross section is much larger than the coherent scattering cross section, and where energy exchange between the neutron and atom is significant, since large amounts of energy can be exchanged in the scattering process for light atom nuclei. Thus for hydrogen-containing materials, such as water, the measured neutron PDF diffraction pattern would contain the extremely large inelastic incoherent neutron scattering signal, which is very challenging to be removed in the data processing, and must be empirically subtracted from the experimental data when present [311].

Some attempts were made for the hydrogen correction. People tried subtracting the entire background by fitting with a polynomial function and spline interpolation and then adding back the baseline expected in the absence of nuclear incoherent scattering [311], as implemented in PDFGETN program [312]. This method assumes that inelastic incoherent scattering contributions are low-frequency oscillations in Q space, which only affect distances shorter than the smallest interatomic distance of the experimental PDF [313]. Furthermore, instead of polynomial fit, people tried to use the data itself to subtract the steep background, for example, a top-hat function can be convoluted with the reciprocal-space data to obtain the inelastic incoherent background [314], which is available in Gudrun program and has been shown to be effective for liquids and glasses [315]. Because the top-hat function can

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broaden all the structural features, and what left after the convolution would be solely the steep background. A Fourier filter is usually applied for correcting large inconsistency of the data, such as removing unrealistic low- r PDF peaks that are not from structure itself but come from incorrect data processing, as implemented as a tool available in some programs such as RMCProfile [316] and Gudrun [315]. So the Fourier filter could be tried to manually subtract the low- r PDF up to the smallest interatomic distance from the structure model so as to remove the steep background in reciprocal space. A Bayesian statistical approach was also tested for easing the hydrogen correction [317]. However, no standard approach has been established as the best method for hydrogen correction so far.

Besides, substituting hydrogen isotopes to the samples can avoid the hydrogen problem in many cases. Once the hydrogen-containing samples are deuterated, i.e., replacing ^1H by its isotope deuterium ^2H , the incoherent scattering signal would be significantly reduced. ^2H has one proton and one neutron in the nucleus, with a nuclear spin of 1, $S^+ = 3/2$ and $S^- = 1/2$ having both positive neutron scattering length. So the difference between $\langle b^2 \rangle$ and $\langle b \rangle^2$ is not very large. As a result, the incoherent neutron scattering length of deuterium would be not that significant (4.04 fm) comparing with ^1H (25.274 fm) [309]. Though deuterated samples are usually much more expensive, meanwhile changing the chemical synthesis protocol into a deuterated process may arise the complexity of preparing samples as well.

2.4.4 Joint neutron and x-ray

Considering the complementary structure information obtained from neutron and x-ray scattering because of their different scattering ability to atom species, the combination of both methods can help comprehensively understand the structures and properties of some materials.

A famous example in the history using the combined technique is the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$

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system, one of the most famous high T_c superconductor. Its crystal structure was first investigated at great scale by many groups all over the world within a few months of its discovery [318]. Almost all of the structural studies on this material used neutron powder diffraction data at that time. Unfortunately, Y and Cu atoms have almost identical neutron scattering length, which resulted in the undetermined sublattices of these two atom species [319]. Though the x-ray atomic form factor for these two atoms are quite distinguishable ($Z = 39$ for Y and $Z = 29$ for Cu), x-ray cannot accurately determine the oxygen atomic positions. So NX co-refinement is an ideal tool to solve this problem. The conventional powder diffraction Rietveld refinement of this structure consisted of fitting four neutron TOF patterns and two x-ray powder patterns simultaneously, using about 120 adjustable parameters fit to totally around 25000 data points, and this study conclusively demonstrated the absence of any cation disorder [320].

So appropriate combination of neutron and x-ray powder diffraction data sets can solve the structural problem that is hard to be understood alone. It has been applied extensively in many studies including both conventional diffraction [321; 322; 323; 324; 325] and PDF analysis [326; 327; 328; 329; 330; 331; 332; 333]

2.5 PDF experimental methods

The real-space resolution, $\pi/Q_{\max}$, needs to be high enough for PDF experiments. To reach high $Q_{\max}$, a short wavelength λ is necessary, as shown in the definition of Q (Eq. 2.3). Though other conditions are also required for PDF experiments, such as high flux for getting a high counting rate for signals from the noisy high- Q range. So as mentioned earlier, PDF experiments are usually carried out at a synchrotron x-ray source or a spallation time-of-flight neutron source.

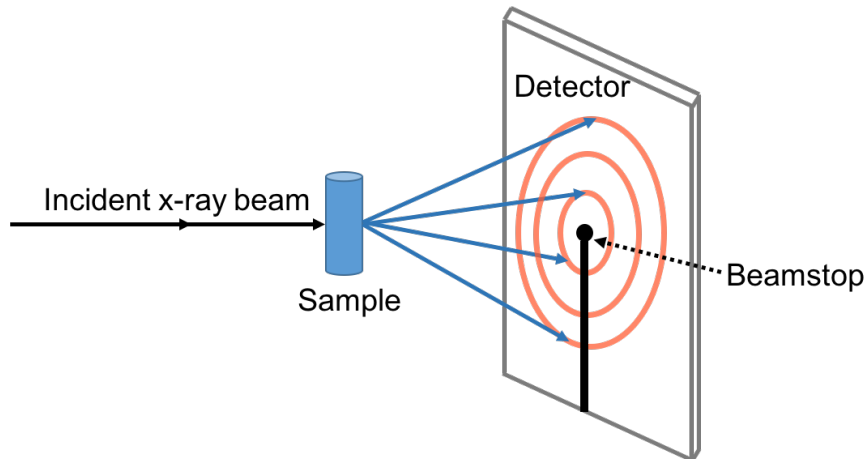


Figure 2.2: The x-ray pair distribution function experimental setup.

2.5.1 PDF experiments at synchrotron x-ray sources

The x-ray PDF experiments for this thesis were performed at the XPD and PDF beamlines of the National Synchrotron Light Source II (NSLS-II) in Brookhaven National Laboratory, which is one of the newest and most advanced synchrotron facilities in the world.

Its PDF experimental setup is quite similar to a conventional fixed-wavelength x-ray powder diffraction experiment with a 2D detector, as shown in Fig. 2.2. The finite-size detector is moved close to the sample such that more high- Q signal can be collected, though as a trade-off, the Q -space resolution is worse [334]. The powdered samples are usually loaded in polyimide capillaries which are weakly scattered by x-rays.

2.5.2 PDF experiments at spallation neutron sources with time-of-flight technique

The neutron PDF experiments for this thesis were carried out at the NOMAD beamline of the Spallation Neutron Source (SNS) in Oak Ridge National Laboratory, which provides the most intense pulsed neutron beams in the world so far, operating at power levels up

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to 1.4 megawatts. The neutron wavelength at the NOMAD can be as small as 0.1 Å, thus achieving $Q_{\max}$ to be 30-50 Å⁻¹ [335].

The epithermal neutron pulse from the spallation process has a spectrum of various velocities or de Broglie wavelengths, which have different time of flight to arrive at the beamline detector. Among them, we can find the short wavelength, 0.1-0.2 Å, which is ideal for PDF. The time-of-flight (TOF) technique means when the distance from the neutron source to the detector is known, the velocity of the neutron can be calculated by counting the time spent to arrive at the detector, then the determined velocity can be used to calculate the de Broglie wavelength of incident neutron beam. The powdered samples are usually loaded in the container made up of low coherent neutron scattering length elements, such as vanadium.

2.6 PDF data analysis

2.6.1 Data processing

After PDF experiments, the measured raw scattering data are converted to PDFs through data processing. For x-rays, at the XPD and PDF beamlines, the 2D image is first azimuthally integrated into 1D powder diffraction pattern using the FIT2D [336] or PYFAI program [337]. Standardized corrections and normalizations were applied to the data to obtain the total scattering structure function, $S(Q)$, which was Fourier transformed to obtain the PDF using PDFGETX3 [338] within xPDFSUITE [339]. These PDF data processing steps are shown in Fig 2.3, from (a) a raw 2D image to (b) the azimuthally integrated into 1D powder diffraction pattern and get processed into $F(Q)$, and finally to (c) the PDF $G(r)$.

For neutrons, at the NOMAD beamline, there are totally six banks of detectors to collect scattering signal. The data reduction is done with custom-built software available at the

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beamline, but the basic principles are the same with other neutron PDF data reduction programs, such as PDFGETN [312], Gudrun [340], and Mantid [341].

In many circumstances, the PDF can be analyzed directly without any structural modeling, which may provide plenty of useful structural information. For instance, when studying the temperature-induced phase transition of the sample, one can compare the PDF collected at low and high temperature together for investigating how the local structure changes versus temperature.

2.6.2 Structural modeling

Once obtained the PDF data, we can then perform PDF modeling analysis to extract the structural information from the PDF. A number of PDF structure modeling programs are available for crystalline or nanocrystalline inorganic materials [342]. Small box modeling programs use a small number of crystallographic parameters with a periodic structure model [79]. Three widely used examples are PDFGUI [343], TOPAS [344], and DIFFPY-CMI [345], among others [346; 347; 348]. Big box modeling programs, which move large numbers of atoms to minimize the difference between the observed and calculated PDFs, usually implement the reverse Monte Carlo (RMC) method [349; 350], such as RMCProfile [316], DISCUS [351; 352], and FullRMC [353]. Other modeling programs use a hybrid approach where a large number of atoms are in the box, but the program refines only a small number of parameters, such as EPSR [354].

There are two ways to compute the PDF [79; 85], one is calculating in the real space (Eq. 2.12), and the other one is in the reciprocal space (Eq. 2.13).

In the real space, the pair density function, $\rho(r)$, is calculated from a crystallographic model with periodic boundary conditions [355; 347; 343], or from a box of atoms that is much larger than the r range of interest [350; 316]. The average number density ρ_0 can be

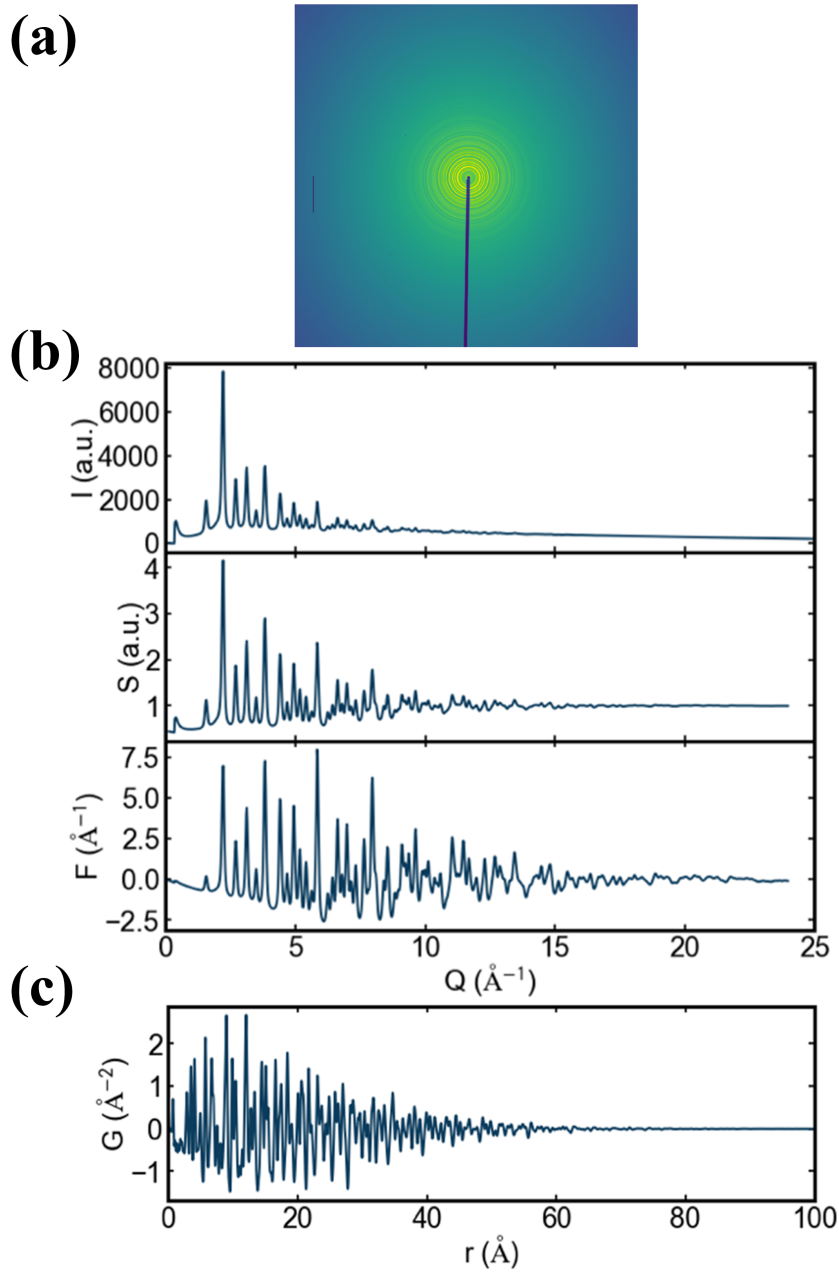


Figure 2.3: (a) The x-ray 2D diffraction image, using the barium titanate nanoparticle powder as an example data. (b) The azimuthally integrated 1D powder diffraction pattern $I(Q)$, the total scattering structure function $S(Q)$, and the reduced total scattering structure function $F(Q)$. (c) The corresponding PDF $G(r)$, obtained by Fourier transforming $F(Q)$.

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calculated from the crystallographic model or the box of atoms in a straightforward way.

A few phase related parameters are refined in the modeling as follows. The Debye-Waller effects [258] accounting for atomic thermal motion can be applied by replacing the delta functions in Eq. 2.30 with Gaussian functions whose widths are given by widths of the atomic displacement factors (ADPs) of atoms. If the nearby atomic motion is correlated, the PDF peak would be sharper, which is described by a δ parameter that accounts for the correlated atomic motions [356]. The Q_{max} termination effects in the Fourier transform can be included by a *sinc* function, since the Fourier transform of a Heaviside step (cutoff) function is a *sinc* function. For nanomaterials, the effects from the finite crystallite size can be approximated by attenuated bulk crystals, which is approximated as $\gamma_0(r)\rho_{bulk}(r)$ [271]. This approach is implemented in the PDFGUI modeling program [343], using a spherical particle diameter (SPD) parameter, in units of Å.

Alternatively, in the reciprocal-space method, the Debye equation (Eq. 2.22) [265] is used to directly calculate the scattering intensity for any given atomic arrangements, and then get Fourier transformed to obtain the PDF. In this way, no periodic boundary condition is needed but with the cost of computational complexity since the Debye equation iterates over all the atom pairs in the system. It can be very slow compared to direct real-space calculation for large systems. It is generally applied for smaller systems such as molecules or small clusters [357]. Some attempts were made for the algorithm that the Debye equation for large systems can be accelerated under certain conditions [358], though in these circumstances the real-space calculation method is still preferred. Similar as in the real-space method, to account for thermal and zero-point motion in the reciprocal-space calculation, the delta functions in Eq. 2.24 are replaced by Gaussian functions that include Debye-Waller effects,

$$F(Q) = \frac{\sum_{i \neq j} f_j^* f_i [\exp(-\frac{1}{2}\sigma_{ij}^2 Q^2)] \frac{\sin(Qr_{ij})}{r_{ij}}}{N\langle f \rangle^2}, \quad (2.37)$$

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where σ_{ij}^2 describes the correlated broadening factor for the atom pair [347; 356]. The termination effects of the finite Q range are already included when we Fourier transform $F(Q)$ to $G(r)$. Note that the $Q_{\min}$ term needs extra care here, because of its effects on the small-angle scattering, which is not included in the definition of $G(r)$, and is not measured, but is included when Fourier transforming the $F(Q)$ calculated from Debye equation unless manually excluded in purpose [343].

The PDF instrument resolution parameters, Q_{damp} and Q_{broad} , which are the parameters that correct the PDF envelope function for the instrument resolution [347; 343], are preferably obtained by measuring a standard calibration material in the same experimental setup geometry as the measured sample, and are fixed in the subsequent structure refinements of the measured sample's PDF.

After calculating the initial PDF from a given model, no matter in which method, it will be compared to the experimental PDF. The PDF refinement procedure is for better matching the calculated PDF onto the experimental PDF. In PDFGUI, the least-squares method is deployed to vary the adjustable parameters of structural model to achieve the best agreement between the calculated and measured PDFs. The minimization step is characterized by a statistical quantity, the goodness-of-fit, R_w , given by

$$R_w = \sqrt{\frac{\sum_{i=1}^n [G_{obs}(r_i) - G_{calc}(r_i, P)]^2}{\sum_{i=1}^n G_{obs}(r_i)^2}}, \quad (2.38)$$

where G_{obs} and G_{calc} are the observed and calculated PDFs, respectively, and P is the set of parameters refined in the model. The lower R_w , the better PDF fit is.

2.7 Candidate structure searching

The PDF modeling is performed by adjusting the parameters of the structure model, such as the lattice parameters, atomic positions, and atomic displacement parameters, to

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maximize the agreement between the calculated PDF from the structure model and the experimental PDF. Though powerful for understanding structure of complex materials, one of the biggest challenge in PDF modeling and structure refinement is that a satisfactory plausible initial model is required to achieve a successful result. Model selection traditionally requires significant chemical knowledge and experience, but can be quite challenging when unknown impurities or reaction products are present in the sample. To address the problem of phase identification, automated search-match algorithms for identifying phases in powder diffraction patterns have been developed and are widely used [359; 360; 361]. There are also programs for helping find candidate structures from structural databases [362; 363; 364; 365; 366]. These search-match programs only work for reciprocal space diffraction patterns, and in general do not allow for automated refinement of structures. Some attempts have been made to couple Rietveld refinement programs to structural databases such as Full Profile Search Match [367; 368], though this is limited to refining structures from the COD database. Alternatively, programs that use scripting such as TOPAS [344] have been used to automatically refine large numbers of candidate structures generated by symmetry-mode analysis from a given high-symmetry starting structure [369]. Furthermore, a structure screening approach where large numbers of algorithmically generated small metal nanoparticle models were compared to PDF data was recently demonstrated [357]. This approach, called cluster-mining, was successful at obtaining significantly improved fits over standard approaches to nanoparticle PDF data from simple models with a small number of refinable parameters. It also returned multiple plausible and well performing structures rather than just one best-fit structure, allowing the user to choose a model based on more information than just the PDF data.

To address the problem of searching for candidate structures for x-ray and neutron PDF, I developed the structure-mining method [370] that works for NXPf, which would be

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described in detail in Chapter 3. It combines the approaches mentioned earlier (database searching, auto-refinement, and screening of large numbers of structures) to the modeling of PDF data in general.

Chapter 3

Structure-mining

3.1 Introduction

Advanced new materials are required to facilitate the development of science and technology [25]. However, the discovery of new materials needs a lot of labor and time. The idea behind materials genomics [371] is to develop collaborations between materials scientists, computer scientists, and applied mathematicians to accelerate the development of new materials through the use of advanced computation such as artificial intelligence (AI), for example, by predicting undiscovered materials with interesting properties [372; 373; 374].

The study of material structure plays a key role in the development of novel materials. Structure solution of well-ordered crystals is largely a solved problem, but for real materials, which may be defective or nanostructured, being studied under real conditions, for example in high-throughput *in situ* and *operando* diffraction experiments such as *in situ* synthesis [229; 230; 231; 232; 233; 234; 235; 236], determining structure can be a major challenge that could itself benefit from a genomics style approach. Here we explore a data-mining methodology for

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the determination of inorganic material structures. The approach can rapidly screen large numbers of structures in a manner that is well matched to the kinds of high-throughput experiments being envisaged in the materials genomics arena.

A number of structural databases are available for inorganic materials containing structures solved from experimental data such as the Inorganic Crystal Structure Database (ICSD) [375; 376], the American Mineralogist Crystal Structure Database (AMCSD) [377], the Crystal Structure Database for Minerals (MINCRYST) [378], and the Crystallography Open Database (COD) [379]. More recently, databases of theoretically predicted structures have begun to become available, such as the Materials Project Database (MPD) [372], the Automatic Flow Library (AFLOWLIB) [380], and the Open Quantum Materials Database (OQMD) [381; 382]. Structural databases such as the International Centre for Diffraction Data [383], have for some time been used for phase identification purposes. In phase identification studies no model fitting is carried out, but phases are identified in a powder diffraction pattern by matching sets of the strongest Bragg peaks from the database structures to peaks in the measured diffractogram [359; 360; 361]. Our goal is not just phase identification, but to speed up the process of finding structural candidates to unknown atomic pair distribution function (PDF) signals.

As described earlier in the thesis, PDF analysis of x-ray and neutron powder diffraction datasets has been demonstrated to be an excellent tool for studying structures of many advanced materials, especially nanostructured materials [88; 216; 89; 90; 218; 219; 91], but also bulk crystalline materials [86; 87; 220; 221].

The experimental PDFs can be analyzed through modeling. As introduced earlier, the PDF modeling is performed by adjusting the parameters of the structure model, such as the lattice parameters, atomic positions, and atomic displacement parameters, to maximize the agreement between the calculated PDF from the structure model and the experimental

PDF. The PDF modeling and structure refinement, no matter using small box [79; 343] or big box modeling [349; 350] methods, are difficult and present a steep learning curve for new users. There are two major challenges. The first is that PDF structure refinement requires a satisfactory plausible starting model to achieve a successful result. The second is that the refinement process is a non-linear regression that is highly non-convex and generally requires significant user inputs to guide it to the best fit whilst avoiding overfitting. A more automated refinement program such as we propose here needs to address both issues.

Here we describe an approach we call structure-mining, to automate and manage structure model selection and PDF refinement. To make the whole procedure as high-throughput and automatic as possible, the required user inputs are kept to a minimum: simply the experimental PDF data and the searching criterion used to filter which structures to fetch from the databases. When finished, the best-fit candidate structures from the data mine are returned to the experimenter for further detailed investigations. Structure-mining currently supports both x-ray and neutron PDF datasets. This software enables high-throughput auto-refinement that may be used right after the PDF is obtained at a synchrotron x-ray or neutron beamline, unlike more traditional human intensive approaches that typically take a large amount of time and effort after the experiment is over. It is designed to solve the problem of searching for candidate structures for NXPf.

3.2 Approach

Structure-mining first obtains a large number of candidate structures from open structural databases. It then computes the PDFs of these structures and carries out structure refinements to obtain the best agreement between calculated PDFs and the measured PDF under study. The initial implementation uses two commonly utilized open structural

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databases: the Materials Project Database (MPD) [372] and the Crystallography Open Database (COD) [379]. The structures are fetched directly from the databases using the RESTful API [384; 385]. There are many rules that could be used for selecting candidate structures to try. In this initial implementation of structure-mining, we are using the following heuristics for filtering which structure models to fetch: (1) all the structures that have the same stoichiometry as prescribed by the experimenter, (2) all the structures containing a prescribed list of elements, (3) all the structures containing the prescribed list of elements plus a number of additional elements specified by a wild-card symbol, (4) all the structures containing a subset of the prescribed elements plus other elements if a wild-card symbol is specified. These heuristics go from more restrictive to less restrictive and may be selected as desired. The results on representative datasets are presented below.

After fetching the structures, structure-mining builds a list of candidate structures and loads their cif files from the database into the DIFFPY-CMI [345] PDF structure refinement program. DIFFPY-CMI works by first building a fit recipe which is the set of information needed to run a model refinement to PDF data, and then executing it. The PDF fit recipe for each structure is generated automatically. By default, the fits are carried out over the range of $1.5 < r < 20$ Å on the Nyquist-Shannon sampling grid [386], however, a different fit range may be specified by the user. The following phase related parameters are initialized and refined: a single scale factor uses initial value 1.0; lattice parameters are constrained according to the crystal systems using the initial lattice parameter values of the structures; isotropic atomic displacement parameter (ADP), U_{iso} , for each element atom of the structure is applied with initial value 0.005 Å^2 ; spherical particle diameter (SPD) parameter can be used if the PDF data are from nano-sized objects, by having the experimenter specify an initial value (in the unit of Å). The instrument resolution parameters, Q_{damp} and Q_{broad} , which are the parameters that correct the PDF envelope function for the instrument resolution [347;

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343], are preferably obtained by measuring a standard calibration material in the same experimental setup geometry as the measured sample, and are fixed in the subsequent structure refinements of the measured sample PDF. They are applied according to the following strategy. If the experimenter specifies Q_{damp} and Q_{broad} values, the experimenter's values are used and they are fixed during the structure refinement. If they are not specified by the experimenter, the program will make a best-effort attempt to allocate meaningful values. This is done currently by storing a table of reasonable values by instruments. So far, we have established reasonable values for the XPD x-ray instrument and the NOMAD and NPDF neutron instruments. If the program cannot find reasonable values in its lookup table for a specified instrument, or if no instrument can be determined, standard global default values are selected. These are $Q_{damp} = 0.04 \text{ \AA}^{-1}$ for rapid acquisition x-ray PDF (RAPDF) experiments [334] and $0.02 \text{ \AA}^{-1}$ for time-of-flight (TOF) neutron PDFs. Similarly, $Q_{broad} = 0.01 \text{ \AA}^{-1}$ and $0.02 \text{ \AA}^{-1}$ are the global defaults for RAPDF x-ray and TOF neutron measurements, respectively. In all the cases where the user does not specify values for Q_{damp} and Q_{broad} , these parameters are allowed to vary in the refinement process.

Different regression algorithms may be used to perform the structure refinement minimizing the fit residual, with the goodness-of-fit R_w , given by Eq. 2.38, The lower R_w , the better PDF fit is. Initially we use the widely applied damped least-squares method (Levenberg-Marquardt algorithm) [387; 388], which is deployed in the Python programming package Scipy [389], to vary the adjustable parameters to achieve the best agreement between the calculated and measured PDFs, since none of the algorithms for nonlinear least-squares problems has been proved to be superior to this standard solution [390; 391], such as Gauss-Newton method [392], modified Marquardt method [393], and conjugate direction method [394]. However, DIFFPY-CMI supports the use of different minimizers and the implementation with different optimizers will be tested in the future. During the

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structure refinement different types of parameters have quite different characteristic behaviors. A systematic parameter turn-on sequence is important to achieve convergence because turning on unstable parameters too early can result in divergent fits or getting trapped at local false minima. To make the structure-mining highly automatic without any human intervention during the whole procedure, here we tested an automatic turn-on sequence that was suggested for conventional full-profile Rietveld refinement [390] as well as considering the difference between PDF and Rietveld refinement procedures. The current structure-mining deploys the following parameter turn-on sequence. (1) Scale factor and lattice parameters are allowed to vary for up to 10 iterations, (2) isotropic ADPs are allowed to vary for up to 100 iterations, (3) if selected, the instrument resolution parameters, Q_{damp} and Q_{broad} , are turned on for up to 100 iterations, and finally (4) if SPD is specified, it will then be turned on for up to 100 iterations. When the whole procedure is finished, if the refinement cannot converge, the refinement will stop, record the latest goodness-of-fit parameter R_w value, and continue with the next structure. If the resulted $R_w > 1.0$ (unconverged fit), it would be marked as 1.0.

This process is repeated for every structure fetched from databases. When the program has looped over all the structures it returns a plot of best-fit goodness-of-fit parameters R_w of each model. We call this plot the structure-mining map (see a representative plot later in Fig. 3.1).

The program also returns a detailed formatted table that is suitable for inserting into a manuscript summarizing the results of the structure-mining process. The experimenter can also select one or multiple structure model entries to save the corresponding results, figures of the data and the fit, the calculated and difference PDF data files, the initial and refined structures in cif format, and the values of initial and refined parameters in a formatted table.

Table 3.1: The experimental PDF datasets for testing the structure-mining approach with relevant parameters. Here L is the sample-to-detector distance and Q_{damp} and Q_{broad} are standard fitting parameters for the PDF that come primarily from instrumental resolution effects. The instrument resolution parameters and L of the CuIr_2S_4 data are not available.

Composition	Scatterer	Beamline	Q_{damp} ($\text{\AA}^{-1}$)	Q_{broad} ($\text{\AA}^{-1}$)	Q_{max} ($\text{\AA}^{-1}$)	X-ray wavelength ($\text{\AA}$)	L (mm)
BaTiO_3 [256]	x-ray	XPD	0.037	0.017	24.0	0.1867	202.8031
Ti_4O_7	x-ray	XPD	0.041	0.009	25.0	0.1866	202.9990
$\text{NaFeSi}_2\text{O}_6$ [395]	x-ray	XPD	0.035	0.016	22.0	0.18288	204.2825
$\text{Ba}_{0.8}\text{K}_{0.2}(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ [396]	neutron	NOMAD	0.018	0.019	20.0	-	-
CuIr_2S_4 [215]	x-ray	XPD	-	-	25.0	0.183	-
MnO [397]	neutron	NPDF	0.0198	0.0195	35.0	-	-
$\text{V}_2\text{N}+\text{VN}$ [398]	x-ray	XPD	0.0369	0.0131	25.0	0.1847	205.3939

3.3 Testing the methodology

To test the method, we selected PDFs of seven different materials from x-ray and neutron total scattering data, as listed in Table 3.1.

The sample synthesis information can be found in the corresponding publications [256; 395; 396; 215; 397; 398]. The introduction of x-ray and neutron PDF experiments on these testing materials are available in the papers as well but summarized as below for convenience.

The total scattering measurements were conducted at one synchrotron x-ray facility, the XPD beamline (28-ID-2) at the National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory, and two neutron time-of-flight facilities, the NOMAD beamline (BL-1B) [335] at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory and the NPDF beamline [304] at the Manuel Lujan Jr. Neutron Scattering Center at Los Alamos Neutron Science Center (LANSCE), Los Alamos National Laboratory. All of the datasets are from previously published work, indicated in the table, except for the Ti_4O_7 , which is unpublished data.

For the XPD beamline the samples were loaded in 1 mm inner diameter polyimide capillaries mounted perpendicular to the beam and the x-ray datasets were collected at room

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temperature, except the vanadium nitride sample that was collected at 100 K [398] and the CuIr_2S_4 sample at 500 K [215], using the rapid acquisition PDF method (RAPDF) [334]. A large area 2D Perkin Elmer detector was mounted behind the samples. The collected data frames were summed, corrected for detector and polarization effects, and masked to remove outlier pixels before being integrated along arcs of constant Q , where $Q = 4\pi \sin \theta / \lambda$ is the magnitude of the momentum transfer on scattering, to produce 1D powder diffraction patterns using the FIT2D program [336]. Standardized corrections and normalizations were applied to the data to obtain the total scattering structure function, $S(Q)$, which was Fourier transformed to obtain the PDF, using PDFGETX3 [338] within xPDFSUITE [339]. The incident x-ray wavelengths and the calibrated sample-to-detector distances are listed in the Table 3.1.

For the NOMAD and NPDF beamlines, the samples were loaded in vanadium cans. The $\text{Ba}_{0.8}\text{K}_{0.2}(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ data from the NOMAD beamline were collected at room temperature [396] and the data were reduced and transformed to the PDF using the automated data reduction scripts at the NOMAD beamline. The MnO data from the NPDF beamline were collected at 15 K [397] and the data were reduced and transformed to the PDF using the PDFGETN program [312].

The full experimental details may be found in Refs. [256; 395; 396; 215; 397; 398]. The maximum range of data used in the Fourier transformation, Q_{max} , was chosen to give the best trade-off between statistical noise and real-space resolution. The instrument resolution parameters, Q_{damp} and Q_{broad} , which are relevant parameters for our structure-mining activity, were obtained by calibrating the experimental conditions in each case using a well crystallized standard sample. The values are reproduced in the Table 3.1.

In the following, the brief structure-mining results on a series of materials, including both x-ray and neutron PDFs, are shown.

3.4 Results and discussions

We first apply this approach to the measured PDF from barium titanate (BTO) nanoparticles, BaTiO_3 . BTO is one of the best studied perovskite ferroelectric materials [159; 156]. Because BaTiO_3 has the well-known candidate structures, we first use it as a demonstration of the structure-mining method.

The structure of this measured BaTiO_3 nanoparticle dataset will be carefully studied in Chapter 5, and more details of the results can be found in the reference [256]. In that work, it was reported that the structure of this nanoparticle sample was non-centrosymmetric at room temperature and had one of the ferroelectric forms of the BaTiO_3 structures [156], among one of the distorted structures with space groups $Amm2$, $P4mm$, and $R3m$. All these structures gave somewhat comparable fit to the data and it was difficult to distinguish which among them was definitively the correct structure because of the Bragg peak broadening and the relatively weak x-ray scattering of oxygen sublattice. Nearby centrosymmetric space groups also performed well based on R_w but could be ruled out by careful consideration of refined ADPs of Ti ions (we note that in table V of [156] there is a typo where the s.g. $P4mm$ structure is described as $P4/mmm$, which is the centrosymmetric parent, but in the body of the table the Ti ion is shown as displacing off the center of unit cell, breaking centrosymmetry).

Heuristic-1 is applied, fetching all structures that have the same composition as input BaTiO_3 . The structure-mining results from the MPD and COD are shown in Fig. 3.1(a) and (b), and Table 3.2 and Table 3.3, respectively. The best-fit structures from each data mine were MPD structure No. 5 [399] and COD structure No. 20 [156] with $R_w = 0.144$ and 0.143, respectively. The calculated and measured PDFs are shown in Fig. 3.2(a) and (b), respectively. Unlike the traditional manual PDF structure refinement methodology, the

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Table 3.2: Structure-mining results for the BaTiO₃ nanoparticle x-ray data using heuristic-1 from the MPD. Here No. refers to the structure index (Fig. 3.1(a)), which is the order fetched from the database, and s.g. represents the space group of the structure model. The initial isotropic atomic displacement parameter (U_{iso}) of all atoms in each structure is set to 0.005 Å² to start the structure refinements. The a , b , and c are the lattice parameters of the structure model. The subscript i indicates an initial value before refinement and the subscript r indicates a refined value. DB ID represents the database ID of the structure model. $Q_{max} = 24.0$ Å⁻¹, $Q_{damp} = 0.037$ Å⁻¹, and $Q_{broad} = 0.017$ Å⁻¹ were set and not varied in the refinements (see Section 3.2 for details).

No.	R_w	s.g.	Ba U_{iso} (Å ²)	Ti U_{iso} (Å ²)	O U_{iso} (Å ²)	a_i (Å)	a_r (Å)	b_i (Å)	b_r (Å)	c_i (Å)	c_r (Å)	DB ID
5	0.144	<i>Amm2</i>	0.0021	0.0070	0.0126	5.81	5.67	5.86	5.76	3.99	3.99	mp-5777
6	0.160	<i>P4mm</i>	0.0027	0.0074	0.0116	4.00	4.00	-	-	4.22	4.07	mp-5986
9	0.165	<i>R3m</i>	0.0027	0.0074	0.0123	5.75	5.66	-	-	7.11	7.05	mp-5020
10	0.170	<i>P4/mmm</i>	0.0026	0.0105	0.0174	4.03	4.00	-	-	4.04	4.07	mp-2998
7	0.530	<i>C222₁</i>	0.0047	0.0023	0.0373	5.84	5.69	10.02	9.84	14.14	13.98	mp-558125
1	0.571	<i>P6₃/mmc</i>	0.0070	0.0041	0.0468	5.79	5.69	-	-	14.10	13.97	mp-5933
2	0.956	<i>P4/mmm</i>	0.0172	0.0011	0.0884	4.11	4.16	-	-	5.04	4.73	mp-19990
3	0.969	<i>Amm2</i>	0.0003	0.0941	0.0090	5.31	5.26	5.33	5.44	8.88	8.80	mp-1076932
8	0.977	<i>Amm2</i>	0.0075	0.0006	0.0010	6.64	6.76	8.63	8.60	3.75	3.86	mp-644497
0	0.990	<i>Amm2</i>	0.0017	0.0031	0.0000	5.81	6.00	5.85	5.98	5.03	4.84	mp-995191
4	1.000	<i>Pm3m</i>	0.0115	0.0104	0.0003	4.65	4.78	-	-	-	-	mp-504715

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Table 3.3: Structure-mining results for the BaTiO₃ nanoparticle x-ray data using heuristic-1 from the COD. See the caption of Table 3.2 for an explanation of the entries.

No.	R_w	s.g.	Ba U_{iso} (Å ²)	Ti U_{iso} (Å ²)	O U_{iso} (Å ²)	a_i (Å)	a_r (Å)	b_i (Å)	b_r (Å)	c_i (Å)	c_r (Å)	DB ID
20	0.143	<i>Amm2</i>	0.0021	0.0080	0.0181	5.67	5.67	5.69	5.76	3.98	3.99	9014492
21	0.144	<i>Amm2</i>	0.0020	0.0087	0.0178	5.67	5.67	5.69	5.76	3.98	3.99	9014627
22	0.145	<i>Amm2</i>	0.0020	0.0091	0.0175	5.67	5.67	5.69	5.76	3.99	3.99	9014645
26	0.146	<i>Amm2</i>	0.0020	0.0094	0.0168	5.67	5.67	5.68	5.76	3.99	3.99	9014774
30	0.148	<i>Amm2</i>	0.0020	0.0100	0.0179	5.67	5.67	5.69	5.76	3.98	3.99	9016084
33	0.151	<i>Amm2</i>	0.0025	0.0083	0.0070	5.68	5.68	5.69	5.75	3.99	3.99	9016638
2	0.156	<i>P4mm</i>	0.0027	0.0064	0.0116	3.99	4.00	-	-	4.04	4.07	1513252
8	0.162	<i>P4mm</i>	0.0026	0.0086	0.0162	4.00	4.00	-	-	4.02	4.07	2100858
0	0.162	<i>P4mm</i>	0.0026	0.0086	0.0162	4.00	4.00	-	-	4.02	4.07	1507756
31	0.163	<i>R3m</i>	0.0027	0.0076	0.0163	5.65	5.66	-	-	6.96	7.05	9016152
29	0.163	<i>Amm2</i>	0.0028	0.0054	0.0029	5.62	5.63	5.64	5.70	4.01	4.06	9015715
28	0.163	<i>R3m</i>	0.0027	0.0077	0.0161	5.65	5.66	-	-	6.95	7.05	9015616
27	0.163	<i>R3m</i>	0.0027	0.0079	0.0160	5.65	5.66	-	-	6.95	7.05	9015236
25	0.164	<i>R3m</i>	0.0027	0.0082	0.0160	5.66	5.66	-	-	6.95	7.05	9014756
17	0.164	<i>R3m</i>	0.0027	0.0083	0.0158	5.66	5.66	-	-	6.96	7.05	9014179
24	0.164	<i>R3m</i>	0.0026	0.0084	0.0153	5.65	5.66	-	-	6.95	7.05	9014743
16	0.164	<i>R3m</i>	0.0026	0.0085	0.0157	5.66	5.66	-	-	6.95	7.05	9014074
18	0.165	<i>R3m</i>	0.0026	0.0087	0.0150	5.65	5.66	-	-	6.95	7.05	9014230
32	0.166	<i>R3m</i>	0.0026	0.0091	0.0149	5.65	5.66	-	-	6.96	7.05	9016624
3	0.166	<i>P4mm</i>	0.0026	0.0096	0.0151	3.99	4.00	-	-	4.03	4.07	1525437
9	0.166	<i>P4mm</i>	0.0026	0.0097	0.0158	4.00	4.00	-	-	4.02	4.07	2100859
4	0.168	<i>Pmm2</i>	0.0025	0.0095	0.0151	3.98	3.99	4.01	4.01	4.02	4.07	1540757
23	0.169	<i>P4mm</i>	0.0026	0.0103	0.0163	4.00	4.00	-	-	4.02	4.07	9014668
11	0.170	<i>P4/mmm</i>	0.0026	0.0105	0.0174	4.00	4.00	-	-	4.02	4.07	2100861
10	0.170	<i>P4/mmm</i>	0.0026	0.0105	0.0174	4.00	4.00	-	-	4.02	4.07	2100860
15	0.210	<i>Pm$\bar{3}$m</i>	0.0046	0.0132	0.0172	3.97	4.02	-	-	-	-	5910149
1	0.210	<i>Pm$\bar{3}$m</i>	0.0046	0.0132	0.0172	4.01	4.02	-	-	-	-	1507757
13	0.210	<i>Pm$\bar{3}$m</i>	0.0046	0.0132	0.0172	4.01	4.02	-	-	-	-	2100863
12	0.210	<i>Pm$\bar{3}$m</i>	0.0046	0.0132	0.0172	4.01	4.02	-	-	-	-	2100862
5	0.210	<i>Pm$\bar{3}$m</i>	0.0046	0.0132	0.0172	4.00	4.02	-	-	-	-	1542140
14	0.210	<i>Pm$\bar{3}$m</i>	0.0046	0.0132	0.0172	4.03	4.02	-	-	-	-	4124842
6	0.367	<i>Pm$\bar{3}$m</i>	0.0058	0.0126	0.0799	4.08	4.02	-	-	-	-	1542189
7	0.573	<i>P6₃/mmc</i>	0.0070	0.0041	0.0469	5.72	5.69	-	-	13.96	13.97	2009488
19	0.708	<i>P4mm</i>	0.0042	0.2490	0.0479	3.99	4.04	-	-	4.03	3.98	9014273

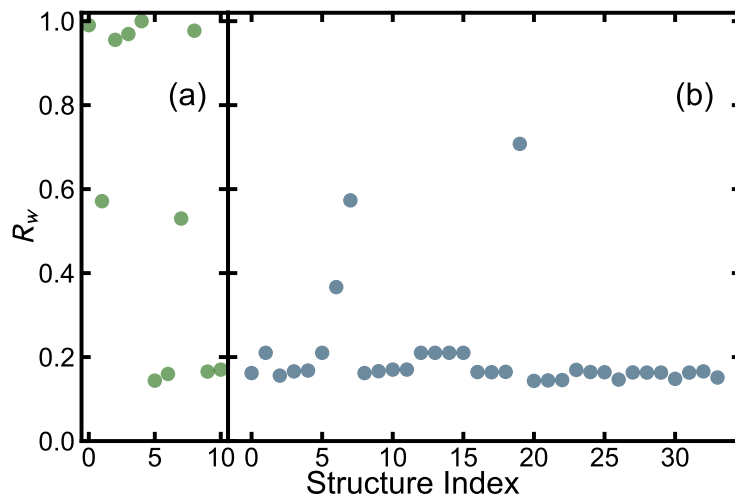


Figure 3.1: R_w values for each of the structures fetched from the databases for the BaTiO_3 nanoparticle x-ray data using heuristic-1, filtering for all the structures with composition BaTiO_3 from (a) the MPD (green) and (b) the COD (blue). The R_w parameter represents the goodness-of-fit for each structure.

structure-mining approach followed by the automated fitting resulted in satisfactory and reasonable fits without any human intervention. These structures may be investigated in more detail by traditional manual fitting approaches.

Some structures retrieved from the mine also resulted in very poor fits, as shown in Fig. 3.2(c) and (d), which are the automatically determined fits of MPD structure No. 4 [372] and COD structure No. 19 [399], respectively. We expect that this will be due to the fact that the structure fetched from the database is different from that of our sample, and it is this automated screening of database structures to find the most plausible candidates that is the goal of structure-mining. However, we investigate this in more detail below.

From the MPD result, as shown in Table 3.2, it clearly reveals that the top three best-fit structures are exactly the non-centrosymmetric ferroelectric forms of BaTiO_3 structures with space groups $Amm2$, $P4mm$, and $R3m$. In addition, the closely similar centrosymmetric perovskite model with space group $P4/mmm$ (No. 10, ranked 4) [400] gives slightly worse

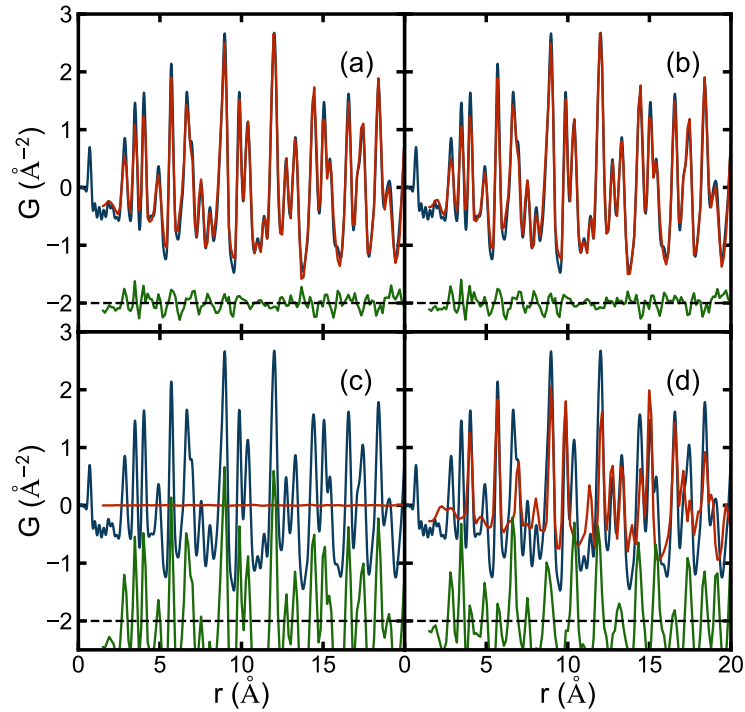


Figure 3.2: PDFs from representative satisfactory and unsatisfactory structures from (a, c) the MPD and (b, d) the COD. Blue curves are the measured PDF of BaTiO_3 nanoparticles. Red curves are the calculated PDFs after retrieving from the databases using heuristic-1 and automatically fitting to the data (see Section 3.2 for details). Offsets below in green are the difference curves.

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but comparable R_w . The heuristic-1 has therefore found the correct candidate structure models from the MPD, as well as returning nearby structures for a more detailed manual comparison.

The COD contained many more candidate structures for this composition (Table 3.3). Again the structure-mining shows that the best three non-centrosymmetric perovskite models are found as expected, along with the similar general barium titanate perovskite models (with slightly worse R_w) with space groups $P4/mmm$ and $Pm\bar{3}m$.

The COD result also returned a space group $Pmm2$ structure (No. 4) [401] with a reasonable fit ($R_w = 0.168$) which turns out to be a general perovskite structure having two half filled Ti ions at (0.5,0.5,0.509) and (0.5,0.5,0.491) sites, similar to a doubled unit cell of the tetragonal barium titanate perovskite model with space group $P4mm$, albeit with a small orthorhombic distortion. This illustrates the power of this structure-mining approach as it does a good job of finding all plausible structures in the database. These can then be considered and ruled out by researchers based on other criteria.

There is also a hexagonal structure (space group $P6_3/mmc$) in the databases for $BaTiO_3$, and this gives very poor fit to the $BaTiO_3$ nanoparticle data from both MPD (No. 1) [402] and COD (No. 7) [402], showing that the approach is capable of finding true positive and true negative results.

The structure-mining gives the COD structure No. 19 (space group: $P4mm$) [399] a bad fit because the model is wrong, with Ti ion sitting at 1b (0.5, 0.5, 0.265) and O2 ion sitting at 2c (0.5, 0, 0.236), which is significantly offset from the correct position such that Ti ion is at or near the center of the unit cell. We checked the reference for this database entry (COD ID: 9014273), and it turned out to be correct in the paper but a wrong entry in the database because the reference reported that Ti ion was at 1b (0.5, 0.5, 0.0515) and O2 ion was at 2c (0.5, 0, 0.486) [399]. This indicates that this structure-mining approach may actually help

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to find errors in the database, but at worst will not return incorrect structures as candidate models.

Interestingly, the mining operation did report one false negative. It missed one of the plausible perovskite structure models in the MPD database, the cubic model with space group $Pm\bar{3}m$ (MPD No. 4) [372], which was correctly found in the COD database. The reason why this did not give a good refinement was that the starting lattice parameters taken from the database were much too large ($a = 4.65 \text{ \AA}$) and the automated refinement could not converge to the correct minimum ($a = 4.02 \text{ \AA}$) due to the 55% cell volume mismatch from the correct one, resulting in a poor fit. Although we refine the lattice parameter during the process, if the starting value is too far away from the correct one, it is possible that the refinement program will not be able to find the right solution in the parameter space and result in a poor fit and a false negative result. In some respect it is a success of the program because we actually hope that incorrect models in the database will fit the data poorly, and if the value of the lattice parameter recorded in the database is far from being correct for the measured sample, in some sense this constitutes a bad model. Similar lattice parameter situations happen for MPD No. 0 [403], 2 [404], 3 [403], and 8 [405]. The entries in the MPD that are taken from the ICSD database have gone through an energy relaxation step using density functional theory (DFT) [406; 407] before the crystal structures are deposited in the MPD. For some reason, the DFT relaxation took some of the lattice parameters somewhat far away from the experimental values in the original structure reports [403; 404; 405]. Overall the heuristic-1 approach already returned the correct structures for BaTiO_3 nanoparticles. The complete mining operation took 29.3 seconds when searching with the MPD and 47.8 seconds for the COD search to complete, using a general laptop.

We would like to further test the more loosely filtered heuristic-2 approach on the BaTiO_3 nanoparticle data. The structure-mining results from the MPD and COD, fetching all

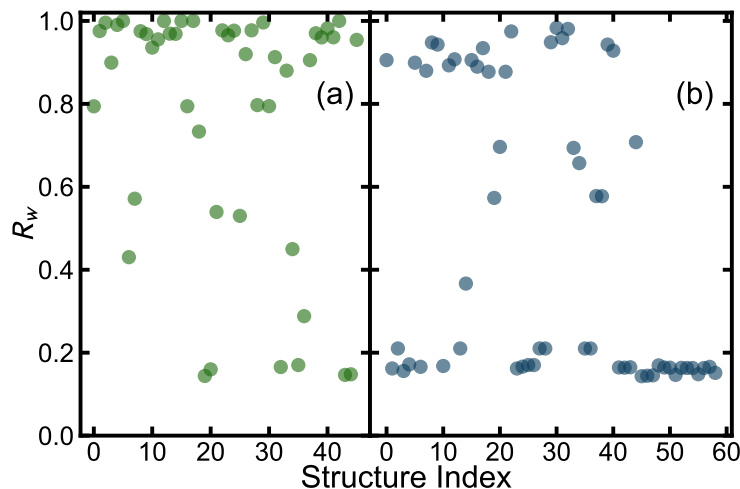


Figure 3.3: R_w values for each of the structures fetched from the databases for the BaTiO_3 nanoparticle x-ray data using heuristic-2, filtering for all the structures with Ba, Ti, and O elements from (a) the MPD (green) and (b) the COD (blue).

structures that contain just Ba, Ti, and O elements with any stoichiometry, are shown in Fig. 3.3(a) and (b), respectively.

Heuristic-2 found all the structures that were found with heuristic-1, as expected. This approach also found a number of additional good structural candidates. The MPD returned three more that were within $\Delta R_w \approx 0.1$ from the best-fit R_w (approximately 0.14), i.e. MPD No. 43 ($\text{Ba}_{12}\text{Ti}_{12}\text{O}_{27}$) [372], 44 ($\text{Ba}_3\text{Ti}_3\text{O}_8$) [408], 36 ($\text{Ba}_4\text{Ti}_4\text{O}_{10}$) [372] and COD returned one, No. 4 model ($\text{Ba}_{0.92}\text{Ti}_{0.9}\text{O}_{2.89}$) [409], where ΔR_w is the deviation in R_w of a structure from the R_w of the best-fit structure. Close inspection of these models indicates that they have a stoichiometry that is approximately the Ba:Ti:O = 1:1:3 ratio and that structure-mining found some nearby defective structures in addition to the standard 113 perovskite structures. This will allow the experimenters to further investigate the defective models to find any physical or chemical insights that they might provide.

The heuristic-2 structure-mining operation also, as expected, returned some structures from the databases for which the atomic composition ratio was not close to 1:1:3. None

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of these additional structures gave reasonable fits to the PDF, resulting in poor R_w values larger than 0.4 for the MPD (such as $\text{Ba}_2\text{Ti}_3\text{O}_8$ MPD No. 6 [372]) and 0.6 for the COD (such as $\text{Ba}_{11}\text{Ti}_{28}\text{O}_{66.48}$ COD No. 34 [410]). The entire search process took 493.7 seconds for the MPD and 469.5 seconds for the COD.

The heuristic-3 approach was also tested on the BaTiO_3 nanoparticle data by fetching all structures that contain Ba, Ti, O elements and one additional element with any stoichiometry. It took about 10.3 and 41.0 minutes for the MPD (in total 57 structures) and COD (in total 103 structures) to finish, respectively. Of these new structures that were found, most of the best-fit structures have slightly worse R_w (~ 0.2) than those in heuristic-1 and 2 (~ 0.14). The new structures are mostly substituting Ba or Ti site by another element and they also have an approximate stoichiometry 113, such as MPD No. 43 ($\text{Ba}_3\text{Sr}_5\text{Ti}_8\text{O}_{24}$) [372] and COD No. 22 ($\text{Ba}_{0.93}\text{Ti}_{0.79}\text{Mg}_{0.21}\text{O}_{2.97}$) [409], which agrees with what has been found in heuristic-2.

Finally we tested the very loose heuristic-4 approach. Here the experimenter can freely choose any searching criteria, such as Ba-Ti-*, Ba-*-O, or even *-*-*, in which an * represents an arbitrary element. In our test case we set the search to be that where the structure contains three elements, including Ba and two other elements, i.e. Ba-*-*. The structure-mining map plot is shown in Fig. 3.4. This search took much longer, 174.3 and 205.2 minutes on a single CPU core for the MPD and COD, respectively. This may be sped up by running on more cores. In total, 1833 structures were fetched from the MPD and 1046 from the COD. The less restrictive heuristic-4 found all the structures that were found with heuristic-1 and 2, as expected. The normal BaTiO_3 perovskite structures are still ranked at the top. Following that, it additionally returns some perovskite structures that have Ti replaced by other species with similar x-ray scattering power as Ti, such as MPD No. 1660 (BaVO_3) [411], MPD No. 1268 (BaMnO_3) [372], and COD No. 683 (BaFeO_3) [412]. These gave agreements

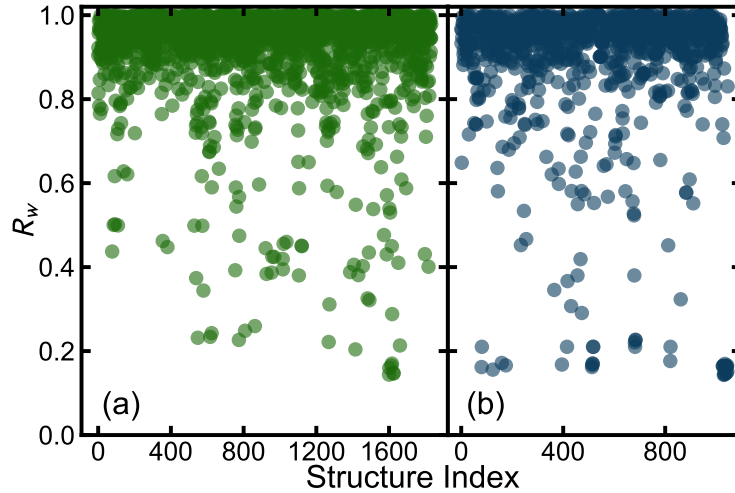


Figure 3.4: R_w values for each of the structures fetched from the databases for the BaTiO_3 nanoparticle x-ray data using heuristic-4, filtering for all the structures with Ba, and two other arbitrary elements from (a) the MPD (green) and (b) the COD (blue).

of $R_w \gtrsim 0.2$ compared to 0.14 for the best-fit structures (BaTiO_3). So the structure-mining is able to distinguish these nearby but incorrect structures from the ones with correct atom species. The perovskite structures with B site element replaced by one with a significantly different x-ray scattering power than Ti resulted in significantly poorer R_w , away from the best-fit structures by $\Delta R_w \sim 0.15$, such as MPD No. 1482 (BaRhO_3) [413] and COD No. 431 (BaNbO_3) [414].

Overall we achieved a satisfactory result for the barium titanate nanoparticle dataset using all the four structure-mining heuristics.

We now test structure-mining for some different materials, for example, the low symmetry Ti_4O_7 system. Its published room temperature crystal structure is a triclinic model (space group $P\bar{1}$) with all the atoms sitting on (x,y,z) general positions [415]. We used the structure-mining heuristic-2 approach, fetching all the structures that contain Ti and O elements with any stoichiometry. The structure-mining map plot is shown in Fig. 3.5. The top seven structure-mining results are also summarized in Table 3.4. The titanium oxides have many

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Table 3.4: The top seven structure-mining results for the Ti_4O_7 experimental x-ray PDF using heuristic-2 on data from the MPD and COD. See the caption of Table 3.2 for an explanation of the entries. The initial lattice parameters and refined ADPs are listed. The refined lattice parameters are not listed because they are close to initial values.

DB No.	R_w	formula	s.g.	Ti U_{iso} ($\text{\AA}^2$)	O U_{iso} ($\text{\AA}^2$)	a_i ($\text{\AA}$)	b_i ($\text{\AA}$)	c_i ($\text{\AA}$)	α_i ($^\circ$)	β_i ($^\circ$)	γ_i ($^\circ$)	Ref.
COD 20	0.168	Ti_4O_7	$P\bar{1}$	0.0051	0.0076	5.60	7.13	12.47	95.1	95.2	108.7	[415]
COD 1	0.169	Ti_4O_7	$P\bar{1}$	0.0050	0.0104	5.59	6.91	7.13	64.1	71.0	75.3	[416]
COD 21	0.170	Ti_4O_7	$P\bar{1}$	0.0050	0.0104	5.59	6.91	7.13	64.1	71.1	75.5	[417]
COD 0	0.173	Ti_4O_7	$P\bar{1}$	0.0048	0.0108	5.59	6.90	7.12	64.1	71.2	75.7	[416]
MPD 38	0.174	Ti_5O_9	$P\bar{1}$	0.0046	0.0065	5.62	7.18	8.56	69.5	75.2	71.3	[418]
MPD 49	0.183	Ti_4O_7	$P\bar{1}$	0.0048	0.0108	5.64	6.96	7.18	64.2	71.1	75.1	[416]
COD 36	0.225	Ti_5O_9	$P1$	0.0053	0.0088	5.57	7.12	8.49	69.8	75.0	71.5	[419]
$\vdots$												

different structures, largely depending on the stoichiometry (98 structures from the MPD and 77 from the COD), but structure-mining returned the published structure for Ti_4O_7 on the top, i.e. COD No. 20 [415].

This is a challenging problem because there are similar structures belonging to the $\text{Ti}_n\text{O}_{2n-1}$ Magnéli homologous series [420; 421]. Among the top 7 entries, the other 4 Ti_4O_7 structures are very similar to COD No. 20. COD 20 is reported in a different structural setting than the other 4 [422], which explains the rather different values for the lattice parameters, but the only real difference in structure between COD 20 and the other Ti_4O_7 structures reported in Table 3.4 is that one oxygen position is shifted by about 0.7 $\text{\AA}$ along the b -axis compared to the other four. This is a significant structural difference yet does not result in a very large difference in R_w and so differentiating these two structures probably deserves some additional consideration by the experimenter. Atomic positions are not refined independently during this structure-mining process and it is possible that this discrepancy may be resolved by a full refinement of the best performing models, as well as suggesting to the user oxygen b -axis position as a possibly relevant variable. Structure-

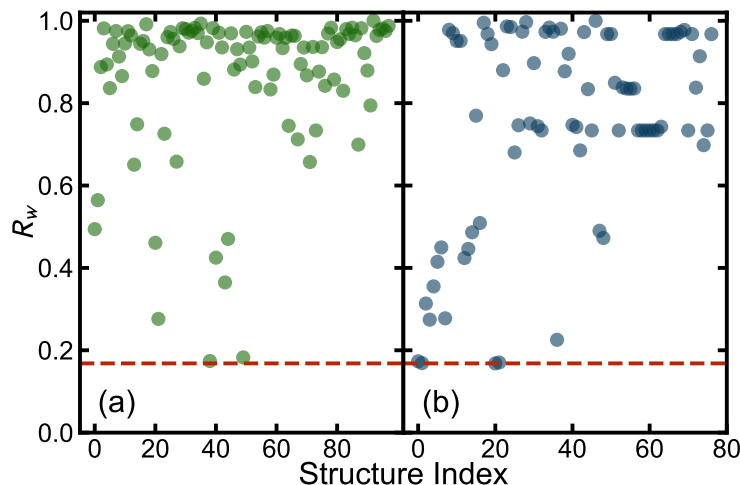


Figure 3.5: R_w values for each of the structures fetched from the databases for the Ti_4O_7 x-ray data using heuristic-2, filtering for all the structures with Ti and O elements from (a) the MPD (green) and (b) the COD (blue). The horizontal dashed line represents the lowest R_w entry found, COD No. 20 (Ti_4O_7 , s.g.: $P\bar{1}$).

mining also returned some results with slightly different stoichiometry with similar R_w values. For example, the MPD No. 38 (Ti_5O_9) [418], which belongs to a different variant in the Magnéli series. The Magnéli phases are constructed from similar TiO_6 octahedral motifs, containing rutile-like slabs extending infinitely in the a - b plane, but the TiO_6 octahedra are stacked along the c -axis in slabs of different widths depending on the composition [420; 421; 418]. In Ti_4O_7 , every oxygen atom connects four octahedra, but in Ti_5O_9 (MPD 38), oxygen atoms link 3 octahedra. Despite these differences, the MPD 38 model performs similarly, albeit somewhat worse, than some of the well performing Ti_4O_7 models, suggesting that it at least warrants being explicitly ruled out as a candidate in a more careful modeling. This illustrates how the structure-mining approach, beyond just automatically finding the “right” structure, additionally can add value by suggesting alternative nearby models to the experimenter. We also note that, from Table 3.4, COD No. 36 (Ti_5O_9 , s.g.: $P1$) [419] performs worse ($R_w > 0.2$), and it is the first model that has a significantly different structure, where

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some Ti atoms are tetrahedrally coordinated by oxygen rather than octahedrally. This model can probably be ruled out on the basis of structure-mining alone.

Now let us turn to a challenging dataset, nanowire bundles of a pyroxene compound with a generic composition of XYSi_2O_6 (where X and Y refer to metallic elements such as but not limited to Co, Na, and Fe). This example is particularly challenging because the samples formed as nanowires that were reported to be ~ 3 nm in width [395]. In that work, a series of candidate structures were tried manually and the best-fit model was found to be monoclinic $\text{NaFeSi}_2\text{O}_6$ with a space group $C2/c$ [423].

The structure-mining heuristic-1 approach was first tested. The MPD found one structure [423] and the COD found six non-duplicated structures [424; 425; 426; 427; 428; 429], all having a quite similar structure, $\text{NaFeSi}_2\text{O}_6$ (s.g.: $C2/c$). The returned structure-mining results have $R_w \approx 0.35$. These are poor fits overall, but comparable to the fits reported in the prior work [395]. Although the R_w is not ideal, possibly due to the sample’s complicated geometry, structural heterogeneity, and defects, the structure-mining approach seems still to be working. Using heuristic-2 (Na-Fe-Si-O) and 3 (Na-Fe-Si-O-*) approaches found similar results, with heuristic-3 finding some Ca and Li doped compounds albeit with the same structure.

The least restrictive heuristic-4 approach was also tried. Here we show the result of fetching all the structures that contain Si and O elements and two other arbitrary elements with any stoichiometry, i.e. *-*-Si-O (Fig. 3.6). The mining operation took about 12 hours for the MPD (in total 1700 structures) and 122 hours for the COD (3187 structures) to finish, respectively. The COD is significantly more time-consuming because many of the COD structures have large numbers of hydrogen atoms, which could be neglected for x-ray PDF calculation to shorten the running time in future work. The top ten entries across the MPD and COD are listed here for convenience in Table 3.5.

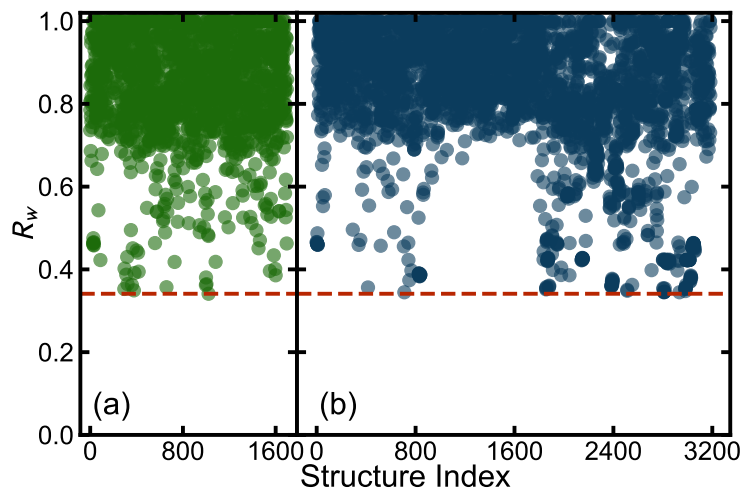


Figure 3.6: R_w values for each of the structures fetched from the databases for the $\text{NaFeSi}_2\text{O}_6$ nanowire x-ray data using heuristic-4, filtering for all the structures with Si, O, and two other arbitrary elements from (a) the MPD (green) and (b) the COD (blue). The horizontal dashed line represents the lowest R_w entry found, MPD No. 1021 ($\text{NaGaSi}_2\text{O}_6$, s.g.: $C2/c$).

Table 3.5: The top ten structure-mining results for the $\text{NaFeSi}_2\text{O}_6$ nanowire experimental x-ray PDF using heuristic-4 on data from the MPD and COD, fetching all the structures that contain Si and O elements and two other arbitrary elements with any stoichiometry, i.e. $*1\text{-}^*2\text{-Si-O}$. The $*1$ and $*2$ represent the first and the second atoms in the formula, respectively. See the caption of Table 3.2 for an explanation of the entries. The refined lattice parameters and ADPs are listed. The initial lattice parameters are not reproduced here because they are all very close to refined values.

DB No.	R_w	formula	s.g.	*1 U_{iso} ($\text{\AA}^2$)	*2 U_{iso} ($\text{\AA}^2$)	Si U_{iso} ($\text{\AA}^2$)	O U_{iso} ($\text{\AA}^2$)	a_r ($\text{\AA}$)	b_r ($\text{\AA}$)	c_r ($\text{\AA}$)	β_r ($^\circ$)	SPD ($\text{\AA}$)	DB ID
MPD 1021	0.341	$\text{NaGaSi}_2\text{O}_6$	$C2/c$	0.0193	0.0053	0.0048	0.0118	9.69	8.81	5.32	107.5	34.0	mp-6822
COD 709	0.345	$\text{NaGaSi}_2\text{O}_6$	$C2/c$	0.0174	0.0054	0.0049	0.0112	9.68	8.81	5.32	107.5	33.8	2004306
COD 2935	0.345	$\text{NaGaSi}_2\text{O}_6$	$C2/c$	0.0174	0.0054	0.0049	0.0112	9.68	8.81	5.32	107.5	33.8	9011383
COD 2809	0.345	$\text{NaGaSi}_2\text{O}_6$	$C2/c$	0.0173	0.0054	0.0048	0.0112	9.68	8.81	5.32	107.5	33.8	9010186
COD 2983	0.348	$\text{NaFeSi}_2\text{O}_6$	$C2/c$	0.0249	0.0033	0.0088	0.0129	9.68	8.82	5.32	107.5	34.1	9013274
COD 2513	0.348	$\text{NaFeSi}_2\text{O}_6$	$C2/c$	0.0214	0.0035	0.0070	0.0144	9.68	8.82	5.32	107.5	34.7	9005439
MPD 377	0.349	$\text{Ca}_{0.5}\text{NiSi}_2\text{O}_6$	$C2$	0.0118	0.0041	0.0052	0.0136	9.68	8.81	5.31	107.4	32.9	mvc-12761
COD 1856	0.352	$\text{NaFeSi}_2\text{O}_6$	$C2/c$	0.0221	0.0033	0.0079	0.0137	9.69	8.81	5.32	107.6	34.6	9000327
COD 2805	0.353	$\text{NaFeSi}_2\text{O}_6$	$C2/c$	0.0227	0.0032	0.0082	0.0135	9.69	8.81	5.32	107.6	34.7	9010095
MPD 294	0.353	$\text{Ca}_{0.5}\text{CoSi}_2\text{O}_6$	$C2$	0.0277	0.0042	0.0050	0.0231	9.68	8.82	5.32	107.3	34.8	mvc-11818
$\vdots$													

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The returned $\text{NaGaSi}_2\text{O}_6$ entries (s.g.: $C2/c$) [430; 431; 432] have a similar structure to $\text{NaFeSi}_2\text{O}_6$ (s.g.: $C2/c$). They both fit experimental data comparably well with $\text{NaGaSi}_2\text{O}_6$ slightly preferred. The $\text{NaGaSi}_2\text{O}_6$ solution can be ruled out on the basis that no Ga was in the synthesis. The x-ray scattering power of Fe and Ga are similar with Ga being slightly higher ($Z(\text{Fe}) = 26$, $Z(\text{Ga}) = 31$). The fact that structure-mining prefers to put a slightly higher atomic number, Z , element at this position suggests that we have the right structure, but some details of the refinement need to be worked out by the experimenter. This example illustrates how careful interrogation of the fits to the database models compared to the original parameters can highlight possible defects or impurities and guide the experimenter towards what things to search for.

The MPD also returned some computed theoretical structures with space group $C2$, MPD No. 377 ($\text{Ca}_{0.5}\text{NiSi}_2\text{O}_6$, s.g.: $C2$) and MPD No. 294 ($\text{Ca}_{0.5}\text{CoSi}_2\text{O}_6$, s.g.: $C2$) [372]. These perform slightly worse than the fully stoichiometric $\text{NaGaSi}_2\text{O}_6$ and $\text{NaFeSi}_2\text{O}_6$ structures. Inspection of these structures indicates that they are very similar in nature but with a lowered symmetry due to missing Ca ions and can probably be ruled out, though the fact that structure-mining finds them may suggest trying sub-stoichiometry models on the A site.

Overall, the heuristic-4 returned a number of isostructural but with different composition structures. For this system, it is possible that the correct structure is not limited to the pure $\text{NaFeSi}_2\text{O}_6$ (s.g.: $C2/c$) stoichiometry only and substituting impurity ions or atom deficiencies may be occurring for such a complicated synthesis [395]. These candidate structures found by structure-mining are valuable to resolve the ambiguity. Furthermore, by taking the structure-mining approach yields different but similarly-fitting models which can also give meaningful information about uncertainty estimates on refined parameters such as metal or oxygen ion positions. This test again shows the huge potential of structure-mining on PDF data to help experimenters be aware of some possible structural solutions that were

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overlooked or not realized in the traditional workflow.

Next, we test structure-mining on a complicated doped material, $\text{Ba}_{1-x}\text{K}_x(\text{Zn}_{1-y}\text{Mn}_y)_2\text{As}_2$. We used the neutron PDF data with composition $(x, y) = (0.2, 0.15)$, which has both A-site and B-site dopings. Its published room temperature crystal structure is a tetragonal structure with the space group $I4/mmm$ [396]. First we applied heuristic-2 specifying all the elements including the dopants, i.e. fetching Ba-Zn-As-K-Mn structures regardless of stoichiometry. This returned no structures from the MPD or the COD. We next tested a heuristic-4 approach with Ba-Zn-As-*-. This did result in two structures being returned, but they were both incorrect compounds, $\text{Ba}_2\text{MnZn}_2\text{As}_2\text{O}_2$ [433] and $\text{BaZn}_2\text{As}_3\text{HO}_{11}$ [372], with R_w values close to 1, as shown in Fig. 3.7(b). We then looked for structures with doping on one site. The “Ba-Zn-As-*” searches the databases for compositions containing four elements, including Ba, Zn, As and one other element. But it still only found incorrect structures, as shown in Fig. 3.7(c). Finally, we resorted to a heuristic-2 approach but only giving the composition of the undoped endmember, Ba-Zn-As. This did find the correct structure, tetragonal phase MPD No. 1 (BaZn_2As_2 , s.g.: $I4/mmm$) [434], as marked by the red circle in Fig. 3.7(d), even though we were fitting to the doped data. This suggests a feasible strategy for doped systems if they are not represented in the databases, which is to try searching for the parent undoped structure, on the basis that the doped structure may be still close to its parent phase, regardless of possible local structure distortions introduced by doping [396]. Starting from this success, the experimenter could then easily change the occupancy of the A-site or B-site, which was also how structural analysis was previously performed on this doped material [435; 436]. So even for the case of doped structures, structure-mining found the correct geometric structure which was from the nearest undoped variant in the database (in this case, there were no structures in the databases that had the same composition as the measured sample). The experimenter can take this structure model and introduce dopants with the known

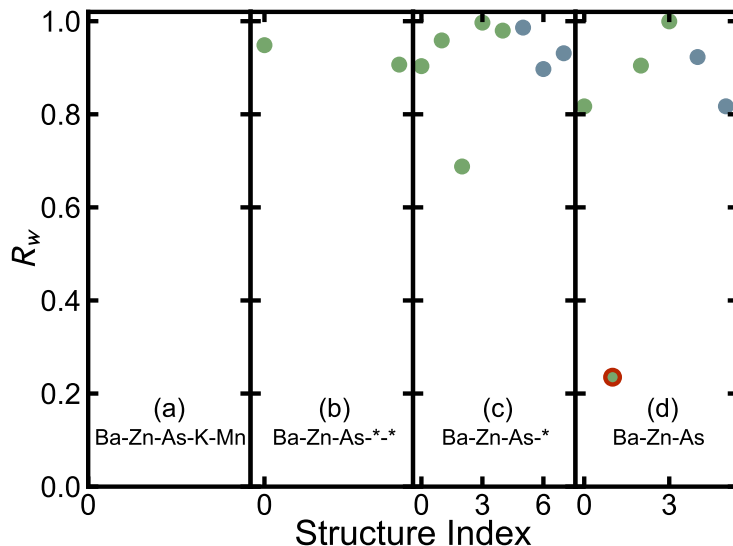


Figure 3.7: R_w values for each of the structures fetched from the databases for the $\text{Ba}_{0.8}\text{K}_{0.2}(\text{Zn}_{0.85}\text{Mn}_{0.15})_2\text{As}_2$ neutron data using the heuristics of (a) Ba-Zn-As-K-Mn, (b) Ba-Zn-As-*-*, (c) Ba-Zn-As-*, and (d) Ba-Zn-As from the MPD (green) and the COD (blue). The best-fit model MPD No. 1 (BaZn_2As_2) in (d) is marked by a red circle.

composition.

Note that the PDF measures the *local* structure of materials, which is not necessarily identical to the long-range ordered crystal structure in some materials [221; 215]. As a result, structure-mining will search for the closest structure in the crystal structure databases to the local atomic arrangement. Here we present the case of the CuIr_2S_4 system, which has a tetragonal local structure (s.g.: $I4_1/amd$) but a cubic long-range ordering (s.g.: $Fd\bar{3}m$) above the metal-insulator transition temperature ($T_{MIT} = 226$ K) [215]. The x-ray data measured at 500 K was tested. when fitting over the narrow range of $1.5 < r < 5$ Å, $1.5 < r < 10$ Å, or $1.5 < r < 20$ Å, structure-mining ranks the tetragonal model above the cubic model. However, when fitting over the broad range of $1.5 < r < 50$ Å, the cubic model fits slightly better than the tetragonal model. The representative results for the $1.5 < r < 5$ Å and $1.5 < r < 50$ Å fit ranges are listed in Table 3.6 and Table 3.7, respectively. As a

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Table 3.6: Structure-mining results for the CuIr_2S_4 x-ray data measured at 250 K data using heuristic-2 from the MPD and COD over the range of $1.5 < r < 5 \text{ \AA}$. Here No. refers to the order that the structures were fetched from the databases, and s.g. represents the space group of the structure model. The initial isotropic atomic displacement parameter (U_{iso}) of all atoms in each structure is set to $0.005 \text{ \AA}^2$ to start the structure refinements. The a , b , and c are the lattice parameters of the structure model. The subscript i indicates an initial value before refinement and the subscript r indicates a refined value. DB ID represents the database ID of the structure model. $Q_{max} = 25.0 \text{ \AA}^{-1}$ (see Section 2 in the manuscript for details).

No.	R_w	formula	s.g.	Cu U_{iso} ($\text{\AA}^2$)	Ir U_{iso} ($\text{\AA}^2$)	S U_{iso} ($\text{\AA}^2$)	a_i ($\text{\AA}$)	a_r ($\text{\AA}$)	c_i ($\text{\AA}$)	c_r ($\text{\AA}$)	DB	DB ID
1	0.079399	CuIr_2S_4	$I4_1/amd$	0.007553	0.002888	0.005664	6.864500	6.885540	10.0257	10.141389	COD	9009940
0	0.090514	CuIr_2S_4	$Fd\bar{3}m$	0.010033	0.003387	0.005496	9.920201	9.873311	-	-	MPD	mp-15065
2	0.092756	CuIr_2S_4	$Fd\bar{3}m$	0.010056	0.003344	0.005495	9.847400	9.871136	-	-	COD	9009941

Table 3.7: Structure-mining results for the CuIr_2S_4 x-ray data measured at 250 K data using heuristic-2 from the MPD and COD over the range of $1.5 < r < 50 \text{ \AA}$.

No.	R_w	formula	s.g.	Cu U_{iso} ($\text{\AA}^2$)	Ir U_{iso} ($\text{\AA}^2$)	S U_{iso} ($\text{\AA}^2$)	a_i ($\text{\AA}$)	a_r ($\text{\AA}$)	c_i ($\text{\AA}$)	c_r ($\text{\AA}$)	DB	DB ID
0	0.108877	CuIr_2S_4	$Fd\bar{3}m$	0.011472	0.004660	0.010181	9.920201	9.855770	-	-	MPD	mp-15065
2	0.109243	CuIr_2S_4	$Fd\bar{3}m$	0.011506	0.004652	0.010912	9.847400	9.855840	-	-	COD	9009941
1	0.111260	CuIr_2S_4	$I4_1/amd$	0.011371	0.004673	0.009709	6.864500	6.967547	10.0257	9.860135	COD	9009940

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result, structure-mining returns the symmetry broken and non-symmetry broken structural candidates whether it is fit over a narrow or broad range, but it also ranks them correctly depending on the r -range fit over in this test case. We note that it is possible in structure-mining for a user to specify a custom fit range, which would allow the researcher to search for structures that are relevant for the measured PDF on different length-scales.

We would also like to test the robustness of the structure-mining approach when the PDF data also include non-atomic structural signals, such as the magnetic PDF (mPDF) signal [437; 397; 438] in a neutron diffraction experiment of a magnetic material.

To test this we consider the MnO neutron PDF data, measured at 15 K, which has a strong mPDF signal. Early neutron diffraction studies reported that MnO has a cubic structure in space group $Fm\bar{3}m$ at high temperature and undergoes an antiferromagnetic transition with a Néel temperature of $T_N = 118$ K, which results in a rhombohedral structure in space group $R\bar{3}m$ [439; 440]. More recently it has been suggested that, at low-temperature, the local structure is even lower symmetry, e.g., monoclinic in s.g. $C2$ [441; 397]. Here we see which of these structural results are returned by the structure-mining process.

The heuristic-2 approach is applied, i.e. fetching all the atomic structures with Mn and O elements. The rhombohedral MnO model is the best performing model (MPD No. 41 [372] with $R_w = 0.236$, Fig. 3.8). The second best fit is the cubic MnO model (COD No. 56 [442] with $R_w = 0.310$). This correctly reflects the fact that at 15 K the material is expected to be in the rhombohedral phase. The monoclinic s.g. $C2$ model was not returned by structure-mining but this is because it is not in any of the databases. The fit agreements are similar to those reported in [397] when the magnetic model is not included in the fit (as is the case here). Therefore, even in the presence of significant magnetic scattering, structure-mining is able to find the correct solution for neutron PDF.

Structure-mining was conceived as a structure selection approach and not for finding

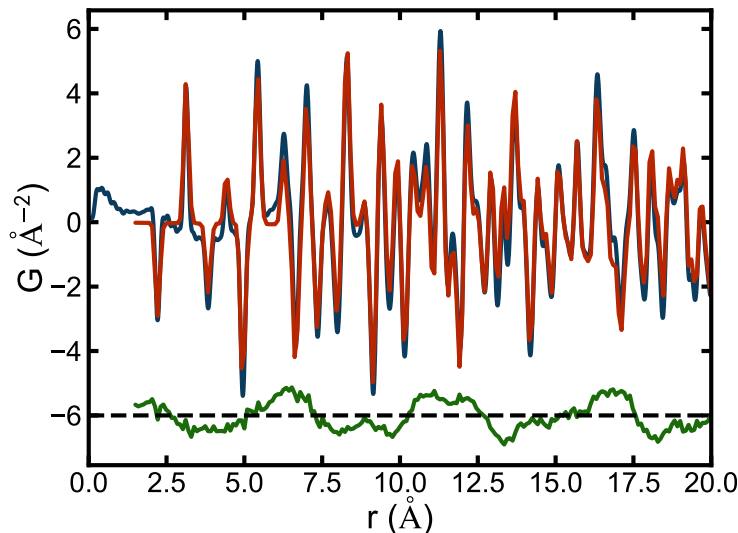


Figure 3.8: The neutron PDF of the MnO data (blue curve) measured at 15 K with the best-fit calculated atomic PDF (red) for the MPD No. 41, rhombohedral MnO model from heuristic-2. The difference curve is shown offset below (green). Notice the strong magnetic PDF signal in the difference curve, which did not confuse structure-mining.

multiple phases in a sample. However, it is interesting to establish how well it performs when the PDF signal consists of more than one phase. For this test we use the x-ray PDF dataset of a vanadium nitride sample [398]. In the original publication [398] it had manually been assigned as consisting of a majority (64%) of V_2N with a structure in space group $P\bar{3}1m$, and a minority (36%) of VN (s.g.: $Fm\bar{3}m$). First we applied the heuristic-2 procedure searching for V-N structures on the measured data. The structure-mining found the correct V_2N structure successfully with $R_w = 0.29$ and with other structures being $R_w > 0.7$. The procedure did not find VN as a candidate structure. We then subtracted the calculated V_2N structure from the measured PDF and carried out structure-mining on the difference. All of the returned structures resulted in values of R_w that were large (0.66 and higher) which is presumably because of the low signal to noise ratio in the subtracted data, and the fact that our definition of R_w (Eq. 2.38) does not account for measurement noise. Nonetheless, the top best-fit structure returned by structure-mining was exactly the correct cubic VN phase

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($R_w = 0.66$). Structure-mining was, therefore, successful at finding both the majority phase and the secondary phase. This shows that, at least in favorable circumstances, multi-phase samples may be successfully structure-mined.

We note that it should be straightforward to extend the structure-mining methodology to study the PDFs of organic materials. However, this is not done in the current version. First, for organic material data, the PDF peaks are sharp at low- r (intra-molecular range) and broad at high- r (inter-molecular range). To handle this correctly, different ADPs should be applied for two separate regions. Especially the sharp intra-molecular peaks cannot be sufficiently fit, which usually require some special treatments on parameters such as the correlated atomic motion parameter δ , sratio, and ADPs [443; 444]. This requires a separation of the molecule from its neighbors which is currently done manually and an automated approach needs to be developed for structure-mining to work. Second, the current heuristics, searching by compositions and elements, are not suitable for organic materials. For example, searching “C-H-O” would return too many candidates, about 16000 entries from COD and MPD databases. Development of new search heuristics, such as searching by organic molecule name, is possible but needs some future work. Third, there are limited organic material entries in the currently supported COD and MPD databases. Supporting some more comprehensive organic structural databases, such as the Cambridge Structural Database (CSD) [445], is necessary for finding organic compounds.

We have shown that structure-mining is able to find the desired structures from the mine on a range of test cases. We now consider its robustness against factors that might prove problematic, specifically data collected at a different temperature to the data in the mine and data measured under a range of different experimental conditions. Structure-mining seems to work well on data collected at different temperatures and so is robust against differences in lattice parameters and ADPs due to temperature effects. This assertion is supported by

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the BaTiO₃ example described above where structure-mining found all the barium titanate structural variants, which were measured at a range of temperatures from 15 K (COD No. 24 in Table 3.3) [156] to 1000 K (COD No. 14 in Table 3.3) [446] when compared to the data measured at room temperature.

Structure-mining also performed well in tests where data were coming from a wide range of different instruments and measurement conditions. In these tests the Q_{max} values for the data varied between $18.6 \text{ \AA}^{-1} < Q_{max} < 25.0 \text{ \AA}^{-1}$, and the ranges of instrument resolution parameters are $0.038 < Q_{damp} < 0.058 \text{ \AA}^{-1}$ and $0.0 < Q_{broad} < 0.048 \text{ \AA}^{-1}$ [217; 396; 447]. All of them worked well in structure-mining which successfully found the correct structures regardless of the fact that different Q_{max} and instrument resolution parameters were in effect. Thus the method should work in general for many other instruments even when Q_{damp} and Q_{broad} vary from one instrument to another.

3.5 PDF in the cloud

Structure-mining is available on a cloud-based platform, PDF in the cloud (PDFITC) [448], at <https://pdfitc.org>. PDFITC is a web applications that hosts software for PDF analysis for studying the local structure of nanostructured materials such as crystalline powders with disorder, nanoparticles and other nanomaterials. It is designed to be a free, powerful and easy-to-use for chemists, materials scientists, earth scientists and anyone who needs to study the structure of materials beyond the average structure.

Beyond that, we hope that it will become a platform for the PDF community to use to share PDF tips, tricks and best practices. It will also be possible for users to “publish” datasets (for example, after the accompanying manuscript is published) facilitating data sharing. Over time we will incorporate new functionality, in the form of new Apps, coming

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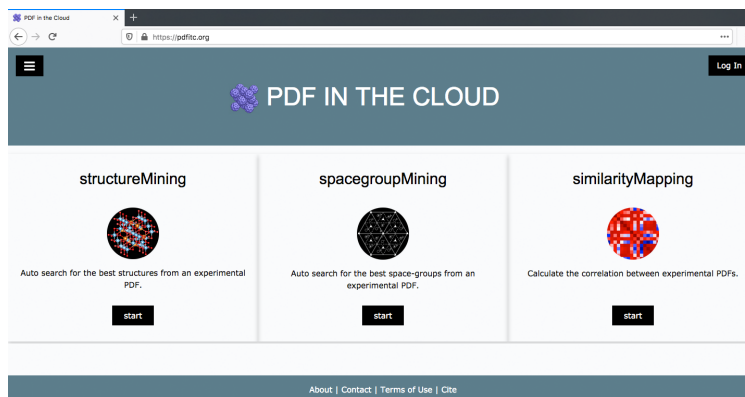


Figure 3.9: The home web page of PDFITC.

from our group. It is also our plan to be able to host Apps contributed by others for the broad use of the community in a way that when the community uses an application proper credit is assigned to the app developer.

Its home web page is shown in Fig. 3.9. Once logged in, the user can use the web applications. For example to use structure-mining, simply upload a PDF and get the answer back once the calculation finishes in the cloud, as we summarize below. More detailed instructions for using PDFITC are available in an “Instructions” link in each application. We present structure-mining as an illustrative example to show the workflow on PDFITC below.

After login, the user clicks on the App of choice to go to the application subpage that is shown in Fig. 3.10 for structure-mining. If users are familiar with the interface they can simply browse for a “.gr” or similar text-format file containing a PDF on their file-system and upload it. Otherwise they can follow the “Instructions” link to get more help.

We use the experimental x-ray PDF of barium titanate nanoparticles [256] again as an example data file here to illustrate the STRUCTUREMINING@PDFITC workflow in steps. In the simplest usage, users just upload the “.gr” format file from their hard-drive, clicks “Submit”, and structure-mining carries out the calculation and returns the result. If there

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Figure 3.10: The subpage of the structure-mining application.

is no compositional data in the header of PDF file, or if it is incorrect, or if the user wants more control over the search heuristic that STRUCTUREMINING@PDFITC uses, the user can specify a chemical composition at the “Composition” text-box, using the heuristics described in Section 3.2.

Here we search for Ba-Ti-O (heuristic 2) as an example. After clicking the “Submit” button, the user will be redirected to an intermediate page, as shown in Fig. 3.11, to wait for structure-mining job to be finished in the cloud. It lists the input data filename and the found or specified chemical composition. It shows the total number of structures meeting the heuristic from all the connected structural databases and has the “Abort” button if anything is wrong in the specification or the search is taking too long and needs to be run with a tighter heuristic.

When finished, STRUCTUREMINING@PDFITC returns a results table sorted by the goodness-of-fit R_w value which can be toggled to a compact or expanded form, as shown in Fig. 3.12. The compact table contains enough information to assess which structures the user may want to download for further study, with the expanded table additionally showing the most interesting starting and refined structural parameters for a slightly more in-depth review of

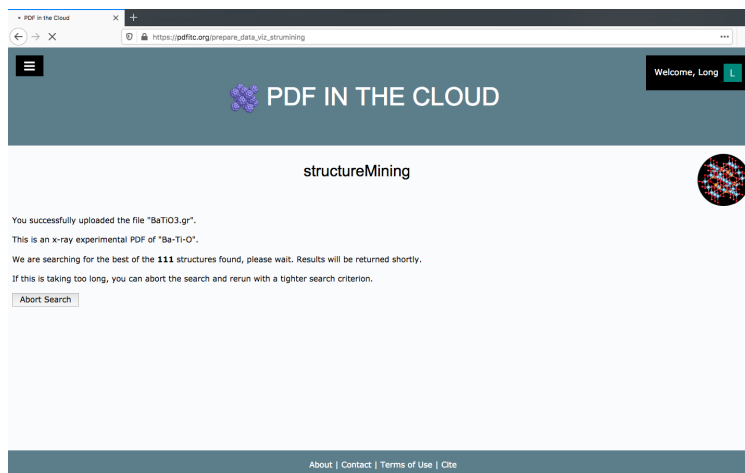


Figure 3.11: The intermediate waiting page after submitting a structure-mining job.

the returned structures, such as the lattice parameters and the isotropic atomic displacement parameters for each element atom.

3.6 Conclusion

We have demonstrated a new approach, called structure-mining, for automated screening of large numbers of candidate structures to the atomic pair distribution function (PDF) data, by automatically fetching candidate structures from structural databases and automatically performing PDF structure refinements to obtain the best agreement between calculated PDFs of the structures and the measured PDF under study. It supports both neutron and x-ray PDFs. The approach has been successfully tested on the PDFs of a variety of challenging quantum materials, including complex oxide nanoparticles and nanowires, low-symmetry structures, complicated doped, magnetic, locally distorted and mixed phase materials. This approach could greatly speed up and extend the traditional structure searching workflow and enable the possibility of highly automated and high-throughput real-time PDF analysis experiments in the future. Structure-mining is available on a cloud-based platform at

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PDF in the Cloud

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https://pdfitc.org/data_structmining

Results

SM found total 110 structures and 32 structures with weighted profile agreement factor, $R_w < 0.5$. [Download All Results](#)

Expand Table							
	rw	formula	space_group	db	db_id	ref	download
0	0.139527	BaTiO ₃	Amn2	COD	9014482	Kwei, Journal of Physical Chemistry, 97 (1993) 2368-2377	download
1	0.139917	BaTiO ₃	Amn2	MPD	mp-5777	Shirane et al. Physical Review (1,1893-132,1963)141,1966-188,1969), 105 (1957) 856-860	download
2	0.140713	BaTiO ₃	Amn2	COD	9014627	Kwei, Journal of Physical Chemistry, 97 (1993) 2368-2377	download
3	0.141875	BaTiO ₃	Amn2	COD	9014645	Kwei, Journal of Physical Chemistry, 97 (1993) 2368-2377	download
4	0.142789	BaTiO ₃	Amn2	COD	9014774	Shirane, Physical Review, 105 (1957) 856-860	download
5	0.142870	BaTiO ₃	C2m	MPD	mp-530879	Jain et al. APL Materials, 1 (2013) 011002	download
6	0.143880	BaTiO ₃	C2m	MPD	mp-33339	(Materials Project)	download
7	0.144699	BaTiO ₃	Amn2	COD	9016084	Kwei, Journal of Physical Chemistry, 97 (1993) 2368-2377	download
8	0.147322	BaTiO ₃	Amn2	COD	9016638	Kwei, Journal of Physical Chemistry, 97 (1993) 2368-2377	download
9	0.151398	BaTiO ₃	P4mm	COD	1513252	Yasuda, Journal of Synchrotron Radiation, 16 (2009) 352-357	download
10	0.153600	BaTiO ₃	P4mm	MPD	mp-5986	Srikahni et al. Inorganic Chemistry, 55 (2016) 4795-4805	download
11	0.157583	BaTiO ₃	P4mm	COD	2100858	Butcher, Acta Crystallographica Section B, 48 (1992) 764-769	download
12	0.157583	BaTiO ₃	P4mm	COD	1507759	Mahmood, Journal of Modern Physics, 2 (2011) 1420-1428	download

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https://pdfitc.org/data_structmining

Results

SM found total 110 structures and 32 structures with weighted profile agreement factor, $R_w < 0.5$. [Download All Results](#)

Collapse Table																
	rw	formula	space_group	db	db_id	Ba_Uiso_r	O_Uiso_r	Ti_Uiso_r	a_r	alpha_r	alpha_r	b_r	b_r	beta_r	beta_r	beta_r
0	0.139527	BaTiO ₃	Amn2	COD	9014482	0.002065	0.017165	0.007918	3.982800	3.991217	NaN	NaN	5.674500	5.672992	NaN	NaN
1	0.139917	BaTiO ₃	Amn2	MPD	mp-5777	0.002205	0.012857	0.007125	5.805908	5.672409	NaN	NaN	5.855292	5.761586	NaN	NaN
2	0.140713	BaTiO ₃	Amn2	COD	9014627	0.002010	0.016971	0.008683	3.980600	3.991070	NaN	NaN	5.671000	5.672059	NaN	NaN
3	0.141875	BaTiO ₃	Amn2	COD	9014645	0.001977	0.016656	0.008694	3.985500	3.990918	NaN	NaN	5.673800	5.671479	NaN	NaN
4	0.142789	BaTiO ₃	Amn2	COD	9014774	0.001968	0.016095	0.009321	3.990000	3.991039	NaN	NaN	5.669000	5.670825	NaN	NaN
5	0.142870	BaTiO ₃	C2m	MPD	mp-530879	0.001784	0.009309	0.007125	11.515188	11.339218	NaN	NaN	8.019176	8.000241	91.616613	90.8318
6	0.143880	BaTiO ₃	C2m	MPD	mp-33339	0.002333	0.015776	0.003795	10.997600	9.976536	NaN	NaN	5.689690	5.647896	91.702595	90.2472
7	0.144699	BaTiO ₃	Amn2	COD	9016084	0.001930	0.016982	0.008628	3.984100	3.990719	NaN	NaN	5.674100	5.670677	NaN	NaN
8	0.147322	BaTiO ₃	Amn2	COD	9016638	0.002567	0.007064	0.008339	3.967400	3.990143	NaN	NaN	5.675100	5.677565	NaN	NaN
9	0.151398	BaTiO ₃	P4mm	COD	1513252	0.002804	0.011780	0.006508	3.990500	4.003749	NaN	NaN	NaN	NaN	NaN	NaN
10	0.153600	BaTiO ₃	P4mm	MPD	mp-5986	0.002723	0.012640	0.007438	4.004457	4.003552	NaN	NaN	NaN	NaN	NaN	NaN

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Figure 3.12: The STRUCTUREMINING@PDFITC result page showing in (a) compact and (b) expanded table forms.

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PDF in the cloud (PDFITC), that hosts applications for PDF analysis at <https://pdfitc.org>. The user can simply upload experimental neutron and x-ray PDFs onto STRUCTUREMINING@PDFITC and get the best-fit candidate structures back once the calculation finishes in the cloud.

Chapter 4

Oxygen vacancies and the loss of electrical conductivity in praseodymium oxides

4.1 Introduction

The lanthanide oxides exhibit electrical conductivities in the range of 10^{-9} - $10^{-1} \Omega^{-1}\text{cm}^{-1}$. The filled or partially filled $4f$ shells of the lanthanide ions have narrow band width and the $4f$ electrons contribute to the electrical conduction [51]. The lanthanide elements can readily be oxidized. For instance, Ce metal oxidizes completely to CeO_2 when exposed to air, and for praseodymium oxides, PrO_2 exists when synthesized under positive oxygen pressure but the oxygen deficient Pr_6O_{11} is more stable at ambient temperatures in air [449; 147].

The phase equilibria in the Pr-O semiconductor system have been extensively studied before [131; 129; 450; 451]. The praseodymium oxides have a series of homogeneous PrO_x

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Table 4.1: The stoichiometry of the homologous PrO_x series. The average oxidation state of Pr ion is also listed.

x in PrO_x	Formula	Pr oxidation
1.500	Pr_2O_3	3.000
1.714	Pr_7O_{12}	3.428
1.778	Pr_9O_{16}	3.556
1.800	Pr_5O_9	3.600
1.818	$\text{Pr}_{11}\text{O}_{20}$	3.636
1.833	Pr_6O_{11}	3.667
2.000	PrO_2	4.000

compositions, where x can be some specific values between $1.5 \leq x \leq 2.0$, and some commonly seen compositions are as listed in Table 4.1, reproduced from Section 1.5.1 for convenience here. Considering that these sub-oxide phases have large concentrations of oxygen vacancies, they are found to have a strong absorption of water when exposed to the air, even at room temperature, which can be explained by the electrically neutral mechanism [452]. The oxide ion vacancies are absorbed to sit at the oxide ions sites, and protons are also absorbed and reside in interstitial sites. On cooling to relatively low temperatures, the water is irreversibly desorbed, and the protons and either hydroxide or oxide ions have high mobility making these potentially interesting in electrochemical applications [132; 453].

The Pr_6O_{11} (or $\text{PrO}_{1.833}$) is an n -type semiconductor, which exhibits ambient temperature and pressure stability [140; 147], extraordinary high oxygen mobility and electrical conductivity [139], due to the electron hopping between different valence state of Pr ions in the lattice [132].

Semiconductor nanoparticles, particles with diameters in the range of 1-20 nm, have important applications in thermoelectric and electronic device fabrications [454; 455; 456; 135].

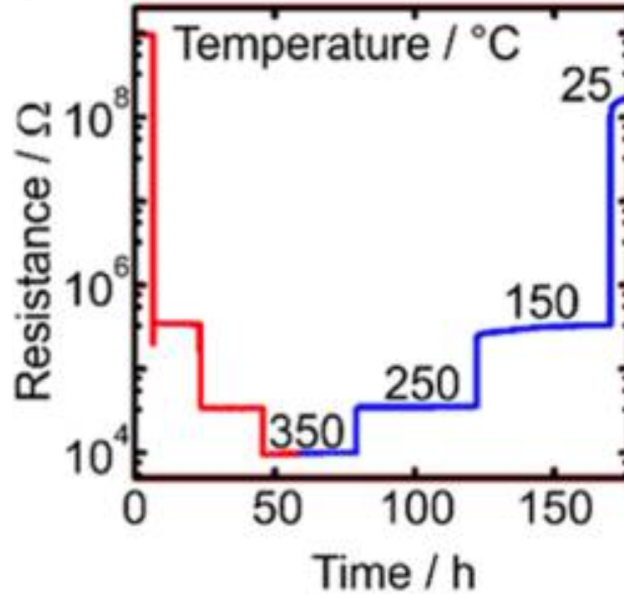


Figure 4.1: The temperature-induced changes of resistance of Pr_6O_{11} nanoparticles.

The resistance of Pr_6O_{11} nanoparticles was reported to have a dramatic change on warming. Only by heating from RT ($10^9 \Omega$) to 150°C ($10^{5.5} \Omega$), the resistance decreases by almost 4 orders of magnitude. The resistance further decreases if keep heating, though with smaller amplitude, by about 1.5 orders of magnitude from 150°C to 350°C . It can recover to the values close to the initial condition after cooling, as shown in Fig. 4.1, adapted from the literature [143].

The polaron model was proposed to explain the conduction mechanism in Pr_6O_{11} , since the band widths in Pr oxides are very small [50; 51; 52]. The interaction between the electron (or hole) and the surrounding ion displacements due to the Coulomb interaction is known as electron-phonon coupling, as first proposed in 1933 by Landau [47]. The charge carrier together with the induced polarization can be considered as one entity, which is called a polaron [48; 49]. The resulting lattice would have local distortions due to the existence of polarons. The formation of polarons can change the conductivity of semiconductors, because the effective mass is larger than that of electron or hole [48], as a result, when the polarons

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formed in a material, the electron conductivity decreases correspondingly.

The polaron model can be classified into large or small polarons, which refer to the case when the polarization phonon cloud is larger than or, with similar size as, the atomic spacing in the material, respectively. The small polaron model is proposed for the Pr_6O_{11} system, where the dimensions of the polarons are of the comparable size as the atomic distance between Pr and O atoms [51], such that the O $2p$ states and Pr $4f$ states would overlap and form a hybridized band, i.e., the O p states have large spatial extent and can reach into the atomic sphere around the Pr atom [457].

In addition, another theory based on the oxygen vacancies in the Pr sub-oxide phases was suggested to interpret the conduction mechanism [458]. The predominant defects can be assigned as neutral oxygen interstitials and neutral or doubly charged oxygen vacancies, and the conduction mechanism is originated from the concentration of 7- or 6-coordinated Pr ions (with one or two less oxygens from the fluorite 8-coordination structure). These are expected to be the easiest sites for trapping electrons. Thus the electron hopping between the mixed metal ion valence state of the lattice can give rise to the electrical conductivity [132]. Similar variable oxidation behavior was also reported in Pr oxide nanoparticles [139].

Consequently, it is crucial to determine the local structure environment of Pr oxides to understand which mechanism can explain the observed dramatic change of conductivity correctly. Our collaborators, from the group of Prof. Dorota Koziej at the University of Hamburg, have successfully synthesized the Pr_6O_{11} nanoparticles. The conventional powder x-ray diffraction measurement was performed and the Rietveld refinement was carried out on the pattern, as shown in Fig 4.2, adapted from [143]. The two candidate structures are the monoclinic Pr_6O_{11} and the cubic PrO_2 , which will be introduced in detail in Section 4.2.4. Because the samples are nanoparticles and x-ray is not sensitive to oxygen atoms, the conventional XRD method is incapable of unambiguously determining which of the two

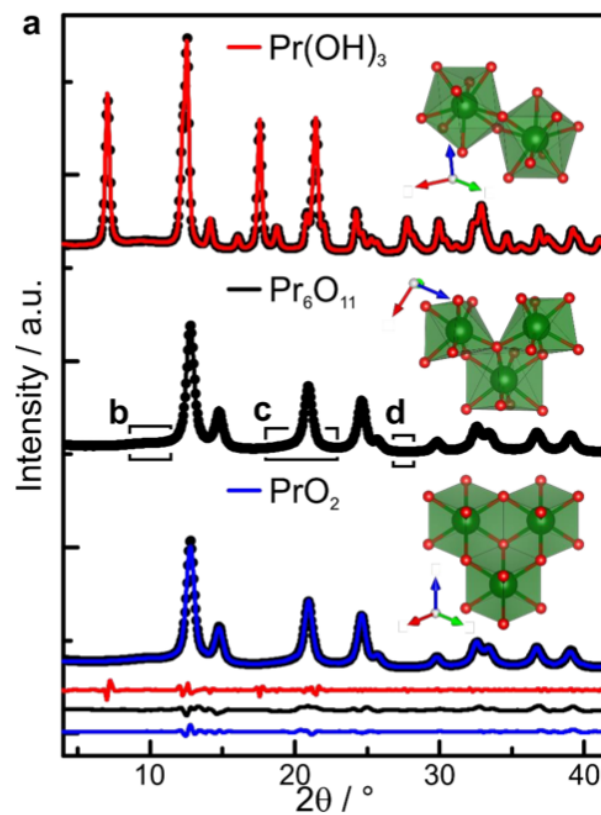


Figure 4.2: Conventional x-ray powder diffraction pattern (dots) and Rietveld refinement (solid lines) of the precursor Pr(OH)_3 (top red) and Pr_6O_{11} (middle black), obtained through heating Pr(OH)_3 to 500°C for two hours. For nanoparticles, the Rietveld refinement cannot distinguish between the monoclinic Pr_6O_{11} and the cubic PrO_2 (bottom blue) structures.

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structures is the correct one. The PDF method using x-ray and neutron diffraction would be the ideal way to distinguish them and to find the best-fit candidate structures.

As a result, joint neutron and x-ray temperature dependent PDF (NXPf) analysis is applied as an effective local structure probe to investigate how the local structure change when temperature increases to study the underlying temperature-induced conduction mechanism. In the x-ray scattering, Pr has larger atomic form factor than O, whereas in the neutron scattering, O scatters more strongly than O. Thus the combination of NXPf can more accurately separate signals from the Pr and O sublattices and better investigate the changes of local structure in Pr_6O_{11} , which is difficult to be fully understood by x-ray or neutron scattering alone.

4.2 Methods

4.2.1 Sample synthesis

The sample synthesis work was done by Sani Harouna-Mayer from the group of Prof. Dorota Koziej at the University of Hamburg, following the similar procedures reported by the collaborator group before [143] and is summarized here for convenience. First, the $\text{Pr}(\text{OH})_3$ nanoparticles were synthesized in an analogous way as the previously reported synthesis of $\text{La}(\text{OH})_3$ [459]. All chemicals were stored and handled in a glovebox under an oxygen- and water-free atmosphere. Acetophenone (4.68 mL, 40 mmol, 99.0% abcr GmbH) was added to $\text{Pr}(\text{O}^i\text{Pr})$ (159.09 mg, 0.5 mmol, 99.9%, REM Chemicals Inc.) with a molar ratio of 1:80 ($\text{Pr}(\text{O}^i\text{Pr})$:Acetophenone) in a reaction vessel containing a stirring magnet. The vessel was sealed with a Teflon cap, and the reaction was carried out in a CEM Discovery microwave reactor at 200°C with 300 W for 20 min. The synthesized particles were separated from the reaction liquid by centrifugation with 4000 rpm for 15 min, washed once with diethyl ether,

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twice with ethanol and once with acetone, and dried at 60°C for 12 h in furnace. Then, the Pr_6O_{11} nanoparticles were obtained by heating the $\text{Pr}(\text{OH})_3$ powder to 500°C for 3 h with a heating rate of 5°C/min. These temperature and heating conditions were investigated in the *in situ* powder x-ray diffraction pattern to determine the ideal parameters for the complete phase transformation from $\text{Pr}(\text{OH})_3$ to Pr_6O_{11} [143].

4.2.2 X-ray and neutron total scattering experiments

The synchrotron x-ray total scattering measurements were carried out at the XPD beam-line (28-ID-2) at the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory (BNL) using the rapid acquisition PDF method (RAPDF) [334]. The Pr_6O_{11} powder sample was loaded in a 1 mm diameter polyimide capillary and measured first on warming from 90 K to 500 K and then on cooling from 500 K to 90 K using a flowing nitrogen cryostream provided by Oxford Cryosystems 700 Series Cryocooler. The experimental setup was calibrated by measuring the crystalline Ni as a standard material. A two-dimensional (2D) PerkinElmer area detector was mounted behind the samples perpendicular to the primary beam path with a sample-to-detector distance of 215.8934 mm. The incident x-ray wavelength was 0.1875 Å. The PDF instrument resolution effects are accounted for by two parameters in modeling, Q_{damp} and Q_{broad} [347; 343]. The x-ray instrument resolution parameters Q_{damp} and Q_{broad} were refined to a nickel dataset collected under the same experimental conditions and then fixed in the refinements of samples under study, which were determined as $Q_{damp} = 0.034 \text{ Å}^{-1}$ and $Q_{broad} = 0.015 \text{ Å}^{-1}$ by fitting the x-ray PDF from a well crystallized sample of Ni.

The collected x-ray data frames were summed, corrected for detector and polarization effects, and masked to remove outlier pixels before being integrated along arcs of constant momentum transfer Q , to produce 1D powder diffraction patterns using the PYFAI pro-

CHAPTER 4. OXYGEN VACANCIES AND THE LOSS OF ELECTRICAL CONDUCTIVITY IN PRASEODYMIUM OXIDES

gram [337]. Standardized corrections and normalizations were applied to the data to obtain the reduced total scattering structure function, $F(Q)$, which was Fourier transformed to obtain the PDF, using PDFGETX3 [338] within xPDFSUITE [339]. The maximum range of data used in the Fourier transform was chosen to be $Q_{max} = 23.7 \text{ \AA}^{-1}$, so as to give the best trade-off between statistical noise and real-space resolution (π/Q_{max}).

The time-of-flight (TOF) neutron total scattering measurements were conducted at the NOMAD beamline (BL-1B) [335] at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. The Pr_6O_{11} powder sample was loaded into a 3 mm diameter vanadium can inside a furnace high-temperature sample environment, and data were collected at a few high temperature points in time series (first heating then cooling), RT, 100, 150, 200, 250, 350, 450, 350, and 250°C. The neutron PDF instrument resolution parameters were determined as $Q_{damp} = 0.022 \text{ \AA}^{-1}$ and $Q_{broad} = 0.020 \text{ \AA}^{-1}$ by fitting the neutron PDF of a NIST standard 640e crystalline silicon sample.

The neutron data were reduced and transformed to the PDF with $Q_{max} = 20.0 \text{ \AA}^{-1}$ using the automated data reduction scripts available at the NOMAD beamline.

Unfortunately, the hydrogen signal was found in the sample from neutron scattering data, which “pollutes” the PDF data due to the extremely strong incoherent inelastic interaction between hydrogen and neutron, as introduced in Section 2.4.3. We suspect this may be due to the water adsorption from the air. The raw neutron diffraction total scattering function $S(Q)$ at all the measured temperatures on warming are shown in Fig. 4.3(a). The steep background clearly indicates the strong incoherent inelastic scattering signal from hydrogen. We also found that the hydrogen scattering signal becomes weaker when heating up to high temperature. So the room temperature data have the most amount of hydrogen signal. Different methods were spent to try hydrogen correction on neutron PDFs, and the Fourier filter method, as implemented as a tool in the RMCProfile software [316], was chosen for the

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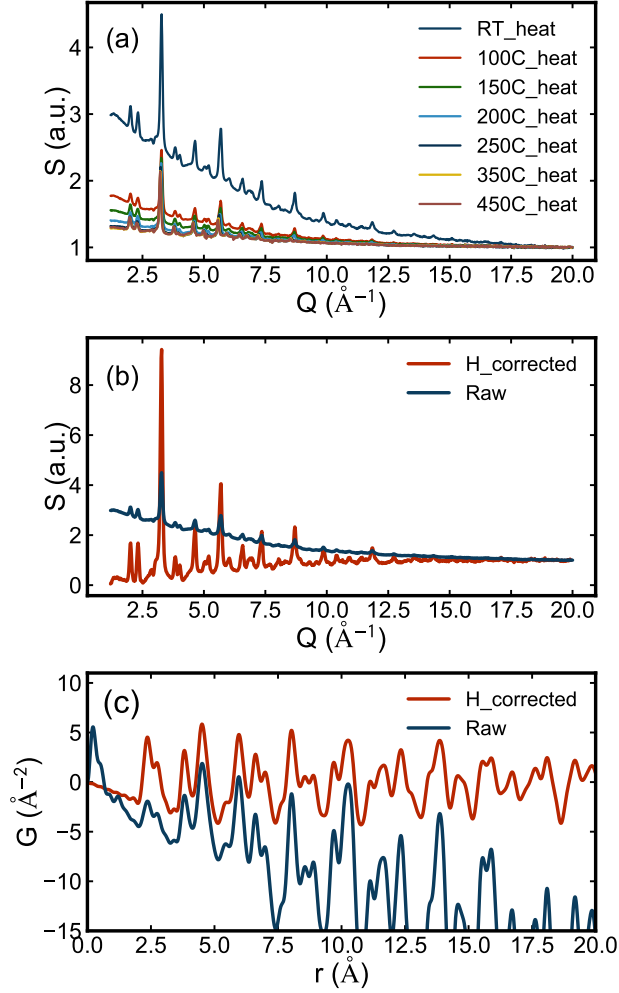


Figure 4.3: (a) The raw neutron diffraction total scattering function $S(Q)$ at all the measured temperatures on warming. (b) The raw (blue) and hydrogen corrected (red) $S(Q)$ data collected at room temperature. (c) The raw (blue) and hydrogen corrected (red) $G(r)$ data collected at room temperature.

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hydrogen correction here. All the neutron $S(Q)$ data were corrected to start from 0 at low- Q and approach 1 at high- Q , and then Fourier transform into correct PDFs. In the rest of this chapter, we will analyze the best hydrogen corrected neutron PDFs achieved so far, using the RT data as an example to represent the raw (blue) and hydrogen corrected (red) data in Fig. 4.3(b) and (c) for $S(Q)$ and $G(r)$, respectively. However, hydrogen correction is still one of the most complicated data processing problem for neutron PDF, and no standard approach has been established as the best method for hydrogen correction yet [313; 311; 317]. Notice that the hydrogen correction does not quite affect the PDF peak positions, as indicated in Fig. 4.3 (c), because the most severe signal from hydrogen is the steep background in $S(Q)$, and the adsorbed water may be mainly located on the surface of the sample, contributing only to the low- r region (much smaller than the shortest Pr-O bond length from Pr oxide sample), not affecting the atom bonding inside the sample. Thus the atomic pair distances obtained from the PDF analysis would still be reliable regardless how well the hydrogen correction is achieved.

4.2.3 Structure-mining

The structure-mining approach was applied on both neutron and x-ray experimental PDFs of Pr_6O_{11} in order to find its candidate structures. The heuristic-2 (Pr-O) is applied, fetching all structures that contain Pr and O elements with any stoichiometry. The corresponding structure-mining results from the Crystallography Open Database (COD) [379] are shown in Fig. 4.4, using the NXPf data collected at the 200°C (475 K) on warming as an example here.

The detailed results are shown in Table 4.2 and Table 4.3 for x-ray and neutron PDF, respectively. Both x-ray and neutron PDF consistently returns the best-fit structure to be the cubic PrO_2 fluorite model with s.g. $Fd\bar{3}m$ [451; 460; 461; 462] from the database

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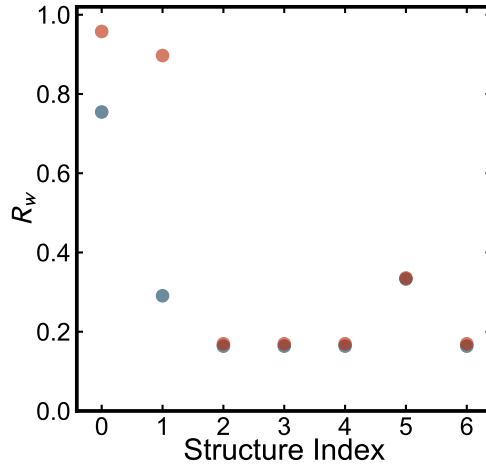


Figure 4.4: R_w values for each of the structures fetched from the databases for the Pr_6O_{11} nanoparticle x-ray (blue) and neutron (red) data collected at 200°C (475 K) on warming using heuristic-2, filtering for all the structures with Pr and O elements from the COD. The R_w parameter represents the goodness-of-fit for each structure.

Table 4.2: Structure-mining results for the Pr_6O_{11} nanoparticle x-ray data collected at 475 K using heuristic-2 from the COD, fetching all structures that contain Pr and O elements with any stoichiometry. Here No. refers to the structure index (Fig. 4.4), which is the order fetched from the database, and s.g. represents the space group of the structure model. The initial isotropic atomic displacement parameter (U_{iso}) of all atoms in each structure is set to $0.005 \text{ \AA}^2$ to start the structure refinements. The a , b , and c are the lattice parameters of the structure model. The subscript i indicates an initial value before refinement and the subscript r indicates a refined value. The spherical particle diameter (SPD) parameter is used with an initial value $60.0 \text{ \AA}$ and get refined for the nano-sized objects. DB ID represents the database ID of the structure model in COD. $Q_{max} = 23.7 \text{ \AA}^{-1}$, $Q_{damp} = 0.034 \text{ \AA}^{-1}$, and $Q_{broad} = 0.015 \text{ \AA}^{-1}$ were set and not varied in the mining operation (see Section 3.2 for details).

No.	R_w	Formula	s.g.	Pr U_{iso} ($\text{\AA}^2$)	O U_{iso} ($\text{\AA}^2$)	a.i ($\text{\AA}$)	a.r ($\text{\AA}$)	b.i ($\text{\AA}$)	b.r ($\text{\AA}$)	c.i ($\text{\AA}$)	c.r ($\text{\AA}$)	SPD ($\text{\AA}$)	DB_ID
2	0.164	PrO_2	$Fm\bar{3}m$	0.0099	0.0399	5.402	5.432	-	-	-	-	43.7	1523192
4	0.164	PrO_2	$Fm\bar{3}m$	0.0099	0.0399	5.394	5.432	-	-	-	-	43.7	1541458
3	0.164	PrO_2	$Fm\bar{3}m$	0.0099	0.0399	5.381	5.432	-	-	-	-	43.7	1537779
6	0.164	PrO_2	$Fm\bar{3}m$	0.0099	0.0399	5.469	5.432	-	-	-	-	43.7	9009031
1	0.291	Pr_5O_9	$P2_1/c$	0.0010	2.0018	6.728	6.724	19.319	19.236	15.48	16.641	60.0	1523024
5	0.333	Pr_7O_{12}	$R\bar{3}$	0.0048	0.0537	10.278	10.192	-	-	9.607	9.399	67.7	2107311
0	0.755	Pr_2O_3	$P321$	0.0057	1.3602	3.850	3.857	-	-	6	6.069	24.7	1010280

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Table 4.3: Structure-mining results for the Pr_6O_{11} nanoparticle neutron data collected at 200°C using heuristic-2 from the COD, fetching all structures that contain Pr and O elements with any stoichiometry. Here No. refers to the structure index (Fig. 4.4), which is the order fetched from the database, and s.g. represents the space group of the structure model. The initial isotropic atomic displacement parameter (U_{iso}) of all atoms in each structure is set to $0.005 \text{ \AA}^2$ to start the structure refinements. The a , b , and c are the lattice parameters of the structure model. The subscript i indicates an initial value before refinement and the subscript r indicates a refined value. The spherical particle diameter (SPD) parameter is used with an initial value $60.0 \text{ \AA}$ and get refined for the nano-sized objects. DB ID represents the database ID of the structure model in COD. $Q_{max} = 20.0 \text{ \AA}^{-1}$, $Q_{damp} = 0.022 \text{ \AA}^{-1}$, and $Q_{broad} = 0.020 \text{ \AA}^{-1}$ were set and not varied in the mining operation (see Section 3.2 for details).

No.	R_w	Formula	s.g.	Pr U_{iso} ($\text{\AA}^2$)	O U_{iso} ($\text{\AA}^2$)	a.i ($\text{\AA}$)	a.r ($\text{\AA}$)	b.i ($\text{\AA}$)	b.r ($\text{\AA}$)	c.i ($\text{\AA}$)	c.r ($\text{\AA}$)	SPD ($\text{\AA}$)	DB.ID
4	0.170	PrO_2	$Fm\bar{3}m$	0.0082	0.0305	5.394	5.452	-	-	-	-	54.2	1541458
6	0.170	PrO_2	$Fm\bar{3}m$	0.0082	0.0305	5.469	5.452	-	-	-	-	54.2	9009031
2	0.170	PrO_2	$Fm\bar{3}m$	0.0082	0.0305	5.402	5.452	-	-	-	-	54.2	1523192
3	0.170	PrO_2	$Fm\bar{3}m$	0.0082	0.0305	5.381	5.452	-	-	-	-	54.2	1537779
5	0.336	Pr_7O_{12}	$R\bar{3}$	0.0026	0.0182	10.278	10.215	-	-	9.607	9.442	53.2	2107311
1	0.897	Pr_5O_9	$P2_1/c$	2e-07	0.2539	6.728	6.683	19.319	19.816	15.48	15.527	162.8	1523024
0	0.958	Pr_2O_3	$P321$	4e-05	0.0430	3.8500	3.894716	-	-	6	5.833	300.6	1010280

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(the top four PrO_2 entries are quite similar despite some tiny difference of the initial lattice parameter), which is the parent phase of Pr_6O_{11} stoichiometry [129; 130]. The same results also apply other temperature data from RT to the highest 450°C on both warming and cooling directions, that the fluorite model is always ranked on the top. So the structure-mining results on Pr_6O_{11} data establish that no phase transition was observed on the synthesized Pr_6O_{11} nanoparticles from RT to 450°C , supported by both x-ray and neutron PDF.

Though most of the pulled structures gave consistent results for x-ray and neutron data. Interestingly, the mining operation did report one obvious mismatch between the x-ray and neutron results in the mapping plot (Fig. 4.4). The COD No. 1 structure, i.e., monoclinic Pr_5O_9 with s.g. $P2_1/c$ [463], gives a much better fit in x-ray ($R_w = 0.291$) than neutron PDF ($R_w = 0.897$). To further investigate this, we simulated the NXPDF of the refined monoclinic Pr_5O_9 structure and the correct top-ranked cubic fluorite PrO_2 structure obtained from the x-ray PDF, i.e., the refined COD No. 1 and No. 2 in Fig. 4.4. The simulated x-ray partial PDF of the Pr sublattice (only account for the Pr-Pr pairs) of both structures is shown in Fig. 4.5(a). The partial PDFs have similar peak positions, though the peak are much broadened for monoclinic Pr_5O_9 , which has lower symmetry than cubic PrO_2 , thus the Pr atomic positions are quite similar in both structures, in other words, the Pr atoms in the Pr_5O_9 structure are close to correct values for the Pr_6O_{11} sample. We then simulate neutron partial PDF of the O sublattice, i.e., the signals from all O-O pairs, of both structures, as shown in Fig. 4.5(b). It clearly indicates that the O atomic positions are very different from each other in these two structures, as a result, the O atoms sit at wrong atomic positions for the Pr_6O_{11} sample. This can also be supported by the quantitative results in the refinement parameter values (Table 4.2). Even though Pr_5O_9 gives reasonable R_w value for fitting the x-ray data, however the refined ADP of oxygen atom is getting into an extraordinary large value, $2.0018 \text{ \AA}^2$, which is unphysical, thus the model tries to omit all the oxygen atoms and

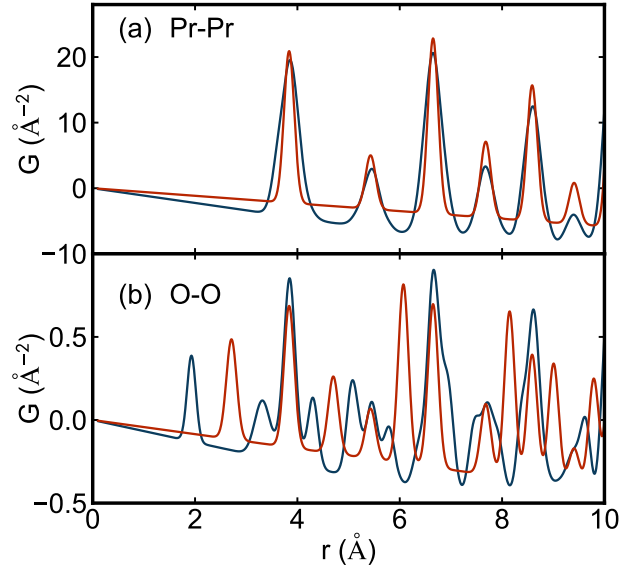


Figure 4.5: The simulated x-ray partial PDF of the (a) Pr and (b) O sublattices. The results of monoclinic Pr_5O_9 and cubic PrO_2 model (s.g. $Fm\bar{3}m$) are shown in blue and red curves, respectively. The isotropic atomic displacement parameter (U_{iso}) of all atoms in both structures is set to $0.005 \text{ \AA}^2$ in order to solely compare the atomic positions of two models.

only fit to Pr-Pr peaks during the refinement.

Overall, this demonstrates that the monoclinic Pr_5O_9 structure have correct Pr atom positions but wrong for O atom positions, with respect to the synthesized Pr_6O_{11} nanocrystals. As a result, structure-mining incorrectly returns Pr_5O_9 as a candidate structure for x-ray PDF because Pr sublattice dominates the x-ray scattering signal whereas neutron PDF marks it as incorrect structure since the O sublattice is evident in the neutron PDF. This is an illustrative example to establish why joint neutron and x-ray PDF would provide the comprehensive results, whereas only using one data may lead to biased incorrect analysis, as the case of only staring at the x-ray PDF structure-mining result shown here (blue dots in Fig. 4.4).

In addition, the rhombohedral Pr_7O_{12} model with s.g. $R\bar{3}$ returned by structure-mining was further tested by a manual fit to both neutron and x-ray PDFs, and the fit quality is

much worse than the best-fit PrO_2 fluorite model.

4.2.4 PDF structural modeling

The PDF modeling program PDFGUI was used for PDF structure refinements [343]. In these refinements U_{iso} ($\text{\AA}^2$) is the isotropic atomic displacement parameter (ADP) and the ADPs of the same type of atoms are constrained to be the same; δ_1 ($\text{\AA}$) is a parameter that describes correlated atomic motions [356]. In the two-phase fits, δ_1 is only applied for one phase to get stable fitting results. The SPD ($\text{\AA}$) parameter is used to account for the finite size of the nanoparticles, or more correctly, the domain of coherent scattering in the nanocrystals, which gives the diameter of the domain in Angstrom units, assuming the shape to be spherical. The PDF instrument parameters Q_{damp} and Q_{broad} determined by fitting the PDF from the well crystallized standard sample under the same experimental conditions are fixed in the structural refinements on Pr_6O_{11} dataset.

Based on the results of structure-mining, the cubic Pr_6O_{11} fluorite model was used as the best possible candidate structure fit against the experimental data. In the cubic Pr_6O_{11} fluorite model (space group: $Fd\bar{3}m$), the atoms sit at the following Wyckoff positions: Pr at 4a (0, 0, 0), and O at 8c (0.25, 0.25, 0.25). The initial lattice parameters are $a = 5.394 \text{ \AA}$ [460]. The oxygen occupancy in the parent PrO_2 crystallographic structure can be set as 0.917 to meet the stoichiometry of Pr_6O_{11} , as a virtual crystal model. The structure of cubic Pr_6O_{11} fluorite model projected along the a -axis is shown in Fig. 4.6(a). Each Pr atom is linked with 8 oxygen atoms.

In addition, the cubic Pr_2O_3 bixbyite model, found by structure-mining from the Materials Project database [372] with database ID mp-16705 [464] was used as a distorted phase in two-phase model of fluorite and bixbyite structures. During the two-phase fit, the ADPs of the Pr and O ions are constrained to be the same in the two phases. The δ_1 parameter

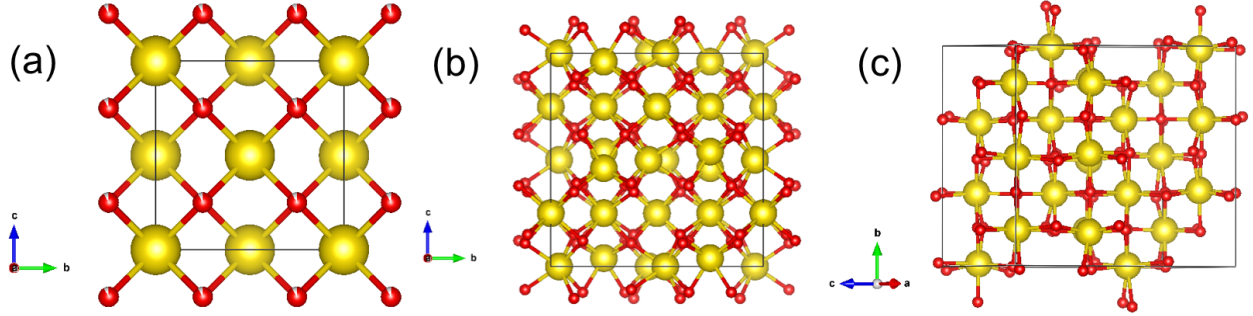


Figure 4.6: The crystal structures of (a) cubic PrO_2 fluorite structure projected along the a -axis, (b) cubic Pr_2O_3 bixbyite structure projected along the a -axis, and (c) monoclinic Pr_6O_{11} structure. The Pr and O atoms are shown in yellow and red, respectively.

for the bixbyite model is not applied during the refinement to get stable fitting results.

In the cubic Pr_2O_3 bixbyite model (space group: $Ia\bar{3}$), the atoms sit at the following Wyckoff positions: Pr1 at 8b (0.25,0.25,0.25), Pr2 at 24d (x , 0, 0.25), and O at 48e (x , y , z). The initial lattice parameters and atomic positions are $a = 11.15$ Å, Pr2 at (0.961, 0, 0.25) and O at (0.391, 0.15, 0.2379) [464]. The structure of bixbyite Pr_2O_3 is shown in Fig. 4.6(b). Each Pr atom is linked with 6 oxygen atoms within a distorted octahedral environment.

The monoclinic Pr_6O_{11} model, found from a conventional XRD study [143], is a low-symmetry phase [465] monoclinic Pr_6O_{11} model (space group: $P2_1/c$), as shown in Fig. 4.6(c). All the Pr and O atoms sit at general positions, 4e (x,y,z). The initial lattice parameters are $a = 6.6850$ Å, $b = 11.6004$ Å, $c = 12.8271$ Å, $\beta = 99.974^\circ$. The atomic positions are listed in the Table 4.4 [465]. For the Pr sites, two of the six Pr atoms (Pr^{3+}) are connected to 8 oxygen atoms, and the coordination number of the other four Pr atoms (Pr^{4+}) is 7. This model was not found by structure-mining since the entry is from the Inorganic Crystal Structure Database (ICSD) [375; 376] (ICSD ID: 82107) [465], which is a commercial database that has not been supported by structure-mining yet.

The summarized information of these three candidate models, including the oxidation states and coordination number of Pr sites, are listed in Table 4.5. For convenience, the

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Table 4.4: The initial atomic positions of the monoclinic Pr_6O_{11} model (space group: $P2_1/c$) to start PDF structural refinements, along with the coordination number and oxidation state of each Pr cation sites.

Parameter ($\text{\AA}$)	Value	Pr Coordination #	Oxidation state
Pr1 (x,y,z)	(0.8607,-0.0136,0.1181)	7	4+
Pr2 (x,y,z)	(0.4095, 0.1682, 0.1275)	7	4+
Pr3 (x,y,z)	(0.8719,0.3469,0.1235)	7	4+
Pr4 (x,y,z)	(0.8636,0.6670,0.1088)	7	4+
Pr5 (x,y,z)	(0.3736,0.5045,0.1321)	8	3+
Pr6 (x,y,z)	(0.3564,0.8332,0.1275)	8	3+
O1 (x,y,z)	(0.1744,0.0158,0.0762)	-	-
O2 (x,y,z)	(0.7492,0.1613,0.0775)	-	-
O3 (x,y,z)	(0.1735,0.3180,0.0876)	-	-
O4 (x,y,z)	(0.6920,0.5140,0.0540)	-	-
O5 (x,y,z)	(0.1769,0.6648,0.0579)	-	-
O6 (x,y,z)	(0.6635,0.8247,0.0473)	-	-
O7 (x,y,z)	(0.5696,0.0005,0.1762)	-	-
O8 (x,y,z)	(0.5821,0.3389,0.1814)	-	-
O9 (x,y,z)	(0.0366,0.5228,0.2059)	-	-
O10 (x,y,z)	(0.5912,0.6719,0.2040)	-	-
O11 (x,y,z)	(0.0244,0.8199,0.1925)	-	-

Table 4.5: The summarized information of Pr sites in the three candidate models. S.G. represents the space group of the model. # refinable parameters stand for the total number of structural fitting parameters used in the PDF fits. In the c-778 model, two thirds of Pr sites have coordination number seven, and one third is eight-coordinated.

Name	Composition	S.G.	# Refinable Parameters	Pr Coordination #	Pr oxidation
c-8	PrO_2	$Fd\bar{3}m$	6	8	4+
c-778	Pr_6O_{11}	$P2_1/c$	60	$\frac{2}{3}$ 7 & $\frac{1}{3}$ 8	3.667+
c-6	Pr_2O_3	$Ia\bar{3}$	10	6	3+

Pr site coordination number of each model is used as the name. So c-8 represents the cubic fluorite PrO_2 model because the coordination number is 8 (c stands for coordination); similarly, c-6 represents the cubic bixbyite Pr_2O_3 model; c-778 stands for the monoclinic Pr_6O_{11} model since two thirds of Pr sites have coordination number seven, and one third has eight. In addition, the total number of refinable structural parameters used in the PDF fits for each model clearly shows that the c-778 has a much lower symmetry than other two candidate models, with correspondingly a much higher degree of freedom for varying parameters in the model.

Notice that these models have a similar structure motif. For instance, the atom clusters shown in the insets of Fig 4.2 highlight that both polymorphs of c-8 and c-778 models have a fluorite structure with oxygen sites either fully or partially occupied for PrO_2 and Pr_6O_{11} stoichiometry, respectively.

4.3 Results and discussions

Before digging into the detailed experimental data analysis, the simulated neutron and x-ray PDFs of the cubic Pr_6O_{11} model are shown in the blue and red curves in Fig. 4.7(a), respectively. The atomic pairs that contribute to the first few peaks are labeled correspondingly. Praseodymium is scattered much more strongly by x-rays than by neutrons. For example, the strong PDF peak at $r = 3.8 \text{ \AA}$ in the x-ray PDF is mainly from the nearest Pr-Pr, whereas the nearest O-O (peak at $r = 2.7 \text{ \AA}$) can be easily found in neutron PDF but is almost hidden in the x-ray case. This is a direct visualization for the importance of applying joint NXPf to fully understand the structure of Pr_6O_{11} system. Correspondingly, the experimental x-ray and neutron PDFs measured at RT are shown in Fig. 4.7(b), which agree well with the simulated patterns. For instance, we can clearly see the nearest O-O

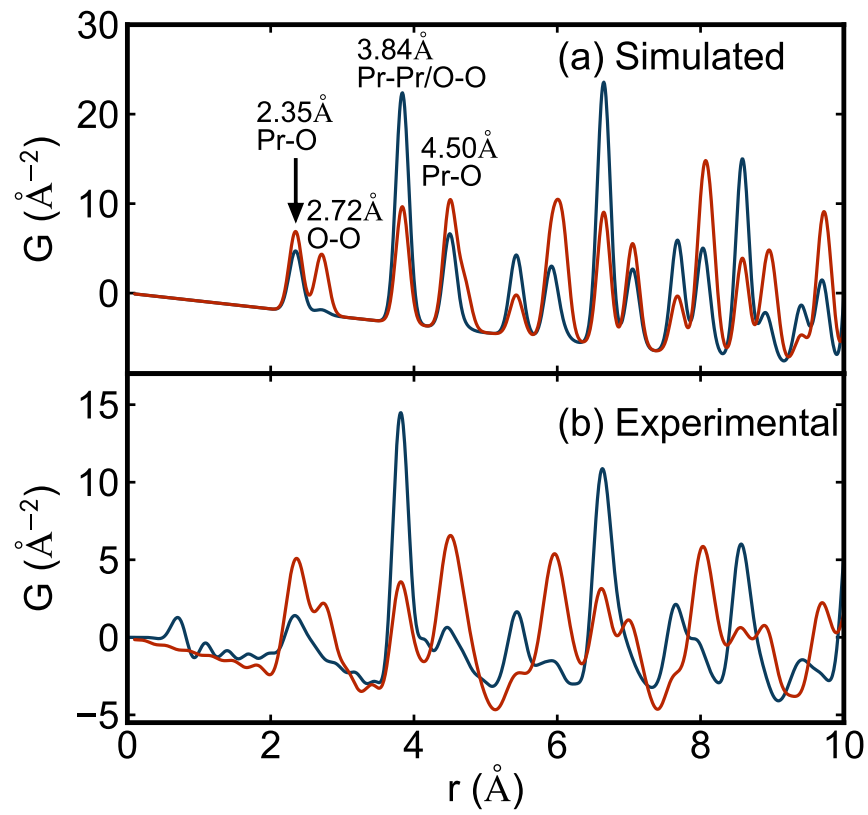


Figure 4.7: The (a) simulated and (b) experimental x-ray (blue curve) and neutron (red) PDFs of the cubic Pr_6O_{11} model. The experimental NXPDFs are collected at room temperature.

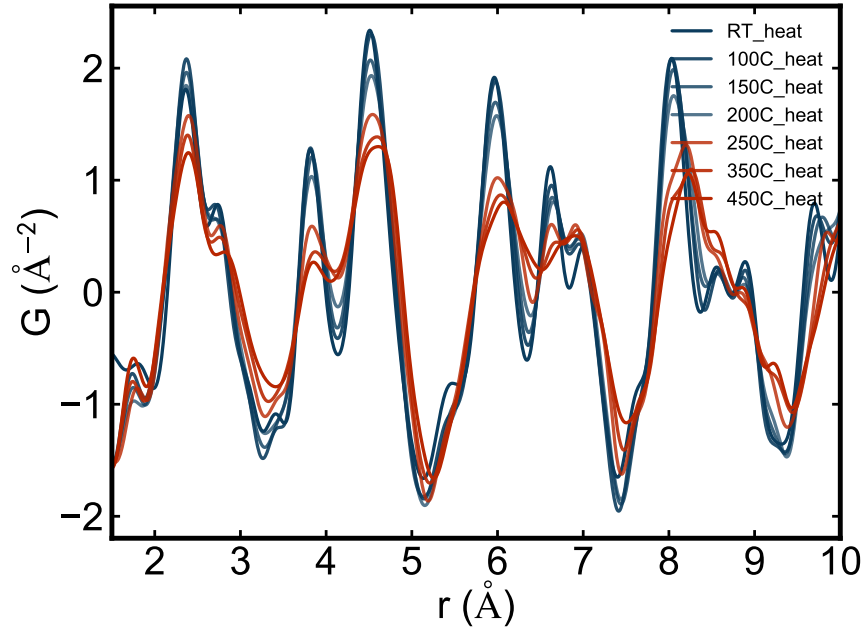


Figure 4.8: The experimental neutron PDFs measured on warming from RT (dark blue curve) to 450°C (dark red curve).

atom pair distance (peak at about 2.72 Å) in neutron PDF which is hardly observable in x-ray, and the nearest Pr-Pr atom pair (about 3.84 Å) is evident in x-ray but much weaker in the neutron data.

We first qualitatively analyze the experimental data collected from RT to high temperature. All the experimental neutron PDFs from RT to 450°C on warming after hydrogen correction are plotted in Fig. 4.8. A close inspection of the data reveals that data from RT to 200°C are similar to each other, as are the data from 250°C to 450°C. However, there is an abrupt change in structure from 200°C to 250°C indicating that the local structure changes at around 200-250°C on warming.

We focus here on the low-temperature behavior below this structure change. Based on the resistance characterization [143], there is a very significant change on the conducting behavior between RT and 200°C, which we now know cannot be attributed to any significant

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change in local structure. We therefore investigate in more quantitative detail the structure that persists in the region below 250°C by focusing on the room-temperature PDF. Having established reasonable starting models to investigate structural distortions associated with polaronic or oxygen vacancy effects, we now turn to the detailed quantitative fitting to the data of these models.

The parent PrO_2 fluorite structure is first tried to fit the PDF data, as shown in Fig. 4.9(b). This model does well indicating that the overall structure is close to the fluorite model. However, careful examination of Fig. 4.9 suggests that the fits are not optimal since there are signals left over in the difference curve. These are from structural distortions in the material that are not captured in the fluorite model. This is not unexpected because of the presence of oxygen vacancy defects which cannot be accurately modeled by the highly ordered fluorite structure, whether or not the oxygen site is set as partially filled in this virtual crystal model. To better investigate the oxygen vacancies in the system, the two other candidate models, described in Section 4.2.4, are fit to the data separately. The representative fits for the neutron room-temperature PDF over the range of $1.5 < r < 50$ Å are shown in Fig. 4.9. The refined R_w values show that the low-symmetry c-778 model (Pr_6O_{11} with s.g. $P2_1/c$) fits best, whereas the high-symmetry c-8 and c-6 models perform worse. Additionally, a close inspection of the difference curves, plotted together in Fig. 4.9(d), shows that the misfit of c-778 model, indicated by the green curve, has the smallest amplitude than those of the two other models at all r points. Consequently, the c-778 model can describe the local structure environment of synthesized praseodymium oxides better than other candidate structures.

However, there are two problems with the c-778 model. First, as discussed above, it has many refinable degrees of freedom (totally 60 refinable parameters) which can easily result in overfitting during the PDF structural refinement. As a comparison, the cubic c-8 and c-6 models only have 6 and 10 fitting parameters, respectively. Second, to better understand

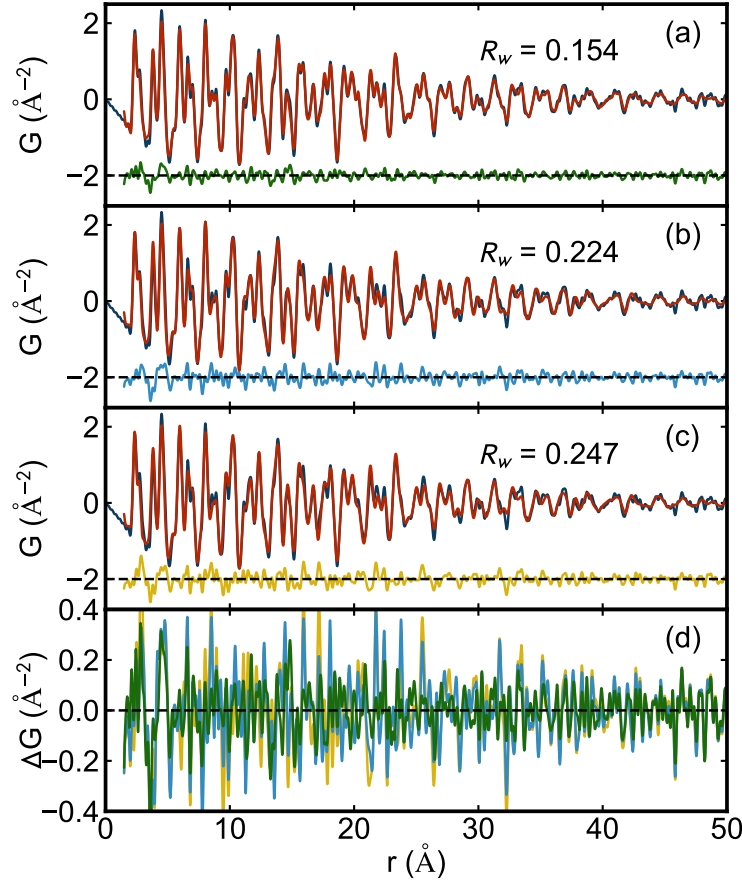


Figure 4.9: The room-temperature neutron PDF data (blue curves) with the best-fit calculated PDF (red) for the (a) c-778 (monoclinic) (b) c-8 (cubic fluorite) and (c) c-6 (cubic bixbyite) models over the range of $1.5 < r < 50$ Å, where c stands for the coordination number of Pr sites in the models. The difference curves are shown offset below in green, blue, and yellow, respectively, and are re-plotted together in (d). R_w is the goodness of fit.

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the mechanism behind the electrical conductivity, a model with a variable number of oxygen vacancies, and therefore a continuously variable average Pr coordination, is needed, which cannot be achieved by the c-778 model (i.e., the Pr oxidation state is locked-in as 3.667+).

We would like to achieve a similar fit quality as the c-778 model, but with a simpler model with variable oxygen vacancies to address both issues. The two-phase model of c-8 plus c-6 is tried for this purpose. Because we are fitting local structure, the two-phase model does not imply the presence of two distinct bulk phases, but rather a distribution of local environments for the Pr. Rather, the fraction of each phase in the PDF modeling can be expected to tell us how many sites of each coordination are present in the single-phase bulk sample. The c-6 model actually contains oxygen di-vacancies (resulting in the 6-fold coordination) which may or may not be present in our Pr_6O_{11} sample, but the main point is that it contains Pr sitting in reduced coordination oxygen environments so it is interesting to see if a model that contains a mixture of fully coordinated Pr (fluorite, c-8 model) and oxygen deficient Pr sites (bixbyite, c-6 model) can actually give a good fit despite having many fewer refinable parameters than the c-778 monoclinic model.

The two-phase model of c-8 plus c-6 is tried for this purpose. Because we are fitting local structure, the two-phase model does not imply the presence of two distinct bulk phases, but Considering that the oxygen contents of PrO_2 and Pr_2O_3 are higher and lower than Pr_6O_{11} , respectively, it is worthwhile combining the highly ordered fluorite and locally distorted bixbyite phases to mimic the c-778 model, in which the number of coordination number and oxidation states on Pr are between c-8 and c-6 models, as listed in Table 4.5. The c-6 model actually contains oxygen di-vacancies (resulting in the 6-fold coordination) which may or may not be present in our Pr_6O_{11} sample, but the main point is that it contains Pr sitting in reduced coordination oxygen environments so it is interesting to see if a model that contains a mixture of fully coordinated Pr (fluorite, c-8, model) and oxygen deficient Pr sites (c-6

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model) can actually give a good fit or not despite having many fewer refinable parameters than the c-778 monoclinic model.

The mixed-phase model improves the neutron data fit quality from $R_w = 0.224$ (single-phase c-8 model, Fig. 4.9(b)) to 0.153 (mixed-phase c-6 + c-8 model, Fig. 4.10(c)). This results in a comparable fit to the c-778 model ($R_w = 0.154$) but with only 13 refinable parameters compared to 60. The improvement in the model is also seen in fits in the x-ray data as well, as shown in Fig. 4.10(b) and (d) for single-phase c-778 and mixed-phase c-6 + c-8 models, respectively. This establishes that both Pr and O sublattices of the nanoparticles can be reasonably described by the mixed-phase model, within the similar reasonable fit quality as the low-symmetry c-778 model.

The detailed refinement results are listed in Table 4.4, using neutron data as the representative results. Notice that unlike neutron data, in the x-ray data fits, not all the oxygen atomic positions can be fully refined due to the fit instability, since the signals of oxygen sublattices are fairly weak in the x-ray PDF. In the mixed-phase model, the average Pr cation oxidation state can be calculated from the refined ratio (per formula-unit) for two phases, with unit cell stoichiometry as Pr_4O_8 (Pr^{4+}) and $\text{Pr}_{32}\text{O}_{48}$ (Pr^{3+}) for c-8 and c-6 phases, respectively. The resulting valence state of the Pr cation is 3.56 obtained from RT neutron data and 3.53 from x-ray data, which are close to the value of 3.53 reported from the earlier high-energy resolution fluorescence detected x-ray absorption near edge structure (HERFD-XANES) analysis [143]. This consistency, together with the fitting stability, suggests that the mixed-phase model is able to capture the underlying local structure distortions of synthesized praseodymium oxides as being a mixture of fully 8-fold coordinated Pr with oxygen deficient Pr sites present as well.

The flexibility of varying the oxygen deficiency is promising to describe the PrO_x homogeneous stoichiometry series [129] with a simpler model and allows us to see whether the

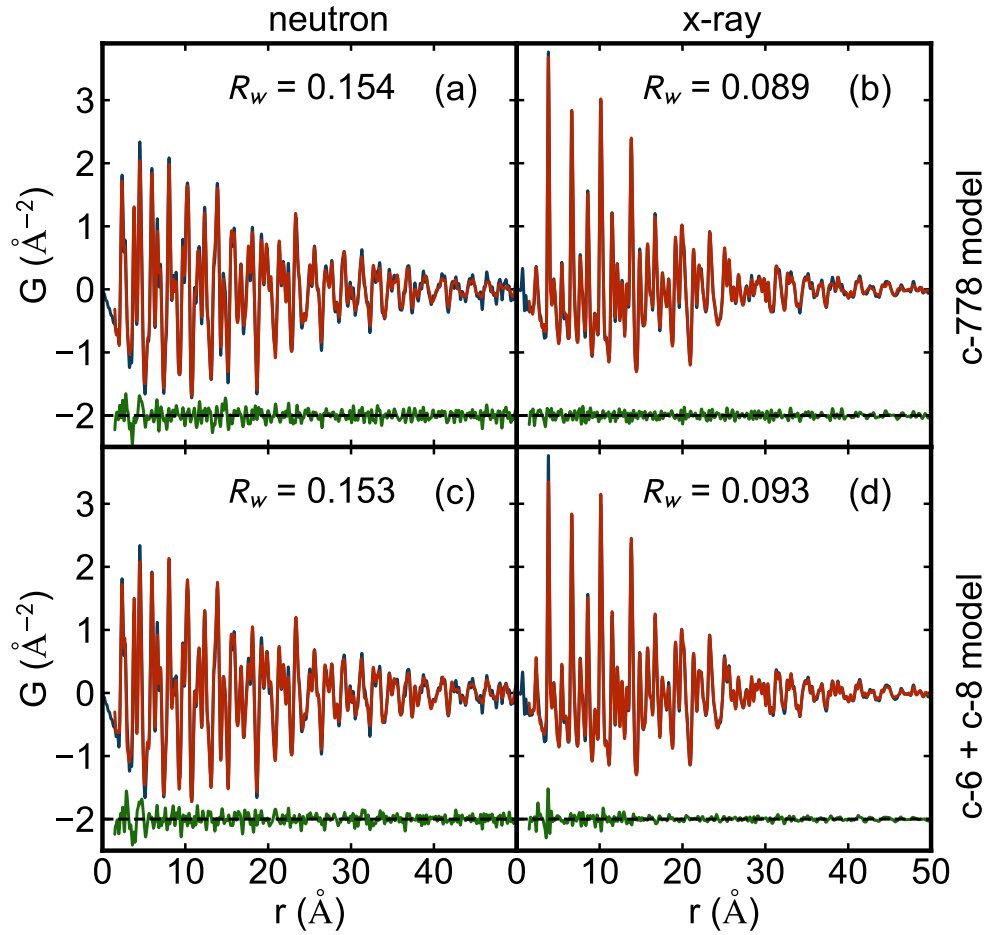


Figure 4.10: The room-temperature (a,c) neutron and (b,d) PDF data (blue curves) with the best-fit calculated PDF (red) for the (a,b) single-phase c-778 and (b,d) c-6 + c-8 mixed-phase models over the range of $1.5 < r < 50$ Å. The difference curves are shown offset below in green. R_w is the goodness of fit.

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Table 4.6: The structure refinement results of neutron and x-ray PDFs measured at RT on warming, fit to the single-phase c-778 structure and the mixed-phase model of c-6 and c-8 structures over the range of $1.5 < r < 50$ Å. In the mixed-phase model, the isotropic atomic displacement parameter of Pr atom (Pr U_{iso}) and O atom (O U_{iso}) were constrained in the same way in both phases. The correlated atomic motion δ_1 parameter was not applied for the c-6 phase due to fit stability. The average Pr cation oxidation state was calculated from the number of unit cell ratio of Pr₄O₈ to Pr₃₂O₄₈, for c-8 and c-6 phases, respectively. The Q_{damp} and Q_{broad} parameters were refined in a fit to a standard calibration sample and then fixed to 0.022 Å⁻¹ and 0.020 Å⁻¹, respectively. The SPD parameter presents the spherical particle size for nanoparticles. The 51 refinable atomic positions of c-778 model are not reported here, since they are not far away from the initial values as listed in Table 4.4. Notice that the oxygen atomic positions cannot be fully refined for x-ray data fits for the sake of the fit instability, since the signals of oxygen sublattices are fairly weak in the x-ray PDF.

Data	Neutron			X-ray		
Phase	c-8	c-6	c-778	c8	c-6	c-778
R_w	0.153		0.188	0.093		0.089
Avg. Pr Oxidation	3.56+		3.667+	3.53+		3.667+
Mass Ratio (%)	57	43	-	53	47	-
Unit Cell Ratio (%)	91	9	-	90	10	-
a (Å)	5.4070	10.9635	6.7361	5.4049	10.9408	6.6312
b (Å)	-	-	11.4679	-	-	11.4645
c (Å)	-	-	12.6397	-	-	12.8312
β (°)	-	-	99.8226	-	-	98.813
Pr U_{iso} (Å ²)	0.0094	0.0094	0.0090	0.0089	0.0089	0.0062
O U_{iso} (Å ²)	0.0156	0.0156	0.0047	0.0472	0.0472	0.0241
δ_1 (Å)	1.33	-	2.13	2.00	-	1.98
SPD (Å)	88.7	86.5	78.1	81.3	87.0	85.9
Pr x	-	0.0206	-	-	0.9882	-
O x	-	0.3778	-	-	0.3573	-
O y	-	0.1089	-	-	0.1168	-
O z	-	0.3628	-	-	0.3833	-

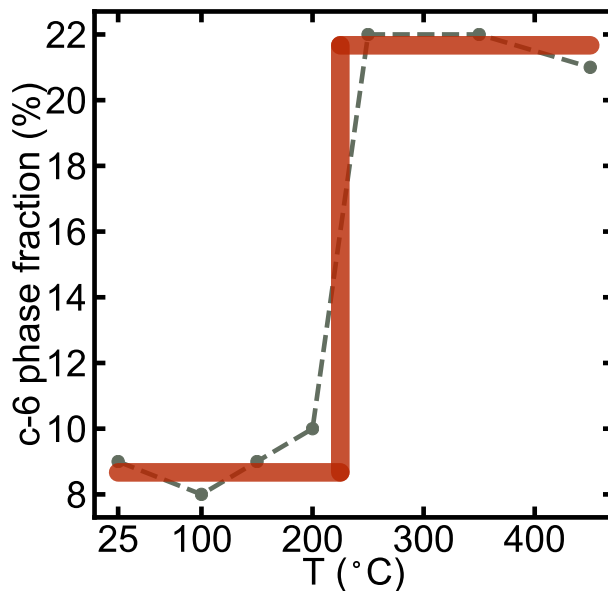


Figure 4.11: The refined phase fraction (ratio per formula-unit) of the under-coordinated c-6 phase from the mixed-phase model when fit against the neutron data collected on warming over the range of $1.5 < r < 50$ Å, as plotted in grey dots. The red guiding lines are plotted based on the average value over two temperature regions separated by 250°C. The step up indicates an abrupt increase in the oxygen vacancy concentration between 200 and 250°C.

number of oxygen vacancies varies with temperature. The mixed-phase model is fit onto all the measured neutron PDFs at different temperature points. The refined phase fraction (ratio per formula-unit) of the under-coordinated Pr phase (c-6 model) from each fit, over the range of $1.5 < r < 50$ Å, is shown in Fig. 4.11. It is consistent with the earlier qualitative observation on the experimental PDFs, as shown in Fig. 4.8, that the structure does not change from RT to 200°C, thus the oxygen vacancies contributed from the under-coordinated c-6 phase are kept almost the same over this temperature range. On the other hand, there appears to be a sharp increase in oxygen vacancies taking place between 200°C and 250°C.

Turning now to the high temperature data, though the structure remains largely similar, neither the low-symmetry c-778 model nor the mixed-phase model can fully describe the underlying high-temperature structure, as evidenced by an increase in the goodness-of-fit

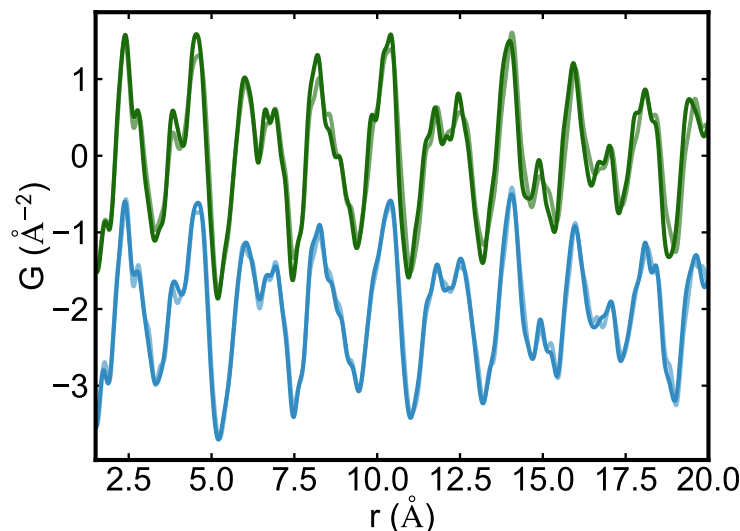


Figure 4.12: The experimental neutron PDFs measured at 250°C (green) and 350°C (blue) on both warming (solid color) and cooling (transparent).

R_w values. As well as a change in the number of under-coordinated Pr ions as indicated in Fig. 4.6 there appears to be an additional change of local oxygen vacancy environment. Though we are not clear about the best model to capture the structure at high temperature at this moment.

Interestingly, we can show that the structural changes at high temperature are reversible. The experimental neutron PDFs collected at 250°C and 350°C on both warming and cooling are plotted together in Fig. 4.12. It shows that the data collected over the high-temperature region are mostly reversible, despite some subtle peak amplitudes, which is mostly likely due to the nonequivalent amount of hydrogen in the sample on warming and cooling. A more careful investigation of this effect requires more data points over this region which is beyond the scope of this study.

We focus our discussion on the low-temperature region where there is a 4-fold decrease in conductivity between RT and 200°C, as shown in Fig. 4.1, with no accompanying change in oxygen vacancy concentration. If the oxygen vacancies serve as trapped states for the

electron charge carriers with the localized energy level lying inside the semiconductor band gap slightly below the conduction band, the density of mobile carries will be determined by thermal excitation of carriers out of these localized states into dispersive states in the conduction band. As temperature increases the mobile carrier density will increase exponentially since the thermal excitation follows the Boltzmann probability, which is proportional to $\exp(-E/k_B T)$, where E is the energy needed to excite charge carriers from the trapped states into the conduction band, consistent with the observation from the conductivity [143]. As a result, the conduction mechanism based on the oxygen vacancies [458] can help explain the collapse of electrical conductivity since the local structure remains unchanged.

4.4 Conclusion

In this work, the local structure of the synthesized Pr_6O_{11} nanocrystals is studied by neutron and x-ray pair distribution function (PDF) analysis. A low-symmetry monoclinic Pr_6O_{11} model with mixed coordination number 7 and 8 for Pr cation sites can fit the PDF better than the high-symmetry fluorite and bixbyite models, with Pr coordinated with 8 and 6 oxygen atoms in the local environments, respectively. A simple mixed-phase model combining the highly ordered cubic undistorted fluorite sublattice and certain number of Pr with oxygen deficient environment can give similar fit quality as the low-symmetry monoclinic model, but with much fewer degrees of freedom on fitting parameters, as confirmed by both neutron and x-ray PDFs. In addition, the mixed-phase model is capable of varying the oxygen vacancies by changing the coordination ratio of Pr sites, which gives the Pr valence state as 3.56 from neutron and 3.53 from x-ray room-temperature data, closer to the reported average oxidation of Pr ions.

The underlying structure hardly changes from RT to 200°C, but the measured electrical

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conductivity has a dramatic increase over this temperature range. The conduction mechanism based on the oxygen vacancies can be a plausible explanation that the oxygen vacancies can be regarded as trapped states for the electron charge carrier slightly below the conduction band, which can be thermally excited into the conducting dispersive states in an exponential manner.

The structure changes largely when heating above 250°C, and is kept similar over the high temperature region. The mixed-phase model indicates that more oxygen vacancies are likely to be formed in the system at high temperature. The high-temperature region are reversible on warming and cooling, which is in agreement with reversibility found from the resistance measurement at 250°C and 350°C.

Chapter 5

Stoichiometric control over multiferroic behavior in iron doped barium titanate nanocrystals

5.1 Introduction

The multiferroic materials that exhibit the coexistence of ferroelectric and ferromagnetic properties have been extensively studied in the recent decade, with their promising unique applications for the revolution in the fields of data storage devices [56; 57], sensors [466], and energy harvesting [467].

From the device fabrication point of view, a device in which the magnetization is controlled by an electric field, preferably at low voltages, at room temperature and with ultrafast switching, is a prime goal [53]. The added dimensions create multiple possibilities for advanced material technology [468; 469; 470], for instance the multi-state memories for future quantum computing [471; 472].

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As introduced in Section 1.5.2, a single-phase multiferroic material would greatly ease the device fabrication, but it was established that there are rare choices in nature for single-phase multiferroics. Hill first pointed out the incompatibility of magnetic and electric order in perovskites [77]. In perovskite structure, the displacive ferroelectricity is achieved when the B site cation is off-centered, which is particularly energetically favorable when the d shell is empty, i.e., d^0 . However, the magnetic ordering for transition-metals require partially filled d shells. This is also called “ d^0 vs. d^n ” problem [77; 473]. One possible way for solving this problem may be a mixed perovskites with d^0 and d^n ions, such as doping ferromagnetic ions into the ferroelectric materials [53]. For instance, people have tried the Fe doping into PbTiO_3 structure [67].

In addition, even though a substantial number of single-phase multiferroic compounds have been investigated, not a single material has been discovered to exhibit large magnetoelectric (ME) coupling at room temperature [75; 65]. In order to ease the device fabrication and making multiferroics useful for industrial applications, it is crucial to find a scalable single-phase synthesis close to room temperature.

The synthesized materials under study are the Fe doped BaTiO_3 nanocrystals, following the concept that doping a magnetic species into a known ferroelectric material can in principle obtain single-phase multiferroics [53].

Barium titanate (BaTiO_3) is one of the most extensively studied perovskite ferroelectric metal oxides because of its versatility in electronic applications, ubiquitous presence in capacitors, and room temperature ferroelectricity [159; 156]. It can be turned into a promising multiferroic candidate for the nanotechnology devices. Since the large ferroelectric polarization nanocrystalline BaTiO_3 can still be observed all the way down to 5 nm crystallite size [170; 171], that can serve as the source of switchable ferroelectricity, and further control the ferromagnetism [474; 158; 170; 171].

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It has been established that the possibility of Fe incorporation could give rise to multiferroic coupling, as supported by a series of theoretical calculations [172; 173; 174; 175; 176]. In the case of nanostructures, multiferroicity is further proposed to be obtainable due to the large number of superficial atoms that significantly affect bulk behavior. As a result, it is of great interest to pursue the development of multiferroic compounds based on the nanoscale BaTiO_3 . Synthesis of BaTiO_3 can be achieved using multiple routes from high temperature solid state syntheses [475] to sol-gel approaches [476] to hydrothermal syntheses [477]. However, these methods require high-temperature synthesis, which may prevent further integration with the nanotechnology device fabrication.

Our collaborators, the group of Prof. Stephen O'Brien from the City University of New York, have developed a simple, green, and scalable gel-collection growth method to produce uniform and aggregate-free colloidal perovskite oxide nanocrystals including BaTiO_3 (BTO), $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) and BaSrTiHfO_3 (BSTH) in high crystallinity and high purity [181]. The synthetic method is solution processed, derived from the sol-gel hydrolysis of metal alkoxides in alcohol solvents such as ethanol by stoichiometric amounts of water in the absence of surfactants and stabilizers. The synthesis is performed under an inert nitrogen or argon atmosphere in a glovebox and the hydrolysis reaction produces nanoscale fully crystallized single domain perovskite metal oxides of the formula ABO_3 where A and B are transition metals. The nanocrystals were shown to have a passivated surface layer of hydroxyl/alkyl groups, which allows the nanocrystals to exist in the form of a super-stable and transparent sol, or a self-accumulate to form a highly crystalline solid gel monolith (hence gel-collection) of 100% yield for easy separation/purification. The dispersibility of the particles in solvents enables the generation of smooth nanocomposite thin films that can be spray printed or spun coat to make single and multilayer capacitors [478]. This advanced synthesis can be performed near room temperature, which is promising to be an

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alternative method to replace the high temperature ceramic processing, so as to allow thin film integration at low temperature, and open more technology avenues such as flexible electronics, novel device topologies, and roll-to-roll fabrication [479; 480; 481].

In the present work, the chemical solution technique was applied to synthesize BaTiO_3 (BTO) as well as $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ (BFT). Textbook data for crystal ionic radii of the Ti/Fe ions shows that a substitution is geometrically feasible in the 6-coordinate B site (Ti(IV): 74.5; Fe(IV): 72.5 Fe(II): 75 (LS), 92 (HS); Fe(III): 69 (LS); 78.5 (HS), values in pm, Shannon ionic radii) [482]. The aim of this study was to adapt gel collection [181] to the synthesis of BTO, BFT ($x = 0.1-0.3, 0.5$, and 0.75), and BaFeO_3 (BFO) and then investigate the structure, magnetic, and electric properties of these materials.

It is crucial to determine whether the compounds have spontaneous polarizations, i.e., whether the synthesized BaTiO_3 nanocrystals exhibit ferroelectricity or not. As introduced in Section 1.5.2, the ferroelectricity, or more precisely the displacive ferroelectric property, in perovskites is solely determined by the local structure. Only the non-centrosymmetric structures can enable the off-centered B site ion (Ti atom for BaTiO_3) to have the electric dipole moment. So studying the structure of the synthesized nanocrystals would play an essential role for investigating the multiferroics. Meanwhile, the characterizations of measuring the electric and magnetic responses to external fields would also help validate the structure-property relationship for the multiferroics.

Recently, the pseudo-Jahn-Teller effect (PJTE) was proposed by Bersuker recently to solve “ d^0 vs. d^n ” problem in perovskite multiferroics [94; 95]. The PJTE theory combines the ground and excited states in vibronic coupling interactions to demonstrate the nature tendency to avoid degeneracy, which results in the symmetry breaking. In the perovskite structure, the PJTE may lead to spontaneous displacements of the center B cation, resulting in the local dipole moments. The vibronic theory to explain the ferroelectricity have been demon-

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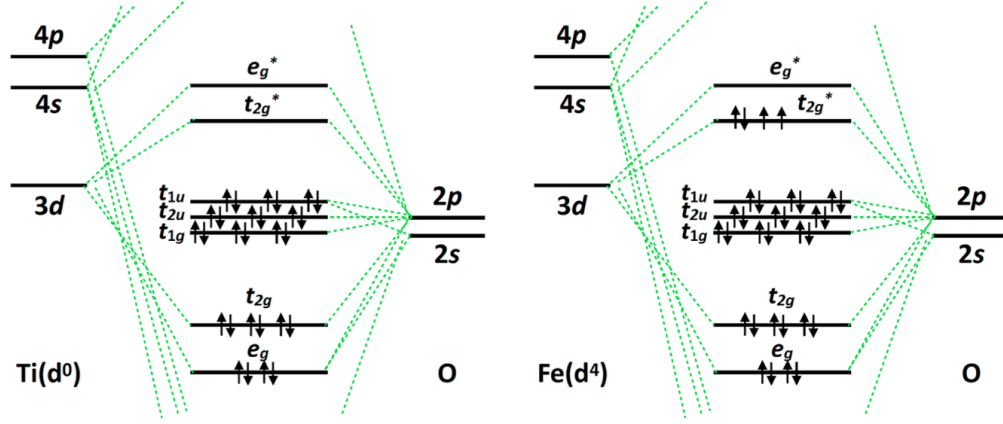


Figure 5.1: MO LCAO scheme for a TiO_6^{8-} octahedron and the analogy energy scheme for a d^4 metal, such as Fe^{4+} .

strated to be successful [483; 484; 485], agreeing well with experimental observations [100; 101; 102], which also interprets the origin of perovskite multiferroics with proper ferroelectricity. Thus, the ABO_3 perovskites with a magnetic d^n configuration of the B ion in principle can possibly exhibit both ferroelectric and ferromagnetic. The typical molecular-orbital (MO) energy scheme for the octahedral fragment TiO_6^{8-} in the approximation of linear combinations of atomic orbitals (LCAO) is shown in Fig. 5.1, adapted from [94; 256]. It shows that Ti^{4+} has an empty t_{2g}^* orbital. However, with the introduction of d^n ($n > 0$) elements, for example, when Fe ions are added to the Ti site, as shown in the right panel of Fig. 5.1, the resulting t_{2g}^* orbital would be partially filled. As a result, the unpaired spins in the perovskite structure could lead to a nonzero magnetic moment, meeting the requirements for the multiferroicity. Conclusively, PJTE predicts that only transition metal ions B with configurations d^3 -LS, d^4 -LS, d^5 -LS and HS, d^6 -HS, d^7 -HS, d^8 , and d^9 can produce multiferroics in principle, where LS represents low-spin state and HS represents high-spin state. Whereas the B ions with d^1 , d^2 , d^3 -HS, d^4 -HS, d^6 -LS, and d^7 -LS, and d^{10} would not result in multiferroics, as summarized in Fig. 5.2, adapted from [94; 256]. In summary, in the $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ system, only Fe^{4+} -LS and Fe^{3+} -LS and HS could

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d^n	ion	HOMO, EC, and GS term	LUMO, EC, and LUES term	FE	MM	MF
d^0	Ti ⁴⁺	$(t_{1u})^6, {}^1A_{1g}$	$(t_{1u})^5(t_{2g}\uparrow)^1, {}^1T_{1u}$	yes	no	no
d^1	Ti ³⁺	$(t_{1u})^6(t_{2g}\uparrow)^1, {}^2T_{2g}$	$(t_{1u})^5(t_{2g}\uparrow)^2, {}^4T_{1u}$	no	yes	no
d^1 , LS	Fe ⁴⁺	$(t_{1u})^6(t_{2g}\uparrow)^3(t_{2g}\downarrow)^1, {}^3T_{2g}$	$(t_{1u})^5(t_{2g}\uparrow)^3(t_{2g}\downarrow)^2, {}^3T_{1u}$	yes	yes	yes
d^1 , HS	Fe ⁴⁺	$(t_{1u})^6(t_{2g}\uparrow)^3(e_g\uparrow)^1, {}^5T_{2g}$	$(t_{1u})^5(t_{2g}\uparrow)^3(e_g\uparrow)^2, {}^7T_{1u}$	no	yes	no
d^5 , LS	Fe ³⁺	$(t_{1u})^6(t_{2g}\uparrow)^3(t_{2g}\downarrow)^2, {}^2T_{2g}$	$(t_{1u})^5(t_{2g})^6, {}^2T_{1u}$	yes	yes	yes
d^5 , HS	Fe ³⁺	$(t_{1u})^6(t_{2g}\uparrow)^3(e_g\uparrow)^2, {}^6A_{1g}$	$(t_{1u})^5(t_{2g})^4(e_g\uparrow)^2, {}^6T_{1u}$	yes	yes	yes

Figure 5.2: Conditions that ABO₃ perovskites with the electronic d^n configuration for Ti/Fe as the B site cation exhibiting multiferroics. EC means electronic configuration, GS means ground state, LUES means lowest ungerade excited state, FE means ferroelectric, MM means magnetic, MF means multiferroic, LS means low-spin, and HS means high-spin.

produce multiferroicity under the PJTE mechanism.

In this work, the PDF analysis was used to study the local structure of synthesized Fe doped nanoparticles. We sought to (a) determine whether these samples have a non-centrosymmetric structure; (b) reveal which state of Fe was being incorporated into the structure; and (c) look for any structure changes with increased Fe content.

5.2 Methods

5.2.1 Sample synthesis

The sample synthesis work [256] was done by Julien Lombardi from Prof. Stephen O'Brien's group in the City University of New York. Barium isopropoxide Ba(OCH(CH₃)₂) and 2.5% w/v iron isopropoxide Fe(OCH(CH₃)₃) in isopropanol were purchased from Alfa Aesar, titanium isopropoxide Ti(OCH(CH₃)₄) and polyvinylpyrrolidone (avg. mol wt. 10,000), and furfuryl alcohol 98% were purchased from Sigma Aldrich. Pure ethanol (200 proof) was purchased from Decon Labs, Inc. All chemicals were used without any further purification. 8 nm BaTiO₃ nanoparticles were synthesized using the gel collection method under an inert nitrogen or argon atmosphere in a glovebox [181]. Stoichiometric amounts of Ba(OCH(CH₃)₂) (3.37 mmol or 0.861 g) were added to 40 mL of 200 proof ethanol and mag-

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netically stirred until the powder dissolved (about 15 min). Then 1 mL of $\text{Ti}(\text{OCH}(\text{CH}_3)_4)$ was added to the solution and magnetically stirred for 15 min. A solution of 2 mL deionized H_2O and 8 mL 200 proof ethanol is prepared and then added 0.5 mL every 10 s and stirred for 5 minutes after the entire solution is added. The solution is then transferred into a sealed container (e.g. a centrifuge tube with a cap) and left to age overnight in the glovebox. A solid gel rod began to form after 8 hours and the container was transferred out of the glovebox and heated to 60°C for 12 hrs in order for condensation of the gel rod to occur. The gel rod was then washed 3 times with 200 proof ethanol and dried in a vacuum oven overnight at 90°C in order to be analyzed using conventional x-ray powder diffraction (XRD) and x-ray photoelectron spectroscopy (XPS). Alternatively, the gel rod can be washed and suspended in 200 proof ethanol or furfuryl alcohol (FA) and then spin coated for dielectric measurements. $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ nanoparticles were synthesized using the same method but with the addition of stoichiometric amounts of $\text{Fe}(\text{OCH}(\text{CH}_3)_3)$. BaFeO_3 nanoparticles were synthesized in the absence of $\text{Ti}(\text{OCH}(\text{CH}_3)_4)$ using the gel collection method outlined above.

BTO, BFT ($x = 0.1-0.3, 0.5$, and 0.75), and BFO nanocrystals were synthesized using the gel collection method. Gel collection employs a treatment of reactive alkoxide precursors that are initially reacted under an inert atmosphere (N_2 or Ar) in the absence of oxygen/moisture. Following formation of a homogenized solution, in which precursors have co-reacted, stoichiometric levels of deionized water are used to initiate hydrolysis and further promote polycondensation, using low temperature (60°C) heating step. All of the reactants are consumed and collected as the product, which insures that the reactant stoichiometry input is equivalent in molarity output. It can therefore be assumed that a reaction with a specific molar ratio (e.g. $x = 0.3$) will yield a defined product, (e.g. $\text{BaFe}_{0.3}\text{Ti}_{0.7}\text{O}_3$), later confirmed by structural and spectroscopic characterization. The synthesized nanoparticles are nanocrystalline, and readily dispersed in polar organic solvents, suitable for preparing

thin films.

5.2.2 Sample characterizations

A few different characterizations on the synthesized nanoparticles were performed by the collaborators, such as x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), energy-dispersive x-ray spectroscopy (EDS), scanning electron microscopy (SEM), and magnetic properties measurement system (MPMS). The detailed description on the characterization measurements can be found in the reference [256].

5.2.3 X-ray total scattering experiment

The x-ray total scattering measurements on these iron doped $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0, 0.1, 0.2, 0.3, 0.5, 0.75, 1.0$) samples were carried out at the XPD beamline (28-ID-2) at the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory (BNL). The nanocrystalline powders were sealed in polyimide capillaries and the data were collected at room temperature using the rapid acquisition PDF method (RAPDF) [334]. The experimental setup was calibrated by measuring the crystalline nickel as a standard material. A large area 2D PerkinElmer detector was mounted behind the samples with a sample-to-detector distance of 202.8031 mm. The incident x-ray wavelength was $\lambda = 0.1867 \text{ \AA}$. The PDF instrument resolution is explained by two parameters in modeling, Q_{damp} and Q_{broad} [347; 343], which were determined as $Q_{damp} = 0.037 \text{ \AA}^{-1}$ and $Q_{broad} = 0.017 \text{ \AA}^{-1}$ by fitting the PDF from a well crystallized sample of Ni.

The detector exposure time was 0.1 s for all the samples to avoid detector saturation, and the number of frames taken for the sample was adjusted to be 1200 for sufficient counting statistics on the data, so the total exposure time per sample was 120 s. The collected data frames were summed, corrected for polarization effects, and masked to remove outlier pixels

before being integrated along arcs of constant Q , where $Q = 4\pi \sin \theta / \lambda$ is the magnitude of the momentum transfer on scattering, to produce 1D powder diffraction patterns using the FIT2D program [486]. Standardized corrections and normalizations were then applied to the data to obtain the reduced total scattering structure function, $F(Q)$, which was Fourier transformed to obtain the PDF, using PDFGETX3 [338] within xPDFSUITE [339]. The maximum range of data used in the Fourier transform was chosen to be $Q_{max} = 24.0 \text{ \AA}^{-1}$, so as to give the best tradeoff between statistical noise and real-space resolution. For consistency, all PDFs were transformed with the same settings.

5.2.4 Structure-mining

The detailed results of applying structure-mining to the synthesized undoped barium titanate nanoparticles have been discussed in Chapter 3 that all the centrosymmetric and non-centrosymmetric candidate perovskite models can be found successfully. Here we show the structure-mining results on the BFO endmember sample data. The mining approach was applied to search for all the possible Ba*-O candidate structures against the experimental PDF of BFO sample. The corresponding structure-mining results from the Crystallography Open Database (COD) [379] are shown in Fig. 5.3. Totally 441 structures were fetched from the COD. Many of the top ranked entries fetched from the COD are duplicated, fetched from a pressure [487] and temperature [488] series study with each temperature and pressure point being recorded in COD. The top six non-duplicated entries with $R_w < 0.7$ are listed in Table 5.1. It clearly shows that the most possible structure for the BFO endmember was found to be the BaCO_3 structure with space group $Pm\bar{c}n$ [323] from the mining operation. However, the resulting goodness-of-fit is not satisfactory ($R_w \approx 0.4$), which indicates that the BFO sample may have complicated structures, or have other signals contributed by multi-phases. The detailed analysis on BFO will be introduced in the following by careful

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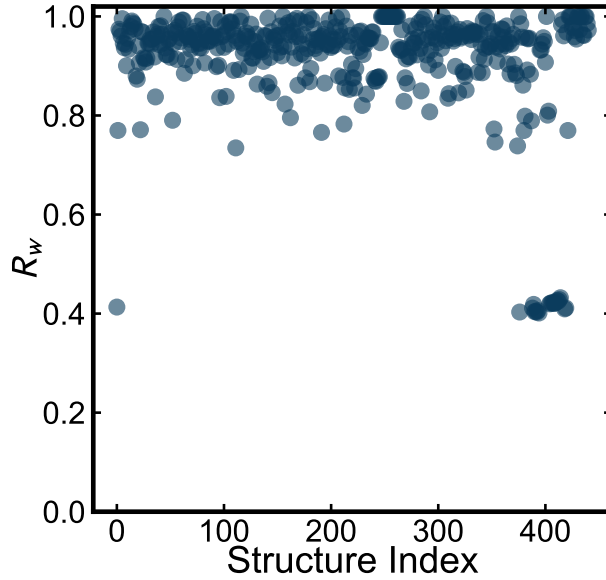


Figure 5.3: R_w values for each of the structures fetched from the databases for the BFO endmember x-ray data searching for all the structures with Ba, O and another arbitrary element from the COD. The R_w parameter represents the goodness-of-fit for each structure.

Table 5.1: The top structure-mining results with $R_w < 0.7$ for the BFO endmember x-ray data fetching all structures with Ba, O and another arbitrary element with any stoichiometry from the COD. Here No. refers to the structure index (Fig. 5.3), which is the order fetched from the database, and s.g. represents the space group of the structure model. The initial isotropic atomic displacement parameter (U_{iso}) of all atoms in each structure is set to $0.005 \text{ \AA}^2$ to start the structure refinements. The a , b , and c are the lattice parameters of the structure model. The subscript i indicates an initial value before refinement and the subscript r indicates a refined value. DB ID represents the database ID of the structure model in COD. $Q_{max} = 24.0 \text{ \AA}^{-1}$, $Q_{damp} = 0.037 \text{ \AA}^{-1}$, and $Q_{broad} = 0.017 \text{ \AA}^{-1}$ were set and not varied in the mining operation (see Section 3.2 for details).

No.	R_w	Formula	s.g.	Ba U_{iso} ($\text{\AA}^2$)	C U_{iso} ($\text{\AA}^2$)	O U_{iso} ($\text{\AA}^2$)	a.i ($\text{\AA}$)	a.r ($\text{\AA}$)	b.i ($\text{\AA}$)	b.r ($\text{\AA}$)	c.i ($\text{\AA}$)	c.r ($\text{\AA}$)	DB_id DB_id
394	0.401	BaCO ₃	<i>Pnma</i>	0.0062	0.0077	0.0057	5.260	5.281	8.846	8.953	5.89500	6.449	9006844
376	0.403	BaCO ₃	<i>Pnma</i>	0.0067	0.0085	0.0039	5.290	5.281	8.850	8.956	6.49000	6.450	8103832
418	0.409	BaCO ₃	<i>Pnma</i>	0.0058	0.0027	0.0072	5.315	5.285	8.904	8.950	6.43409	6.451	9013804
419	0.411	BaCO ₃	<i>Pnma</i>	0.0060	0.0029	0.0066	5.316	5.286	8.906	8.950	6.43383	6.450	9013805
0	0.413	BaCO ₃	<i>Pnma</i>	0.0056	0.0031	0.0073	5.313	5.287	8.896	8.950	6.42840	6.450	1000033
404	0.420	BaCO ₃	<i>Pnma</i>	0.0051	0.0013	0.0106	5.310	5.288	8.912	8.946	6.43650	6.450	9010928

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Table 5.2: Summary of the structural models used for BaTiO₃ PDF fits.

Model name	CC	CT	NT	NR	NO
Crystal System	Cubic	Tetragonal	Tetragonal	Rhombohedral	Orthorhombic
Centrosymmetric	Yes	Yes	No	No	No
Space Group	$Pm\bar{3}m$	$P4/mmm$	$P4mm$	$R3m$	$Amm2$
Ba position	(0,0,0)	(0,0,0)	(0,0,0)	(0,0,0)	(0,0,0)
Ti position	(0.5,0.5,0.5)	(0.5,0.5,0.5)	(0.5,0.5, z)	(z,z,z)	(0.5,0, z)
O1 position	(0.5,0.5,0)	(0.5,0.5,0)	(0.5,0.5,0)	(x,y,x)	(0,0, z)
O2 position		(0.5,0,0.5)	(0.5,0,0.5)		(0.5, y,z)

PDF fits.

5.2.5 PDF structural modeling

The PDF modeling program PDFGUI was used for structure refinements [343]. In these refinements U_{iso} ($\text{\AA}^2$) is the isotropic atomic displacement parameter (ADP), and in multi-phase fits, the ADPs of the same type of atoms are constrained to be the same in different phases; δ_1 ($\text{\AA}$) is a parameter that describes correlated atomic motions [356]; SPD ($\text{\AA}$) is a parameter that accounts for the finite size of the particle, or more correctly, the domain of coherent scattering in the particle, which gives the diameter of the domain in angstrom units, assuming it to be spherical. Q_{damp} and Q_{broad} were refined to a nickel dataset collected under the same experimental conditions and then fixed in the nanoparticle refinements.

As already shown in Chapter 3 for the structure-mining on the undoped barium titanate nanoparticles, five candidate BaTiO₃ perovskite models were fit to the experimental PDFs to determine the structure of the gel nanoparticles. All the structure models, based on the perovskite structure of BaTiO₃, are defined in detail in Table 5.2 [159; 156].

The NT model was extended for the samples that have iron incorporated in them. Designated NT-BFTO, this model (space group: $P4mm$) is built from the NT model by sub-

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stituting Fe into the Ti site, with variable occupancies on the Fe and Ti sites constrained to keep the total site occupancy as 1.0. The atomic positions and ADPs of Fe and Ti ions are constrained to be the same as each other during the refinement, i.e. $z(\text{Ti}) = z(\text{Fe})$ and $U_{iso}(\text{Ti}) = U_{iso}(\text{Fe})$.

Furthermore, as supported by the structure-mining results, we found evidence for this BaCO_3 structure as an impurity phase for doped samples and modeled it with the following orthorhombic (BCO) model (space group: $Pm\bar{c}n$): with Ba at $(0.25, y, z)$, C at $(0.25, y, z)$, O1 at $(0.25, y, z)$ and O2 at (x, y, z) [489; 490]. When using the BCO model as an impurity phase in two-phase fits for $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ datasets, the ADP of the C ion is fixed as $U_{iso}(\text{C}) = 0.04007 \text{ \AA}^2$, and atomic positions of all atoms were fixed as Ba at $(0.25, 0.4164, 0.7544)$, C at $(0.25, 0.7556, -0.0783)$, and O, O1 at $(0.25, 0.9011, -0.0894)$ and O2 at $(0.4601, 0.6832, -0.0820)$, where these numbers were taken from [323], and δ_1 and SPD parameters are not applied during the refinement since the impurity BCO component is too short-range to get stable fitting results.

For high Fe content samples, we also used the cubic perovskite BaFeO_3 (BFO) model (space group: $Pm\bar{3}m$) [491]: with Ba at $(0, 0, 0)$, Fe at $(0.5, 0.5, 0.5)$, and O at $(0.5, 0.5, 0)$; and the orthorhombic BaFe_2O_4 (BF2O4) model (space group: $Pm\bar{c}n$) [492]: with Ba1,2 at $(0.25, y, z)$, Ba3 at (x, y, z) , Fe1,2,3,4 at (x, y, z) , O1-7 at (x, y, z) , O8,9 at $(0.25, y, z)$.

5.3 Results and discussions

To study the multiferroics, it is important to investigate the structure of synthesized nanoparticles, the x-ray PDF analysis is performed over the full range of compositions ($x = 0, 0.1, 0.2, 0.3, 0.5, 0.75, 1.0$). The corresponding sample names used in the PDF analysis is listed in Table 5.3.

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Table 5.3: The information of $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ samples, from undoped ($x = 0$) to fully doped ($x = 1.0$).

#	Sample name	Composition
1	BTO	BaTiO_3
2	BFT1	$\text{BaFe}_{0.1}\text{Ti}_{0.9}\text{O}_3$
3	BFT2	$\text{BaFe}_{0.2}\text{Ti}_{0.8}\text{O}_3$
4	BFT3	$\text{BaFe}_{0.3}\text{Ti}_{0.7}\text{O}_3$
5	BFT5	$\text{BaFe}_{0.5}\text{Ti}_{0.5}\text{O}_3$
6	BFT75	$\text{BaFe}_{0.75}\text{Ti}_{0.25}\text{O}_3$
7	BFO	BaFeO_3

5.3.1 BaTiO_3

We first consider the undoped pristine BTO nanoparticles and would like to know whether it has centrosymmetric or non-centrosymmetric structure. This would provide evidence for whether a paraelectric or ferroelectric phase could be retained in the synthesized nanocrystals and provide further insights into the structure-property relationship in nanoscale BaTiO_3 , a topic that has fascinated the community for many years [493; 494].

All five of the perovskite models fit quite well after refinement. The centrosymmetric models gave comparable agreements as each other ($R_w = 0.133$), but slightly worse than the N models ($R_w \sim 0.115$). The refinement results are given in Table 5.4 and representative fits are shown in Fig. 5.4. This is the first indication that the synthesized nanoparticles are non-centrosymmetric.

Concluding that the underlying structures are non-centrosymmetric based on R_w values alone is insubstantive, because the non-centrosymmetric models have more freedom of variables. However, strikingly, the Ti atoms refine to values away from the center of symmetry in all the non-centrosymmetric models, and the ADPs of the Ti ions are significantly smaller, in the non-centrosymmetric models compared to the centrosymmetric models. This

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Table 5.4: Structure refinement results of all candidate perovskite models fit to the BaTiO₃ dataset over a range of $1.5 < r < 50$ Å. The models are introduced in Section 5.2.5 and are summarized in Table 5.2. Briefly, the models are centrosymmetric-cubic (CC), centrosymmetric-tetragonal (CT), non-centrosymmetric-tetragonal (NT), non-centrosymmetric-rhombohedral (NR), non-centrosymmetric-orthorhombic (NO). Here, R_w is the goodness of fit; x , y and z are the refinable atomic positions in fractional coordinates (see Table 5.2 for details), U_{iso} , in units of (Å²), is the isotropic atomic displacement parameter (ADP); δ_1 is a correlated motion related PDF peak sharpening coefficient; SPD, in units of (Å), is the spherical particle diameter.

Model:	CC	CT	NT	NR	NO
R_w	0.133	0.133	0.118	0.119	0.115
a (Å)	4.0246	4.0211	4.0170	4.0254	4.0147
b (Å)	-	-	-	-	5.6863
c (Å)	-	4.0318	4.0424	-	5.7141
α (°)	90	90	90	89.795	90
Ba z	-	-	-0.0011	0.0046	-0.0039
Ti z	-	-	0.5328	0.4834	0.5218
O1 x	-	-	-	0.0125	-
O1 z	-	-	-0.0180	0.5157	0.4644
O2 y	-	-	-	-	0.2695
O2 z	-	-	0.4756	-	0.2479
Ba U_{iso}	0.0083	0.0082	0.0083	0.0085	0.0086
O U_{iso}	0.0287	0.0284	0.0255	0.0264	0.0204
Ti U_{iso}	0.0177	0.0176	0.0099	0.0088	0.0087
δ_1 (Å)	1.44	1.43	1.57	1.55	1.71
SPD	120.0	122.1	132.4	126.4	129.77

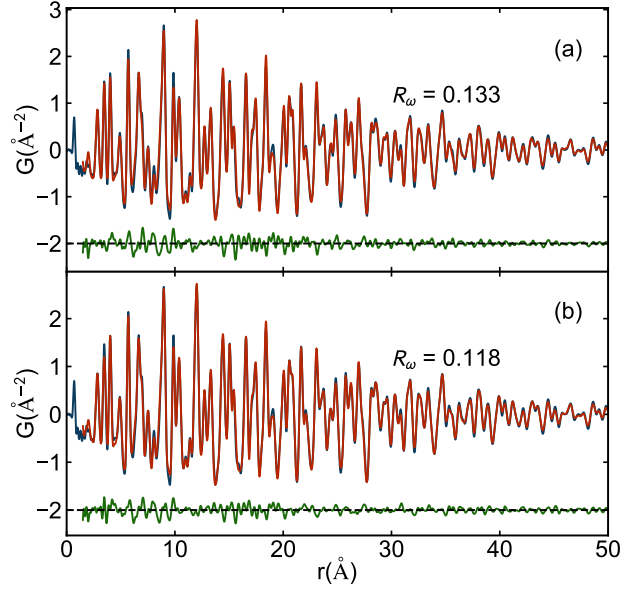


Figure 5.4: X-ray PDFs of the undoped BTO data (blue curves) with the best-fit calculated PDFs (red) for the (a) CC and (b) NT models. The difference curves are shown offset below in green. R_w is the goodness of fit.

is strong evidence that the underlying structure has Ti off the (0.5, 0.5, 0.5) center of symmetry. We also note that the ADPs of the Ba and O ions are comparable between the non-centrosymmetric and centrosymmetric models, which again suggests that the main difference is that Ti is moving off the center of symmetry and that the data strongly support the fact that the gel nanoparticles are non-centrosymmetric. It is not possible with our x-ray PDF data to determine unambiguously which of the non-centrosymmetric symmetry lower distortions that we tried is the correct one.

5.3.2 Low-doped $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ ($0 < x \leq 0.3$)

To verify Fe incorporation into the BaTiO_3 lattice in the doped $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ samples. We therefore fit the NT model, with Fe substituted onto the Ti site (we refer to this as the NT-BFTO model, described in Section 5.2.5), to the low-doped $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0.1, 0.2$,

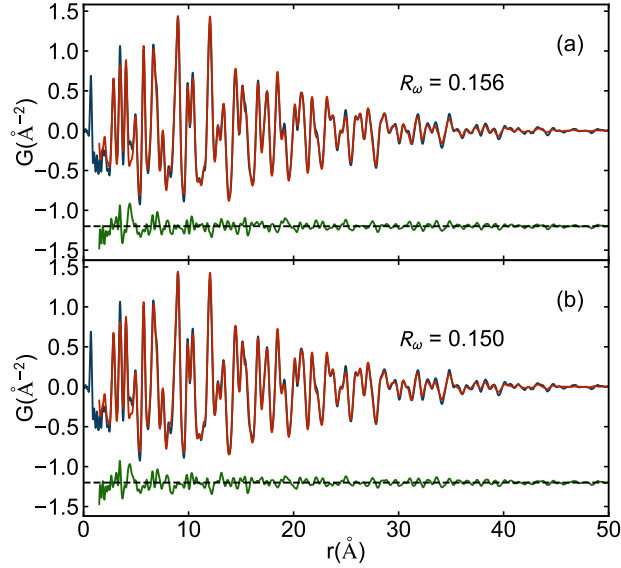


Figure 5.5: X-ray PDFs of the the BFT3 ($x = 0.3$) data (blue curves) with the best-fit calculated PDFs (red) for the (a) NT-BFTO and (b) NT-BFTO + BCO two-phase models. The difference curves are shown offset below in green. R_w is the goodness of fit.

0.3) datasets.

The fits are satisfactory showing that the perovskite structure survives. A representative fit of the BFT3 sample PDF with the NT-BFTO model is shown in Fig. 5.5(a).

However, following the discovery of BaCO_3 impurity in the higher-doped samples (see below) we looked for its presence in these samples by adding it as a second phase to these refinements, i.e. NT-BFTO+BCO model. This led to a small improvement in the goodness-of-fit, R_w , value with the BaCO_3 present at the few percent level. Barium carbonate (BCO) is known to occur in barium containing oxides in which exposure to atmospheric $\text{CO}_2(\text{g})$ can adsorb to, and react with, the surface, to form small quantities of carbonate [489]. The refinement results are given in Table 5.5 and the representative fit is shown in Fig. 5.5(b). It was not possible to refine occupancies on the Ti and Fe sites into stable values. This is not unexpected because Ti and Fe have the similar x-ray scattering power. However, another way of telling if the Fe is doping into the material is to monitor the lattice parameters. In

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Table 5.5: Structure refinement results of NT-BFTO+BCO model fit to the low-doped $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0.1, 0.2, 0.3$) sample PDFs, i.e. BFT1 to BFT3, over a range of $1.5 < r < 50 \text{ \AA}$. The model is introduced in Section 5.2.5. In NT-BFTO model, the occupancies on the Ti and Fe sites are fixed during the refinement keeping the total site occupancy as 1.0. The occupancies on the Fe site are fixed as 0.1, 0.2, and 0.3 for BFT1, BFT2, and BFT3, respectively. The ADPs of Ba and O ions are constrained to be the same in two phases. Here, R_w is the goodness of fit; z is the refinable atomic position in the fractional coordinate (see Table 5.2 for details), U_{iso} , in units of ($\text{\AA}^2$), is the isotropic atomic displacement parameter (ADP); δ_1 is a correlated motion related PDF peak sharpening coefficient; SPD, in units of ($\text{\AA}$), is the spherical particle diameter. The refinement result from the undoped BTO sample is listed together for easier comparison.

Sample Phase	BTO	BFT1		BFT2		BFT3	
	NT	NT-BFTO	BCO	NT-BFTO	BCO	NT-BFTO	BCO
a ($\text{\AA}$)	4.0170	4.0232	5.2954	4.0271	5.3173	4.0270	5.3228
b ($\text{\AA}$)	-	-	9.0207	-	9.0409	-	9.0111
c ($\text{\AA}$)	4.0424	4.0564	6.3406	4.0683	6.3673	4.0753	6.4076
Ba z	-0.0011	-0.0081	-	-0.0077	-	-0.0068	-
Ti (Fe) z	0.5328	0.5283	-	0.5282	-	0.5282	-
O1 z	-0.0180	-0.0228	-	-0.0267	-	-0.0245	-
O2 z	0.4756	0.4867	-	0.5009	-	0.5059	-
Ba U_{iso} ($\text{\AA}^2$)	0.0083	0.0104	0.0104	0.0117	0.0117	0.0128	0.0128
Ti (Fe) U_{iso} ($\text{\AA}^2$)	0.0099	0.0108	-	0.0121	-	0.0124	-
O U_{iso} ($\text{\AA}^2$)	0.0255	0.0266	0.0266	0.0249	0.0249	0.0236	0.0236
SPD ($\text{\AA}$)	132.4	80.8	-	65.4	-	55.2	-
Mass Ratio (%)	-	96.4	3.6	96.1	3.9	95.7	4.3
δ_1 ($\text{\AA}$)	1.57	1.59	-	1.57	-	1.55	-
R_w	0.118	0.138		0.141		0.150	

Fig. 5.6 we plot the iron concentration dependence of the unit cell volume for the low-doped $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ series of samples fit with the NT-BFTO+BCO model as shown in Table 5.5. We find that the unit cell volume increases monotonically with increasing Fe content. This trend is the evidence that Fe is being incorporated into the lattice of the perovskite BTO structure. This is consistent with the observations of XPS data. The experimental results, independently offer verification of the same trend that an increase in lattice parameters occurs on incorporation of the iron into the perovskite. Since Fe^{4+} is a smaller ion than the

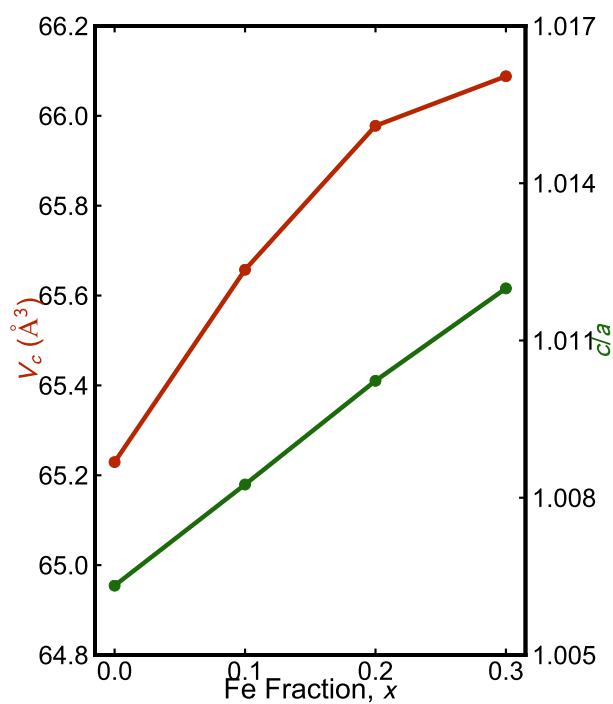


Figure 5.6: The unit cell volume V_c (red curve) and the tetragonality c/a (green curve) from the NT model as a function of Fe doping concentration (x) of $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ samples in the two-phase fits.

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Ti^{4+} that it is replacing, it therefore makes sense to assume that the some of the iron is being incorporated as $3+$ in the high-spin (HS) state, alongside Fe^{4+} .

To maintain charge balance, this would imply that a significant number of oxygen vacancies (V_O^{2+}) would have to also be arriving into the structure [495; 177]. Such vacancies may be more easily accommodated due to the large surface to volume ratio for these sub 10 nm uniform nanocrystals. The XPS data confirms increasing Fe^{3+} (HS). So it is concluded that the nanocrystals have the potential to be multiferroic, as shown in Fig. 5.2, given evidence of retention of tetragonality, lattice expansion to accommodate Fe^{3+} (HS), XPS evidence of Fe^{3+} as well as Fe^{4+} , and confirmed by the magnetic characterization, which would be shown in Section 5.3.4.

The lattice parameters could go up or down with Fe doping depending on the valence and spin state of the iron. According to the Database of Ionic Radii [482], for 6-coordinate octahedral environments, the ionic radius, R_i , of Ti^{4+} , is 0.605 Å. For Fe^{4+} in the same coordination, $R_i = 0.585$ Å, and for Fe^{3+} low spin, $R_i = 0.55$ Å, which are both smaller than Ti^{4+} . On the other hand, for Fe^{3+} high spin, $R_i = 0.645$ Å, which is larger than Ti^{4+} . Therefore, the increase in unit-cell volume with x , 1.3% increase in volume for 30% Fe incorporation, suggests that Fe is being incorporated into the BTO lattice, and the Fe^{3+} high-spin state is present. This reveals the possibility of exhibiting multiferroics in the system under the PJTE mechanism as introduced earlier.

We also note that the tetragonality, c/a , also increases with x , as shown in Fig. 5.6, which may indicate that the ferroicity is strengthening with increasing Fe content. From Table 5.5 we see that the Ti/Fe site refines to a value away from the high symmetry position in all these compounds, indicating that the low-doped structure is still non-centrosymmetric. The ADPs of the Ti/Fe and Ba ions also increase slightly with higher x , consistent with some structural disorder from chemical substitution effects when Fe is doped into the lattice.

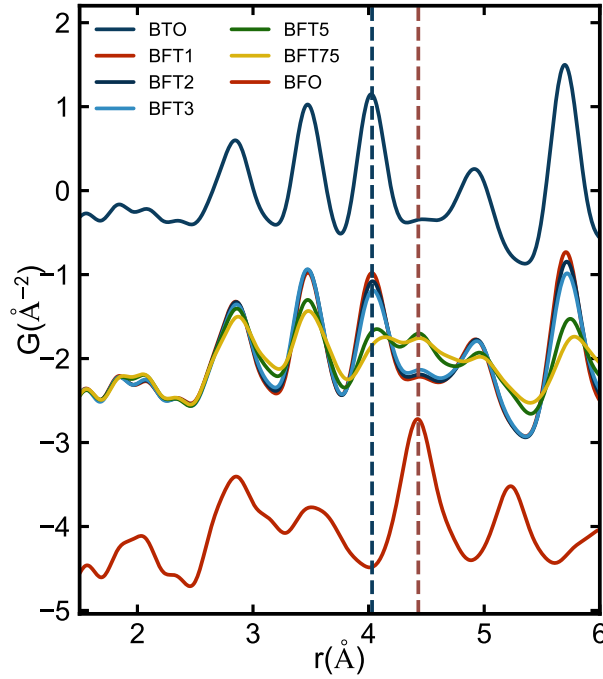


Figure 5.7: Experimental PDFs of iron doped $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ samples. Top curve: pure BTO sample, $x = 0$, (blue). Bottom curve: pure BFO sample, $x = 1$, (brown). Curves in the middle: Ti-Fe mixed composition samples. The blue vertical dashed line highlights the strong $r = 4.03 \text{ \AA}$ peak from the BTO data coming from Ba-Ba, Ti-Ti, and O-O bond lengths. The brown vertical dashed line highlights the strong $r = 4.43 \text{ \AA}$ peak from the BFO data.

5.3.3 High-doped $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ ($x \geq 0.5$)

For higher doped samples there are significant changes in the PDF, as shown in Fig. 5.7. This indicates that the material has either changed its structure, or the sample has become mixed phase with a large amount of the second component. Comparing peaks in the BFO end member sample with the new peaks appearing in the high-doped BFTO samples suggests that the new phase appearing is the same as the BFO sample. This can be seen qualitatively by focusing on some characteristic peaks in the end member models. There is a peak in the BTO data at $r = 4.03 \text{ \AA}$ that is absent in the BFO data and a strong peak at $r = 4.43 \text{ \AA}$ in the BFO end member that is not in BTO. The high-doped BFT5 and BFT75 ($x = 0.5$

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and 0.75) PDFs clearly contains both characteristic peaks, suggesting that these samples are mixed phase. These peaks are highlighted in Fig. 5.7 with vertical dashed lines.

As a result, solving the structure for the BFO sample is the key to understand the high-doped samples. Surprisingly, we were not able to fit the BFO data well with any reported model for BaFeO_3 , where the models we tried, distinguished by their space groups, were $Pm\bar{3}m$ [491], $P4/mmm$ [496], $R\bar{3}m$ [497], $R3c$ [496], $R3m$ [498], $P6_3mmc$ [499]. We finally were able to identify the main signal in this PDF as coming from BaCO_3 , which is a known impurity in these systems arising from the reactive adsorption of CO_2 on the highly basic BaO surface layers of the BTO nanocrystals [489; 490]. The best fit PDF of the BCO model to the BFO data is shown in Fig. 5.8(a).

The BCO model fits the high- r region well, but there is significant extra signal evident in the difference curve in the low- r region. We therefore sought barium ferrite models that might explain this left-over signal. The BaFeO_3 perovskite model worked somewhat. For example, the fit of the BCO+BFO3 (see Section 5.2.5 for details) two-phase model gets slightly better goodness of fit as shown in Fig. 5.8(b). However, a much better fit was obtained using a model for orthorhombic BaFe_2O_4 (named as BF2O4 model, see Section 5.2.5 for details), where a two-phase fit resulted in a significantly improved R_w of 0.155, as shown in Fig. 5.8(c). XPS data suggested the presence of Fe^{4+} for $x > 0.5$, therefore favoring the model of BaFeO_3 , in which the B site oxidation state is formally 4+, compared to BaFe_2O_4 for which Fe is 3+. In addition, the model refined lattice parameters are noticeably different from one previously reported values for BaFe_2O_4 : $a = 18.995 \text{ \AA}$, $b = 6.973 \text{ \AA}$, and $c = 11.300 \text{ \AA}$, compared to $a = 17.347 \text{ \AA}$, $b = 9.336 \text{ \AA}$, and $c = 10.882 \text{ \AA}$ [492].

There is still a small residual signal even from the two-phase fit, so we further tried BFO+BFO3+BF2O4 three-phase fit, and it slightly improve the fit, as shown by the reduced $R_w = 0.130$ and shown in Fig. 5.9. The refined mass ratios of the three phases,

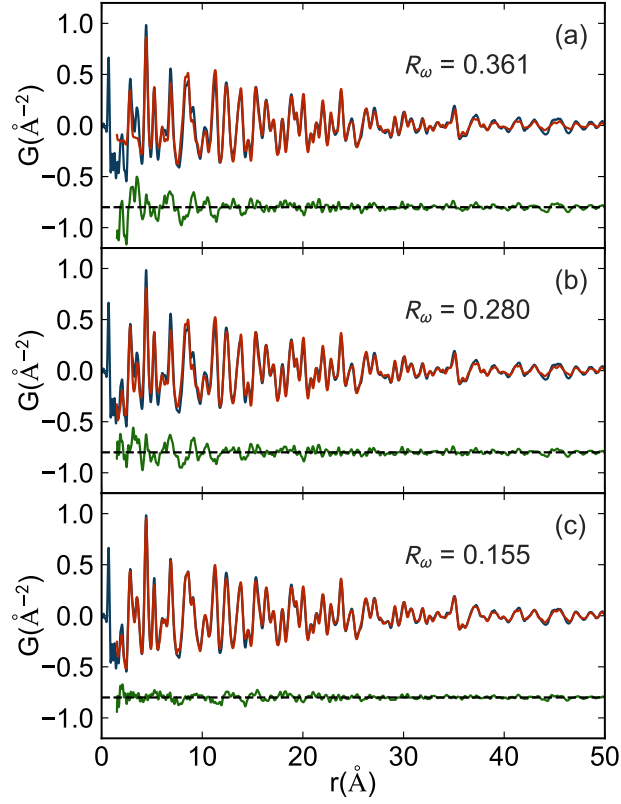


Figure 5.8: X-ray PDFs of the the BFO ($x = 1.0$) data (blue curves) with the best-fit calculated PDFs (red) for the (a) BCO, (b) BCO+BFO3 and (c) BCO+BF2O4 models. The difference curves are shown offset below in green.

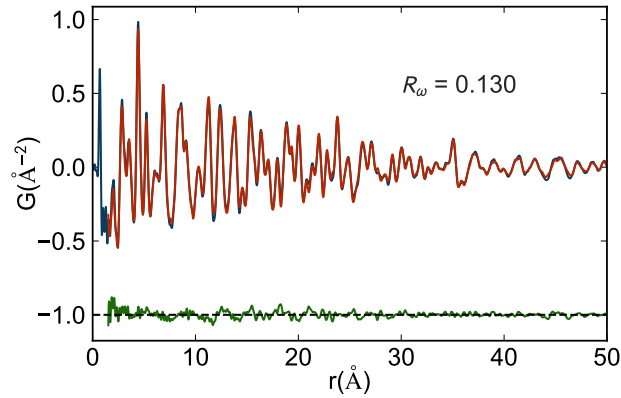


Figure 5.9: X-ray PDF of the the BFO ($x = 1.0$) data (blue curve) with the best-fit calculated PDF (red) for the BCO+BFO3+BF2O4 three-phase model. The difference curve is shown offset below in green.

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BCO:BF₀3:BF₂O₄, are 0.24:0.31:0.45 suggesting that, despite the very strong PDF signal from the BCO in the plot, there are not many mass partials from BCO compared with the barium ferrite phases. The reason why the BCO phase dominates the signal is that it is highly crystalline, compared to the barium ferrite phases that have a very small nanocrystalline particle size. The refined values for the crystallite diameter is 0.51 nm for the BaFeO₃ component and 2.15 nm for the BaFe₂O₄ phase. The crystallite size for the BaFeO₃ component is so small that it may actually be forming an amorphous phase. The refinements were tested for stability and the parameters of the BaFeO₃ model were stable and all refined to reasonable values, so despite the small range of structural coherence we believe that short-range ordered material resembling the perovskite ferrite is present in the sample.

Other refined structural parameters are similar to those we obtained in the two-phase fits, such as ADPs and lattice parameters, noticing that the BF₂O₄ lattice still significantly contracted along the a and b axes ($a = 18.921$ Å, $b = 6.888$ Å, and $c = 11.609$ Å). The refined ADP of the Fe ion (constrained to be the same in both BF₀3 and BF₂O₄ components), 0.001 Å², is much smaller than those of other ions in the model (about 0.010 Å² for Ba and O ions, and 0.031 Å² for the C ion in the BCO model). This value is unphysically small and may indicate a desire for the model to place extra intensity at the Fe position.

Overall, from the PDF analysis, we conclude that, in the nanoscale BaFe _{x} Ti_{1- x} O₃ system for values of $x \leq 0.3$, synthetic substitution occurs seamlessly and a single-phase compound is maintained, with substitution at the B site of Ti for Fe, as a mixture of Fe³⁺/Fe⁴⁺. Although not precisely quantified, it is postulated therefore that the structure may contain oxygen vacancies (especially at the surface) with increasing x , of the form BaFe _{x} Ti_{1- x} O_{3- δ} . With increasing Fe concentration (especially $x \geq 5$), the morphology of the nanocrystals is still largely intact, and the material can be dispersed in organic solvents, converted into films etc., but the perovskite structure appears to be less stable, devolving into additional

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competing phases. Some BaCO_3 is present, and while $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ is evident for $x \geq 0.5$, some BaFeO_3 or BaFe_2O_4 (or possibly both) may be forming.

The collaborators also performed the x-ray photoelectron spectroscopy (XPS) measurements on the samples, and Fe^{3+} was found to exist in the sample from the XPS data [256]. This agrees with the PDF data analysis that the increase in lattice parameters with the increase in the concentration of Fe corresponds to a doping of Fe^{3+} on the Ti^{4+} site within the crystal lattice. A mixture of $\text{Fe}^{3+}/\text{Fe}^{4+}$ may end up residing at the B site such that Fe^{4+} helps stabilize the structure through charge balancing, while Fe^{3+} can be complimented with oxygen vacancies to some extent. Eventually, with increasing Fe ($x > 0.5$), neither Fe^{3+} nor Fe^{4+} can maintain the structure and more thermodynamically stable Ba-Fe-O phases start to emerge.

It would be of great interest to perform neutron PDF analysis on this system for two reasons. First, neutron PDF can provide the accurate oxygen sublattice structure information, so as to determine which of the non-centrosymmetric space groups ($Amm2$, $P4mm$, $R3m$) is the correct structure model for describing the local structures of these synthesized nanocrystals [156; 170]. Second, the magnetic properties of the multiferroic behavior can be further studied from neutron PDF, and the magnetic PDF technique based on neutron PDF [437] can help further investigate the local magnetism.

However, the current gel-collection method would have hydrogenous materials involved during the synthesis, which would result in difficult data reduction because of the hydrogen problem in neutron experiments. Avoid any ^1H left in the material requires extra time and cost to optimize the current chemical synthesis methods, otherwise the strong inelastic incoherent scattering from hydrogen would prevent us obtaining the coherent scattering signal for PDF analysis, as explained in Section 2.4.3. In addition, due to the unexpected COVID-19 pandemic situation, the neutron experiments are suspended in 2020. We did not

have opportunity to perform the neutron measurements on $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ materials at the time of writing thesis.

5.3.4 Dielectric and magnetic characterizations

To validate the multiferroicity in the $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$. Collaborators also performed the dielectric and magnetic characterizations [256].

The fabricated thin film (450 nm) nanocomposites were prepared in order to study the dielectric properties. The result on the stability of the effective dielectric constants over a standard range of frequencies (100 Hz-2 MHz, relatively flat lines) is shown in Fig 5.10, adapted from [256]. The dielectric constants at 1 MHz of 27.0 to 22.2 for $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ samples for $x = 0-0.75$ respectively. This observation is strong evidence that the measurement of the effective dielectric constants acquired using impedance analysis is due to the intrinsic nature of the material, and not from interstitial charging or space charging due to void spaces within the 0-3 nanocomposite. The dielectric loss ($\tan \delta$) values were in the range of 0.02-0.09 with the dielectric loss rising in the higher frequency range as seen in Fig. 5.10(b). This slight increase in dielectric loss at higher frequencies ($> 10^5$ Hz) is due to contact resistance which is known to make a significant contribution to the dielectric loss at higher frequencies [46]. The dielectric loss values at 1 MHz, were however, all $\tan \delta < 0.04$, demonstrating that the nanocomposite can function well as an insulating dielectric, a capacitor or potential multiferroic device. The effective dielectric constants showed a trend in decreasing effective dielectric constants as a function of increasing Fe concentration in the sample (Figure 5.10(a)), likely due to the Fe^{3+} ions providing fewer polarizable dipoles in the crystalline structure. This trend in decreasing effective dielectric constants agrees well with the literature [500]. Using the modified interphase model [501], the estimated dielectric constants of BTO, BFT ($x = 0.1-0.3, 0.5, 0.75$), and

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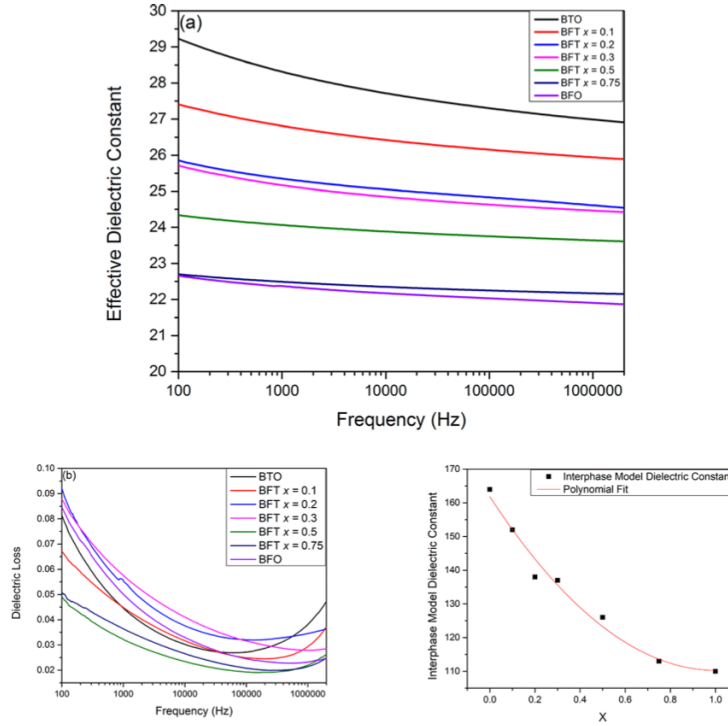


Figure 5.10: (a) Effective dielectric constants as a function of frequency for all $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ samples. (b) Dielectric loss as a function of frequency for all $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ samples. Dielectric constant decreases with increasing Fe concentration. (c) Plot of estimated intrinsic dielectric constants of the $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ nanocrystals as a function of x , calculated by applying the interphase model, with known volume fractions and electrode area.

BFO were shown in Fig. 5.10(c). It has been reported that the bulk dielectric constants of BTO, BFT, and BFO are significantly larger than our calculated values (> 1000) [502; 59]; however, it is known that the size of the size of nanoparticles plays a significant role in the suppression of the ferroelectric behavior of the material, despite evidence of persistence of polarization. This is evident in the dielectric measurements and consistent with other perovskite systems and nanocomposites [493].

The magnetic properties were measured to investigate the ferromagnetic behavior in the system. Characterization of the magnetic properties of $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ samples was performed on a Quantum Designs Magnetic Property Measurement System (MPMS) at Oak Ridge Na-

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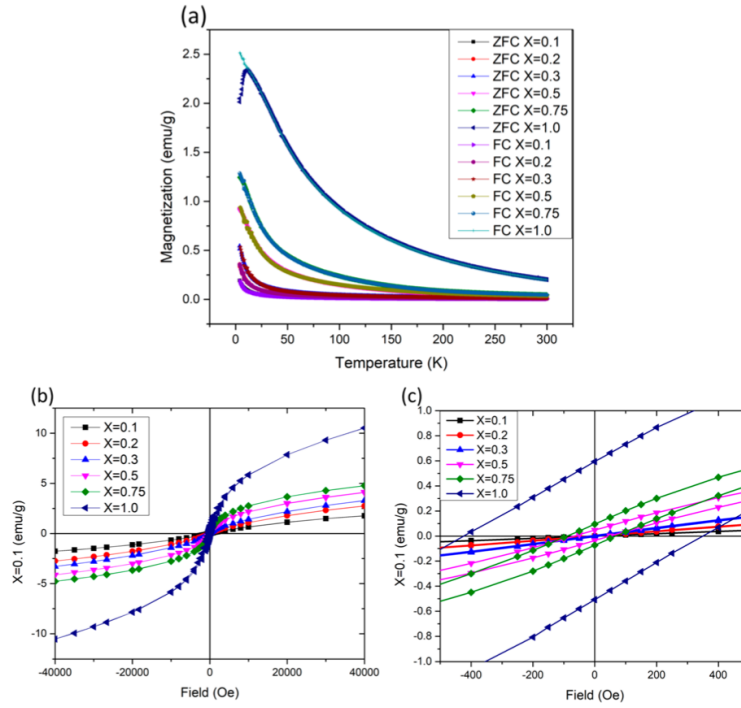


Figure 5.11: (a) ZFC and FC measurements of the doped $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ samples. (b) The magnetic hysteresis measurements of doped $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ samples, and (c) zoomed in portion of (b) to highlight asymmetric hysteresis loops at higher Fe concentration.

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tional Laboratory in Tennessee. ZFC and FC measurement results were shown in Fig 5.11(a), adapted from [256]. For ZFC measurements the samples were cooled to 5 K in the absence of an external magnetic field. Once at 5 K, an external magnetic field of 2000 Oe was applied to the samples and they were slowly heated to 300 K. For the FC measurements, the samples were cooled down to 5 K in the presence of a 2000 Oe field. A sharp increase in magnetization is observed at the increasing temperature point when x increases, and an increase in magnetization as a function of Fe concentration is observed and agrees well with literature [179; 178]. A much larger increase in the magnetization is seen in the $x = 1.0$ sample as there is no presence of Ti^{4+} in the material thus leading to a higher amount of magnetic spins aligning in the presence of a magnetic field and as confirmed by PDF, the presence of Ba-Fe-O phases is also contributing. As the temperature is increased the magnetization decreases due to randomization of the magnetic orderings within the nanoparticles because of the thermal energy. This only becomes drastically apparent below 200 K. There is no observed splitting between the ZFC and FC measurements implying that the nanoparticles may be paramagnetic. Magnetic hysteresis measurement results with a maximum sweeping magnetic field of 40000 Oe are shown in Fig. 5.11(b). A similar trend in increasing magnetization can be seen as a function of increasing Fe content in the nanocrystals. Upon closer inspection of the magnetic hysteresis loops in the zoomed in region in Fig. 5.11(c) it is apparent that there is a weak magnetic coercivity and a small remanence magnetization implying a weak ferromagnetic state at low temperatures (< 5 K) however the samples never reach full magnetic saturation at this magnetic field strength. For lower Fe concentrations ($x \leq 0.2$) it is observed that the magnetic coercivity (H_c) is 11 Oe for BFT1 and 15 Oe for BFT2 with relatively low remanent magnetization of 0.001 emu/g and 0.003 emu/g, respectively. However, when Fe concentration is higher ($x \leq 0.3$) there are different values for the negative and positive magnetic field values. This is seen in both the magnetic coercivity and the remanent

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magnetization. As the Fe concentration increases, the remanent magnetization and magnetic coercivity increase as well, and this is to be expected as more Fe-O octahedra are forming, creating more magnetic moments due to doping concentration. The asymmetric hysteresis loops are thought to be due to the multiple valence states existing within the crystal lattice due to the presence of both Fe^{3+} and Fe^{4+} as seen in the XPS data [256]. As Fe concentration increases, the different magnetic states become more and more apparent. A similar trend in the much larger increase in magnetization is seen in the hysteresis as well as the ZFC and FC curves, and is likely due to the absence of Ti^{4+} in the material as stated above. Thus the characterizations above clearly show both the ferroelectric and ferromagnetic behaviors in the Fe doped samples.

5.4 Conclusion

In this work, the $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ nanocrystals were prepared using a near room temperature ($\leq 60^\circ\text{C}$) hybrid sol-gel chemical solution processing method by collaborators. The local structures of samples are studied by x-ray pair distribution function (PDF) analysis, which reveals that the gel-collected nanoparticles are non-centrosymmetric, whereas the unambiguous determination on one of the non-centrosymmetric symmetry breaking distortions (tetragonal, rhombohedral, or orthorhombic crystal system) requires the neutron PDF experiments for providing the accurate oxygen sublattice structure information. The non-centrosymmetry reveals the ferroelectric property of the samples, since the B site cation is off-centered, which results in the spontaneous polarization phenomenon for the 8-10 nm nanoparticles.

For low-doped $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ ($x \leq 0.3$) samples, the PDF analysis clearly shows the increase in lattice parameters with the increase in the concentration of Fe, which corresponds

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to a doping of Fe^{3+} (high spin) on the Ti^{4+} site within the crystal lattice, due to the larger cationic radii of Fe^{3+} high-spin ions when compared to Ti^{4+} which gives the possibility of multiferroics predicted by the pseudo-Jahn-Teller effect theory. The PDF analysis fully supports the observation that Fe substitution is facile for $x = 0.1, 0.2$, and 0.3 , generating a series of compounds that appear mainly single-phase, but at higher Fe substitutions the $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ nanocrystals show evidence of other (trace) phases being present but still present similar structural characteristics, suggesting that Fe substitution is also possible at $x \geq 0.5$.

For high-doped $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_3$ ($x \geq 0.5$) samples, Fe evidently impacts the structure, but still produces dispersible, relatively monodisperse nanocrystals, with additional phases growing in. It is possible that a mixture of $\text{Fe}^{3+}/\text{Fe}^{4+}$ ends up residing at the B site: Fe^{4+} helps stabilize the structure through charge balancing, while Fe^{3+} may be complimented with oxygen vacancies to some extent, especially at the surface. The structure may therefore be of the form $\text{BaFe}_x\text{Ti}_{1-x}\text{O}_{3-\delta}$ for increasing x . Eventually, with increasing Fe ($x > 0.5$), neither Fe^{3+} nor Fe^{4+} can maintain the structure and the emergence of more thermodynamically stable Ba-Fe-O phases start to emerge.

The multiferroicity is further validated by the frequency dependent dielectric measurements and Magnetic characterization by MPMS (both magnetic hysteresis loops and zero field and field cooling measurements) carried out by the collaborators, for the ferroelectricity and ferromagnetism, respectively.

Chapter 6

Two-orbital degeneracy lifted state as a local precursor to a metal-insulator transition in magnesium titanate spinels

6.1 Introduction

The AB_2X_4 transition-metal spinels, with B cations forming a pyrochlore lattice, the geometrically frustrated network of corner-sharing tetrahedra [185], exhibit a wealth of interesting electronic and magnetic properties, such as spin dimerization [204; 211], spin-lattice instability [503], orbital ordering [504], charge ordering [505], and metal-insulator transitions [506; 209; 507].

For instance, the $CuIr_2S_4$ thiospinel system has many exotic properties, such as a transition from paramagnetic metal to diamagnetic insulator on cooling [200; 201; 202], the forma-

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tion of structural isomorphous octamers [203; 204], and anomalous electrical properties [205; 206]. In particular, CuIr_2S_4 has broken symmetries in its ground state accompanied by the formation of charge order and orbital order and the creation of magnetic spin singlets on dimerized Ir^{4+} - Ir^{4+} pairs [204].

These dimers were shown to disappear on warming through the transition, but surprisingly, preformed local symmetry broken states were seen at high temperature well above the global long-range ordering structure transition [215]. Thus, on cooling, a precursor state exists that has broken local symmetry but is high symmetry over the long range. This behavior was shown to be driven by breaking of d -electron orbital degeneracies, resulting in a local fluctuating orbital-degeneracy-lifted (ODL) state distinct from the spin singlet dimer. This local state is enabled by a direct t_{2g} Ir orbital overlap promoted by the topology of the crystal structure. In the regime of partial filling and high crystal symmetry that imposes the degeneracy of the orbital manifold, a molecular-orbital-like state is formed and accompanied by associated local structure distortion. Many of the interesting physical properties of CuIr_2S_4 could be well explained by the insights gained from understanding the short-range-ordered ODL phenomenon, such as the non-conventional conduction mechanism in the high-temperature metallic phase [205], and the apparently contradictory observation of the destruction of the dimers at the phase transition but the persistence of poor metallic response above the transition [508].

Similar local symmetry-broken ODL states preformed at high temperature were also observed in other non-spinel d -electron systems such as the FeSe superconductor [509; 333]. Even the well studied physics of the perovskite lanthanum manganites (LaMnO_3) could also be interpreted in the same way [510], establishing that the ODL phenomenon is widespread among the many materials with partially filled d -electron manifolds. To gain comprehensive understanding of the phenomenon it is important to seek it out systematically and charac-

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terize it in more materials with potential of revealing novel aspects. Here we show that a similar ODL state exists in MgTi_2O_4 .

MgTi_2O_4 has many similarities to CuIr_2S_4 [207]. They are both cubic spinels at high temperature with a transition metal ion pyrochlore sublattice of corner-shared tetrahedra. In both cases the crystal field splits the d -orbitals into a t_{2g} triplet and an e_g doublet with the t_{2g} orbitals partially occupied and the e_g orbitals empty. They both exhibit a temperature-dependent metal-insulator transition (MIT) [208; 209], the origin of which has been attributed to an orbital-selective Peierls mechanism [207]. They both exhibit a global symmetry lowering, from cubic to tetragonal, at the MIT on cooling. They both have anomalous electrical resistivity behavior in the high-temperature metallic phase [210; 205]. The symmetry lowering at the MIT is accompanied by a dimerization of transition metal ions that results in alternating short and long metal-metal bonds, and a resulting tetramerization [511], along linear chains of ions on the pyrochlore sublattice [207]. The short bonds are associated with spin singlet dimer formation [204; 211]. The charge filling is also almost electron-hole symmetric between the systems with Ti^{3+} having one electron in the t_{2g} manifold, while Ir^{4+} has one hole, although the nominal charge of Ir in CuIr_2S_4 is 3.5+ which would place half a hole per Ir in the t_{2g} anti-bonding band on average in this compound.

Despite the similarities, there are also notable differences. The Ti valence electrons are in $3d$ orbitals whereas for Ir they are $5d$, which are more extended and should result in larger bandwidth. This is reflected in the average separation between the transition metals on undistorted tetrahedral pyrochlore sublattices of their cubic structures follows this expectation: Ti-Ti separation is shorter (~ 3.0 Å) whereas Ir-Ir separation is longer (~ 3.5 Å). Also, experimentally, in MgTi_2O_4 the tetragonal distortion is shown to be compressive ($c < a$) below the MIT [211] but it is tensile ($c > a$) in CuIr_2S_4 [200]. Dimers form helical

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superstructures in MgTi_2O_4 , whereas they form octameric molecules in CuIr_2S_4 , thereby lowering the symmetry further to triclinic. Both materials tetramerize below the MIT; however, CuIr_2S_4 has a $3+-3+-4+-4+$ charge ordering (CO) that accompanies an orbital ordering (OO) [215], whereas no CO is observed in MgTi_2O_4 and the site charge is uniformly $3+$. It is thus interesting to explore whether ODL effects are seen in MgTi_2O_4 despite these differences.

Neutron pair distribution function (PDF) analysis on MgTi_2O_4 has been performed in earlier work [512] to study the dimers, suggesting that they do persist to high temperature. However, due to the weak and negative neutron scattering length of Ti, and appreciable overlap with substantially stronger oxygen signal, neutron PDF itself cannot fully reveal how the local structure behaves with temperature. Here we have applied a combined x-ray and neutron analysis to understand the full picture. We find unambiguously that the Ti-Ti dimers do disassemble on warming through MIT. However, the local structure does not agree with the average structure even at high temperature. In analogy with CuIr_2S_4 , partially filled t_{2g} transition metal orbital manifolds of MgTi_2O_4 , which are triply degenerate in the average cubic symmetry, utilize their favorable overlaps fostered by the pyrochlore sublattice topology to form an ODL state. Its structural signatures are observed up to 500 K, the highest temperature measured. The spatial extent of the local structural response is found to be longer than that observed in CuIr_2S_4 , suggesting a two-orbital character of the ODL state in MgTi_2O_4 , consistent with the electronic filling.

6.2 Methods

6.2.1 Sample synthesis

The sample synthesis work [513] was done by Dr. John Mitchell from Materials Science Division in Argonne National Laboratory. TiO_2 , Ti metal, and an excess of MgO were mixed and reacted in a graphite crucible using a spark plasma sintering technique. Synthesis at 1100°C was complete in ~ 15 minutes. The sample was reground and fired a second time under similar conditions.

6.2.2 Sample characterizations

The conventional x-ray diffraction and magnetization characterization measurements [513] were performed by the collaborators, Dr. John Mitchell and Dr. Hong Zheng from Materials Science Division in Argonne National Laboratory. Powder x-ray diffraction analysis of the product showed well-crystallized MgTi_2O_4 spinel accompanied by an extremely small concentration of Ti_2O_3 as a second phase. Magnetization measurements were conducted using a superconducting quantum interference device (SQUID) magnetometer on a specimen with mass of 6.2 mg, and the Curie-Weiss analysis was performed on the data. The fit to the normalized low-temperature data revealed the Weiss temperature of -0.45 K, consistent with isolated Ti^{3+} , and the Curie constant of 0.023 emu K/mol, which corresponds to about 3 mol% of putative Ti^{3+} spin-1/2 impurities.

6.2.3 X-ray and neutron total scattering experiments

The synchrotron x-ray total scattering measurements were carried out at the PDF beamline (28-ID-1) at the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory (BNL) using the rapid acquisition PDF method (RAPDF) [334]. The MgTi_2O_4

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powder sample was loaded in a 1 mm diameter polyimide capillary and measured from 90 K to 500 K on warming using a flowing nitrogen cryostream provided by Oxford Cryosystems 700 Series Cryocooler. The experimental setup was calibrated by measuring the crystalline Ni as a standard material. A two-dimensional (2D) PerkinElmer area detector was mounted behind the samples perpendicular to the primary beam path with a sample-to-detector distance of 227.7466 mm. The incident x-ray wavelength was 0.1668 Å. The PDF instrument resolution effects are accounted for by two parameters in modeling, Q_{damp} and Q_{broad} [347; 343]. For x-ray PDF measurement, these were determined as $Q_{damp} = 0.039 \text{ Å}^{-1}$ and $Q_{broad} = 0.010 \text{ Å}^{-1}$ by fitting the x-ray PDF from a well crystallized sample of Ni collected under the same experimental conditions.

In order to verify the data reproducibility, an additional set of x-ray data (in the 90 K to 300 K temperature range on warming) was collected at the XPD beamline (28-ID-2) at the NSLS-II at BNL using a similar RAPDF setup but with x-ray wavelength of 0.1901 Å and sample-to-detector distance of 251.1493 mm. The corresponding instrument resolution parameters were determined to be $Q_{damp} = 0.032 \text{ Å}^{-1}$ and $Q_{broad} = 0.010 \text{ Å}^{-1}$, implying similar instrument resolution effects across the two sets of measurements.

The collected x-ray data frames were summed, corrected for detector and polarization effects, and masked to remove outlier pixels before being integrated along arcs of constant momentum transfer Q , to produce 1D powder diffraction patterns using the PYFAI program [337]. Standardized corrections and normalizations were applied to the data to obtain the reduced total scattering structure function, $F(Q)$, which was Fourier transformed to obtain the PDF, using PDFGETX3 [338] within xPDFSUITE [339]. The maximum range of data used in the Fourier transform was chosen to be $Q_{max} = 25.0 \text{ Å}^{-1}$, so as to give the best trade-off between statistical noise and real-space resolution.

The time-of-flight (TOF) neutron total scattering measurements were conducted at the

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NOMAD beamline (BL-1B) [335] at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. The MgTi_2O_4 powder sample was loaded into a 3 mm diameter silica capillary mounted on a sample shifter, and data were collected from 100 K to 500 K on warming using an Ar flow cryostream. The neutron PDF instrument resolution parameters were determined as $Q_{\text{damp}} = 0.0232 \text{ \AA}^{-1}$ and $Q_{\text{broad}} = 0.0175 \text{ \AA}^{-1}$ by fitting the neutron PDF of a NIST standard 640d crystalline silicon sample. The neutron data were reduced and transformed to the PDF with $Q_{\text{max}} = 25.0 \text{ \AA}^{-1}$ using the automated data reduction scripts available at the NOMAD beamline.

6.2.4 Structure-mining

The structure-mining approach was applied on both neutron and x-ray experimental PDFs of MgTi_2O_4 in order to find its candidate structures. The heuristic-2 (Mg-Ti-O) is applied, fetching all structures that contain Mg, Ti, and O elements with any stoichiometry. The corresponding structure-mining results from the Crystallography Open Database (COD) [379] are shown in Fig. 6.1, using the NXPf data collected at the 500 K as an example here. The top ranked entries are mostly the duplicated cubic structure from a temperature series neutron diffraction study with each temperature point being recorded in COD [379]. The top seven non-duplicated entries with $R_w < 0.7$ are listed in Table 6.1 and Table 6.2 for x-ray and neutron PDF, respectively. Both x-ray and neutron PDF consistently return the best possible candidates structures as the cubic (s.g. $Fd\bar{3}m$) and tetragonal (s.g. $P4_122$) magnesium titanate spinel models [514; 515]. Notice that in spinels the A and B sites can switch symmetrically in the structure, and considering that Mg ($b = 5.375 \text{ fm}$) and Ti ($b = -3.438 \text{ fm}$) scatter neutron quite differently, but not that far away for x-ray scattering, it is interesting that neutron PDF ranks the MgTi_2O_4 stoichiometry model on the top but x-ray returns Mg_2TiO_4 in the first

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Table 6.1: The top structure-mining results with $R_w < 0.7$ for the MgTi_2O_4 x-ray data collected at 500 K using heuristic-2 from the COD, fetching all structures that contain Mg, Ti, and O elements with any stoichiometry. Here No. refers to the structure index (Fig. 6.1(a)), which is the order fetched from the database, and s.g. represents the space group of the structure model. The initial isotropic atomic displacement parameter (U_{iso}) of all atoms in each structure is set to $0.005 \text{ \AA}^2$ to start the structure refinements. The a and c are the lattice parameters of the structure model. The subscript i indicates an initial value before refinement and the subscript r indicates a refined value. DB ID represents the database ID of the structure model in COD. $Q_{max} = 25.0 \text{ \AA}^{-1}$, $Q_{damp} = 0.039 \text{ \AA}^{-1}$, and $Q_{broad} = 0.010 \text{ \AA}^{-1}$ were set and not varied in the mining operation (see Section 3.2 for details).

No.	R_w	formula	s.g.	Mg U_{iso} ($\text{\AA}^2$)	Ti U_{iso} ($\text{\AA}^2$)	O U_{iso} ($\text{\AA}^2$)	a.i ($\text{\AA}$)	a.r ($\text{\AA}$)	c.i ($\text{\AA}$)	c.r ($\text{\AA}$)	DB.ID DB.ID
82	0.189	Mg_2TiO_4	$Fd\bar{3}m$	0.0105	0.0042	0.0146	8.438	8.508	-	-	9013398
5	0.190	Mg_2TiO_4	$Fd\bar{3}m$	0.0105	0.0042	0.0145	8.469	8.508	-	-	9001691
72	0.190	Mg_2TiO_4	$Fd\bar{3}m$	0.0105	0.0042	0.0143	8.455	8.508	-	-	9003041
78	0.200	Mg_2TiO_4	$P4_122$	0.0089	0.002943	0.0114	5.975	6.034	8.414	8.457	9011260
7	0.206	Mg_2TiO_4	$P4_122$	0.0087	0.003396	0.0101	6.007	6.035	8.415	8.448	9001695
1	0.227	MgTi_2O_4	$Fd\bar{3}m$	0.0100	0.0069	0.0210	8.474	8.512	-	-	1541493
0	0.253	Mg_2TiO_4	$Fd\bar{3}m$	0.0111	0.0043	0.0125	8.410	8.505	-	-	1011276

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Table 6.2: The top structure-mining results with $R_w < 0.7$ for the MgTi_2O_4 neutron data collected at 500 K using heuristic-2 from the COD, fetching all structures that contain Mg, Ti, and O elements with any stoichiometry. Here No. refers to the structure index (Fig. 6.1(b)), which is the order fetched from the database, and s.g. represents the space group of the structure model. The initial isotropic atomic displacement parameter (U_{iso}) of all atoms in each structure is set to $0.005 \text{ \AA}^2$ to start the structure refinements. The a and c are the lattice parameters of the structure model. The subscript i indicates an initial value before refinement and the subscript r indicates a refined value. DB ID represents the database ID of the structure model in COD. $Q_{max} = 25.0 \text{ \AA}^{-1}$, $Q_{damp} = 0.0232 \text{ \AA}^{-1}$, and $Q_{broad} = 0.0175 \text{ \AA}^{-1}$ were set and not varied in the mining operation (see Section 3.2 for details).

No.	R_w	Formula	s.g.	Mg U_{iso} ($\text{\AA}^2$)	Ti U_{iso} ($\text{\AA}^2$)	O U_{iso} ($\text{\AA}^2$)	a.i ($\text{\AA}$)	a.r ($\text{\AA}$)	c.i ($\text{\AA}$)	c.r ($\text{\AA}$)	DB.ID DB.ID
1	0.242	MgTi_2O_4	$Fd\bar{3}m$	0.0040	0.0089	0.0157	8.474	8.507	-	-	1541493
72	0.256	Mg_2TiO_4	$Fd\bar{3}m$	0.4040	0.0032	0.0109	8.455	8.509	-	-	9003041
82	0.256	Mg_2TiO_4	$Fd\bar{3}m$	0.4382	0.0036	0.0109	8.438	8.509	-	-	9013398
5	0.256	Mg_2TiO_4	$Fd\bar{3}m$	0.4299	0.0035	0.0109	8.469	8.509	-	-	9001691
78	0.277	Mg_2TiO_4	$P4_122$	0.1566	0.0004	0.0104	5.975	6.034	8.414	8.462	9011260
7	0.302	Mg_2TiO_4	$P4_122$	0.2137	0.00003	0.0094	6.007	6.007	8.415	8.536	9001695
0	0.369	Mg_2TiO_4	$Fd\bar{3}m$	0.2148	0.0012	0.014	8.410	8.507	-	-	1011276

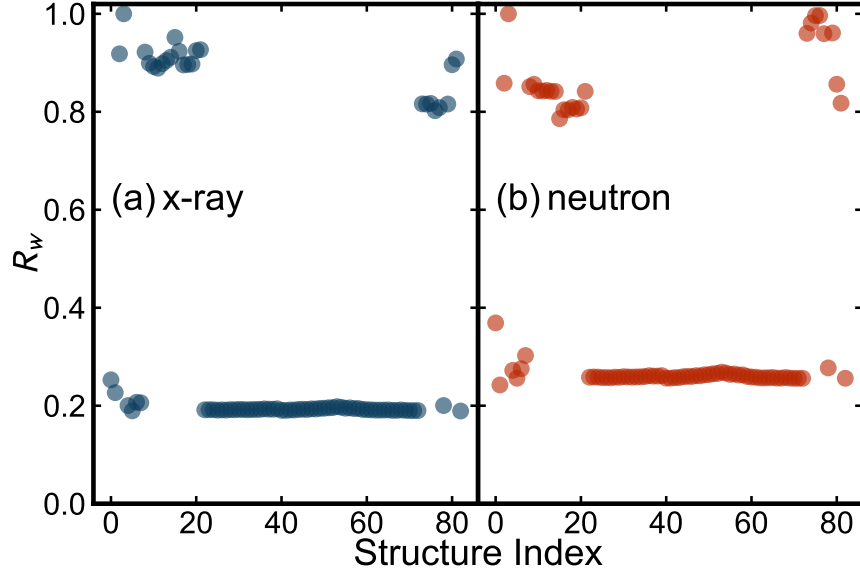


Figure 6.1: R_w values for each of the structures fetched from the databases for the MgTi_2O_4 (a) x-ray and (b) neutron data collected at 500 K using heuristic-2, filtering for all the structures with Mg, Ti, and O elements from the COD. The R_w parameter represents the goodness-of-fit for each structure.

place from the mining operation. Strikingly, neutron data refinement returns extremely high ADP value for Mg atom in Mg_2TiO_4 (about $0.4 \text{ \AA}^2$), whereas the refined parameters of the MgTi_2O_4 model are physically reasonable in the neutron fit. This validates that the underlying structure of the sample is MgTi_2O_4 . So the combination of neutron and x-ray PDFs would help distinguish the best candidate structure for the magnesium titanate spinel system under study, and the spinel composition is more likely to be MgTi_2O_4 based on the structure-mining.

6.2.5 Structural modeling

The PDF modeling programs PDFGUI and DIFFPY-CMI were used for PDF structure refinements [343; 345]. In these refinements, U_{iso} ($\text{\AA}^2$) is the isotropic atomic displacement parameter (ADP) and the ADPs of the same type of atoms are constrained to be the same;

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δ_2 ($\text{\AA}^2$) is a parameter that describes correlated atomic motions [356]. The PDF instrument parameters Q_{damp} and Q_{broad} determined by fitting the PDF from the well crystallized standard sample under the same experimental conditions are fixed in the structural refinements on MgTi_2O_4 dataset.

To estimate the correlation length of local structural distortions, an r_{min} -dependent fit is performed on select high-temperature x-ray data (300 K, 400 K, and 500 K). During the fit, the average high-temperature cubic MgTi_2O_4 model is used, fixing the upper limit of fit range as $r_{max} = 50 \text{ \AA}$, but changing the lower limit r_{min} from $1 \leq r_{min} \leq 36 \text{ \AA}$ in $0.2 \text{ \AA}$ r -steps. Each fit range uses the same initial parameter values and the δ_2 term is not applied since the data fitting range does not consistently include the low- r region in all these refinements.

The Rietveld refinement on the neutron TOF Bragg data was implemented in the GSAS-II software [516]. The instrument parameters were refined to the standard silicon data collected under the same experimental conditions and then fixed in the MgTi_2O_4 Rietveld refinements. The sequential refinement option was used to refine the temperature series dataset collected at the $2\theta = 120^\circ$ detector bank from 100 K to 500 K in a systematic manner.

Based on the structure-mining results, two candidate MgTi_2O_4 models were fit against the experimental data. In the cubic MgTi_2O_4 model (space group: $Fd\bar{3}m$), the atoms sit at the following Wyckoff positions: Mg at 8a (0.125,0.125,0.125), Ti at 16d (0.5,0.5,0.5), and O at 32e (x,x,x). The initial lattice parameters and atomic positions are $a = 8.509027 \text{ \AA}$ and O at (0.25920,0.25920,0.25920) [211]. The Ti pyrochlore sublattice is shown in Fig. 6.2(a), indicating that all the Ti-Ti bonds are of equal length, reflecting regular Ti_4 tetrahedra. In the tetragonal MgTi_2O_4 model (space group: $P4_12_12$), the atoms sit at the following Wyckoff positions: Mg at 4a ($x,x,0$), Ti at 8b (x,y,z), O1 at 8b (x,y,z), and O2 at 8b (x,y,z). The initial lattice parameters and atomic positions are $a = 6.02201 \text{ \AA}$, $c = 8.48482 \text{ \AA}$, Mg at (0.7448,0.7448,0), Ti at (-0.0089,0.2499,-0.1332), O1 at (0.4824,0.2468,0.1212), and O2

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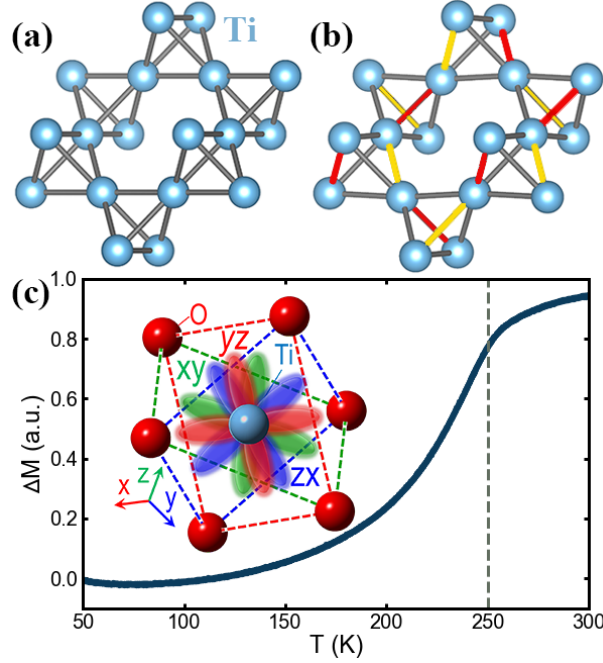


Figure 6.2: (a,b) The Ti pyrochlore sublattice of corner-shared Ti_4 tetrahedra for (a) undistorted (cubic) and (b) distorted (tetragonal) MgTi_2O_4 structure, respectively, highlighting both short (red) and long (yellow) Ti-Ti bonds in the distorted structure. (c) The temperature dependence of magnetization (symbols) with the Curie-Weiss behavior contribution subtracted. The inset shows TiO_6 octahedron and t_{2g} orbitals that point towards O-O edges, where the Ti atom is in blue and the O atom is in red. The vertical grey dashed line at 250 K indicates the MIT temperature.

at $(0.2405, 0.0257, 0.8824)$ [211]. The corresponding distorted Ti sublattice is presented in Fig. 6.2(b), showing that one Ti-Ti bond gets shorter (indicated in red) and one gets longer (in yellow) out of the six Ti-Ti bonds of each Ti_4 tetrahedron. The lattice parameters of these two models have the relationship of $c_c \sim c_t \sim \sqrt{2}a_t$, where the subscripts c and t refer to the cubic and tetragonal models, respectively.

6.3 Results

The magnetization, $M(T)$, of the sample up to 300 K is shown in Fig. 6.2(c), adapted from [513]. A low-temperature Curie-Weiss like component has been subtracted to account for the effect of magnetic impurities contributing to the signal at low temperature. The onset of a broad dimerization transition is observed at around 250 K, which is close to the literature reported MIT temperature of 260 K [209; 517] and implies the canonical behavior of our sample.

We next establish that the average structural behavior of our sample agrees with other observations in the literature [209; 211; 518] by carrying out Rietveld refinements fitting tetragonal and cubic MgTi_2O_4 models to the neutron time-of-flight (TOF) Bragg data measured from 100 K to 500 K. The refinement results from select fits are reproduced in Tab. 6.3, and a representative fit, of the tetragonal model to the 100 K dataset, is shown in Fig. 6.3(a).

The tetragonal distortion, given by $c/\sqrt{2}a$, is small at all temperatures and the data are not of high enough resolution to directly observe distinct peaks that would indicate any tetragonal distortion. However, the temperature dependence of the weighted profile agreement factor, R_{wp} , of the two models is shown in Fig. 6.3(b) and clearly implicates the tetragonal model as preferred at low temperature, but not at high temperature, above around 230-250 K, which is close to the literature-reported MIT temperature 260 K [209].

We investigate the behavior of the local structure by performing a PDF structural refinement of the x-ray total scattering PDF data from 90 K to 500 K. Fits were carried out over the data ranges of $1.5 < r < 4 \text{ \AA}$ and $1.5 < r < 10 \text{ \AA}$ and the results are qualitatively the same. A representative fit, again of the tetragonal model to the 100 K dataset, is shown in Fig. 6.3(c). This time the temperature dependence of the goodness-of-fit parameter, R_w , of the tetragonal and cubic models (Fig. 6.3(d)) indicates that the tetragonal model always fits

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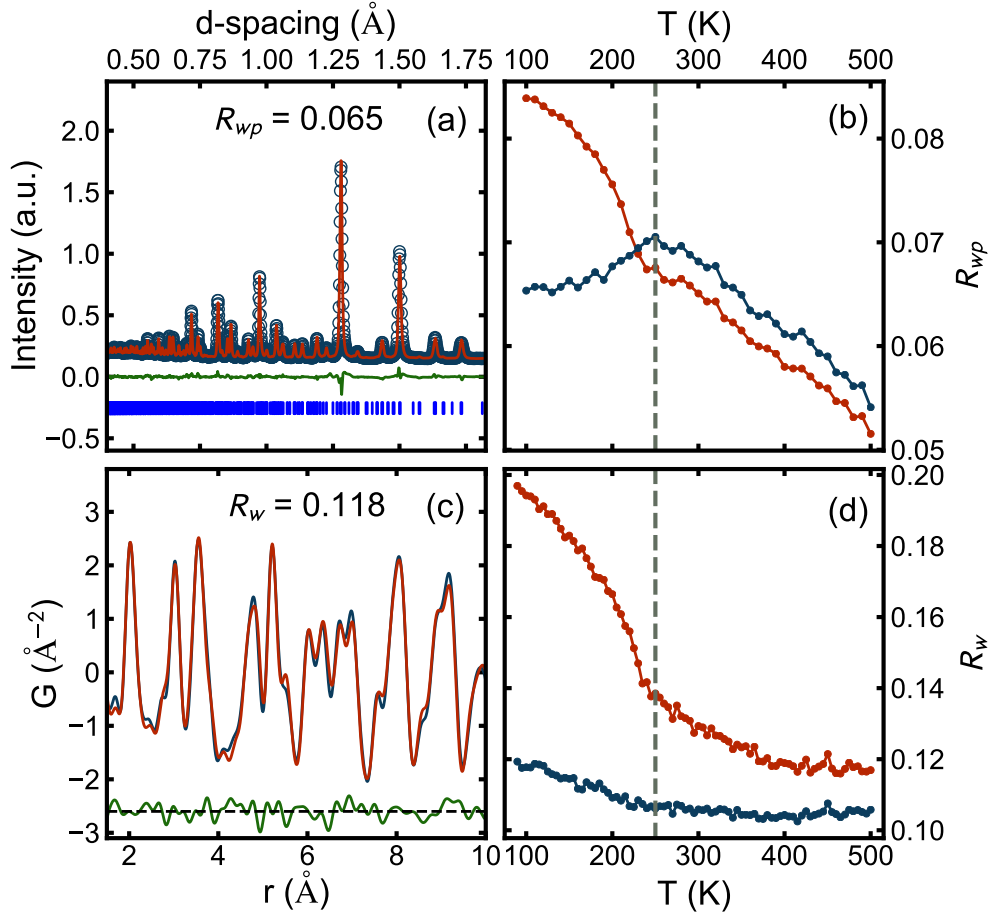


Figure 6.3: (a) The neutron 100 K powder diffraction pattern (blue) collected using $2\theta = 120^\circ$ detector bank fit by tetragonal MgTi₂O₄ model (red) with difference curve (green) offset below. (b) The resulting neutron Rietveld refinement weighted profile agreement factor R_{wp} values versus temperature on neutron TOF Bragg data using tetragonal (blue) and cubic (red) MgTi₂O₄ models from 100 K to 500 K (120° detector bank data). (c) The x-ray PDF of 100 K data (blue) fit by tetragonal model (red) over the range of $1.5 < r < 10$ Å. The difference curve (green) is shown offset below. (d) The resulting x-ray PDF refinement goodness-of-fit parameter R_w values versus temperature on x-ray data using tetragonal (blue) and cubic (red) MgTi₂O₄ models from 90 K to 500 K over the range of $1.5 < r < 10$ Å. The vertical grey dashed line at 250 K indicates the MIT temperature.

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Table 6.3: The Rietveld refinement results of tetragonal and cubic MgTi_2O_4 models fit to the neutron TOF powder diffraction patterns at 100 K and 500 K, respectively. The models are introduced in detail in Section 6.2. Here, R_{wp} is the weighted profile agreement factor; x , y and z are the refinable atomic positions in fractional coordinates; U_{iso} , in units of ($\text{\AA}^2$), is the isotropic atomic displacement parameter (ADP).

Parameter	Model (Temperature)	
	tetragonal (100 K)	cubic (500 K)
R_{wp}	0.065 34	0.051 54
a ($\text{\AA}$)	6.011 97	8.508 33
c ($\text{\AA}$)	8.469 56	-
$c/\sqrt{2}a$	0.996 16	1.0
Mg x	0.7449	-
Ti (x,y,z)	(-0.0112,0.2451,-0.1414)	-
O1 (x,y,z)	(0.4795,0.2480,0.1182)	(0.2595,0.2595,0.2595)
O2 (x,y,z)	(0.2410,0.0219,0.8805)	-
Mg U_{iso} ($\text{\AA}^2$)	0.0063	0.0110
Ti U_{iso} ($\text{\AA}^2$)	0.0093	0.0191
O U_{iso} ($\text{\AA}^2$)	0.0042	0.0071

the local structure better than the cubic model, at all temperatures. In the local structure the tetragonal distortion is always evident. It is noteworthy that the temperature trend of R_w of the cubic model, which reveals the presence of the local distortions above the MIT, is reminiscent of the reported temperature trend of MgTi_2O_4 resistivity [209].

To see visually in the PDF how the cubic model fails, we can consider the low- and high-temperature PDFs and fits with the cubic and tetragonal models, shown in Fig. 6.4. The low temperature PDFs (below the MIT) are shown in the top row ((a) and (b)) and the high temperature (above the MIT) in the lower row ((c) and (d)). The tetragonal model fit is shown in the first column ((a) and (c)) and the cubic fit is shown in the second column ((b) and (d)). At low temperature, as expected, the tetragonal model (Fig. 6.4(a)) fits much better than the cubic model (Fig. 6.4(b)). At 300 K we have already established that the

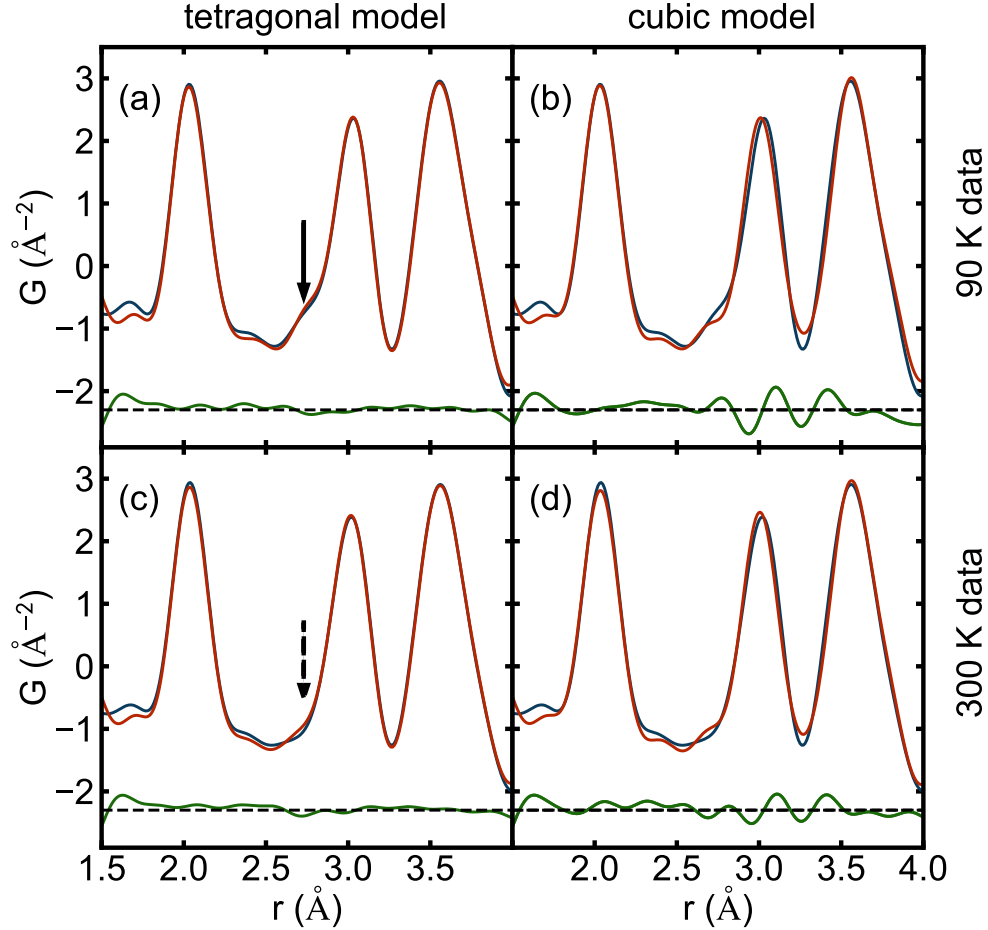


Figure 6.4: (a-d) The x-ray PDF data (blue) collected at the XPD beamline at (a,b) 90 K and (c,d) 300 K fit by (a,c) tetragonal and (b,d) cubic models (red) over the range of $1.5 < r < 4$ Å. The difference curves (green) are shown offset below. (e) The resulting PDF refinement goodness-of-fit R_w values versus temperature on x-ray data using cubic (red) and tetragonal (blue) MgTi_2O_4 models over the range of $1.5 < r < 4$ Å. The Ti-Ti dimer is observed in the 90 K data (marked by the solid arrow) but not present in the 300 K data (dashed arrow).

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global structure is cubic; however, again we see that in these local structural fits the tetragonal model (Fig. 6.4(c)) is superior to that of the cubic model (Fig. 6.4(d)), with smaller oscillations in the difference curve. To emphasize our argument, we note that the difference curves are similar when data collected at distinct temperatures are fit using identical symmetry constraints. Specifically, careful inspection of the difference curves in Fig. 6.4(b) and (d) reveals that the positions of residual maxima and minima are nearly identical, although their amplitudes are smaller in Fig. 6.4(d). Since this difference signal represents the inability of the cubic model to fit the data, it is further support to the idea that a similar tetragonally distorted structure is present in the low- r region at 90 K and at 300 K, but smaller in amplitude at 300 K. To validate that the results are reproducible, Fig. 6.4 represents x-ray PDF data collected at the XPD beamline, whereas data collected from the PDF beamline is shown in Fig. 6.5, and reproduces the same result as discussed above.

In the cubic MgTi_2O_4 structure unit cell, all six Ti-Ti bonds have the same length, 3.008 Å, whereas in the tetragonal MgTi_2O_4 model, one of the six Ti-Ti distances is shortened (2.853 Å), forming dimers, and one Ti-Ti bond is longer (3.157 Å) [518]. From the analysis of the average structure it was understood that the MIT was accompanied by the formation of Ti-Ti structural dimers. Above we showed the observation from the PDF of local tetragonality at high temperature which may indicate that local dimers survive above the MIT. This would seem to be in qualitative agreement with a prior observation from a neutron PDF study that reported the persistence of Ti-Ti dimers up to high temperature [512]. In this picture the dimers survive locally but become disordered at the transition where the structure becomes globally cubic on warming.

However, our PDF analysis clearly shows that the large amplitude structural dimers actually do disappear at the MIT, as described below, and that the local tetragonality that we observe at high temperature in the PDF has a more subtle origin as we discuss in greater

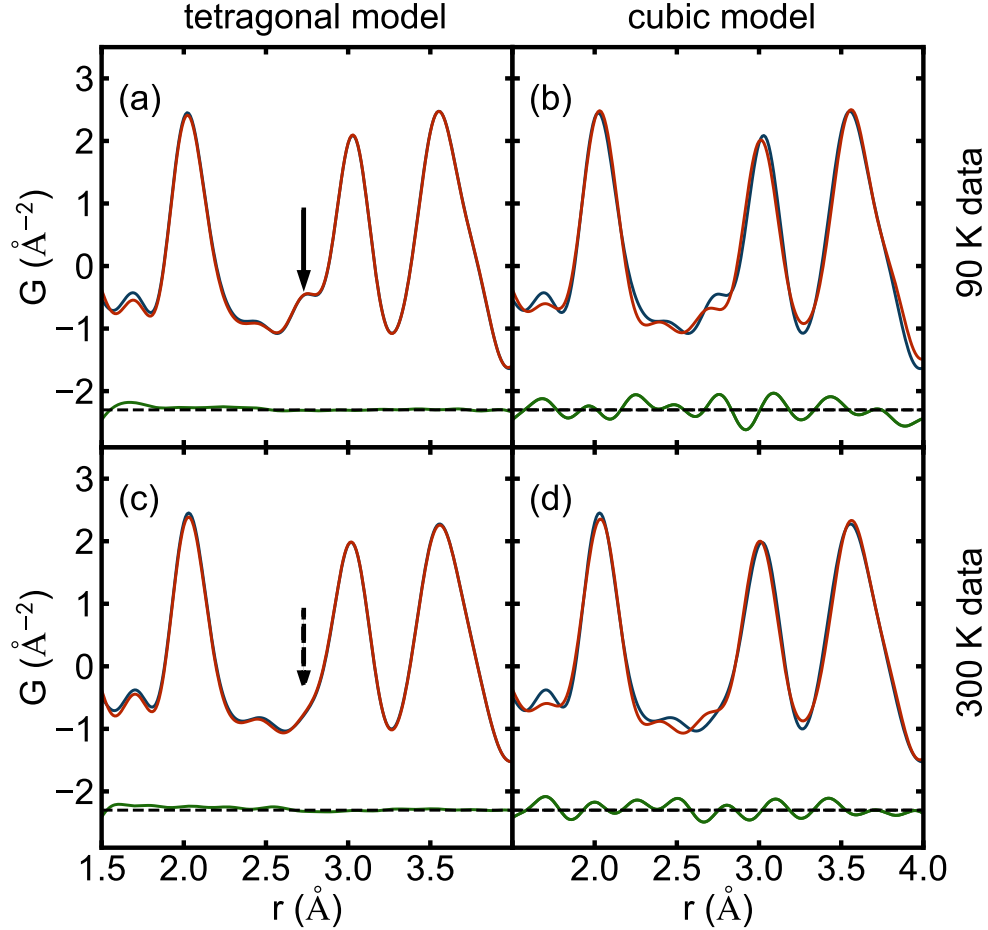


Figure 6.5: (a-d) The x-ray PDFs collected at the PDF beamline of (a,b) 90 K and (c,d) 300 K data (blue) fit by (a,c) tetragonal and (b,d) cubic models (red) over the range of $1.5 < r < 4$ Å. The difference curves (green) are shown offset below. (e) The resulting PDF refinement goodness-of-fit R_w values versus temperature on x-ray data using cubic (red) and tetragonal (blue) MgTi_2O_4 models over the range of $1.5 < r < 4$ Å. The Ti-Ti dimer is observed in the 90 K data (marked by the solid arrow) but not present in the 300 K data (dashed arrow)

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detail in the discussion section. To establish the disappearance of the structural dimers at the phase transition we simulated x-ray PDFs of the cubic (no dimers) and tetragonal (dimers) models. These are plotted as the red and blue curves, respectively, in Fig. 6.6 (a). A number of the PDF peaks are affected on the transition through the MIT, with the largest change observed on the peak at around 3.0 Å which contains the shortest Ti-Ti distances. Based on the change in crystal structure, the expected change in the PDF results in the characteristic M-shaped signature in the difference curve seen in Fig. 6.6 (a) which comes from the disappearance of the long and short Ti-Ti bonds associated with the dimer, leaving all the Ti-Ti distances the same. This can be compared to the difference in the measured PDF data as MgTi_2O_4 crosses the MIT, shown in Fig. 6.6(c) at 300 K (red) and 100 K (blue). First, we see a significant change in the relevant 3.0 Å peak when moving through the MIT. This change is inconsistent with the conclusion from the previous neutron PDF study that the dimers are retained, unaltered, to high temperature in the local structure [512], necessitating an order-disorder scenario in which the local structure across the transition is unchanged, with small or no change in the PDF. Instead we see a significant change in the x-ray PDF at the phase transition, with PDF intensity moving from the short r position towards that of the average Ti-Ti distance, as indicated by the grey circle in Fig. 6.6(c).

It is clear from careful inspection that the observed and simulated difference curves across the transition (Fig. 6.6(c) and (a), respectively) are significantly different. PDF peak intensity redistribution associated with the dimer removal is seen in the differential curve as a transfer of intensity from 2.71 Å to 2.89 Å, i.e., on the low- r side of the average Ti-Ti distance at 3.01 Å marked by the vertical dashed line in the figure. This implies that the very short Ti-Ti ion dimers disappear at the phase transition, but the associated PDF intensity is shifted to a position that is still shorter than that of the average Ti-Ti distance: shortened Ti-Ti contacts in fact do exist at high temperature above the MIT but they are not the

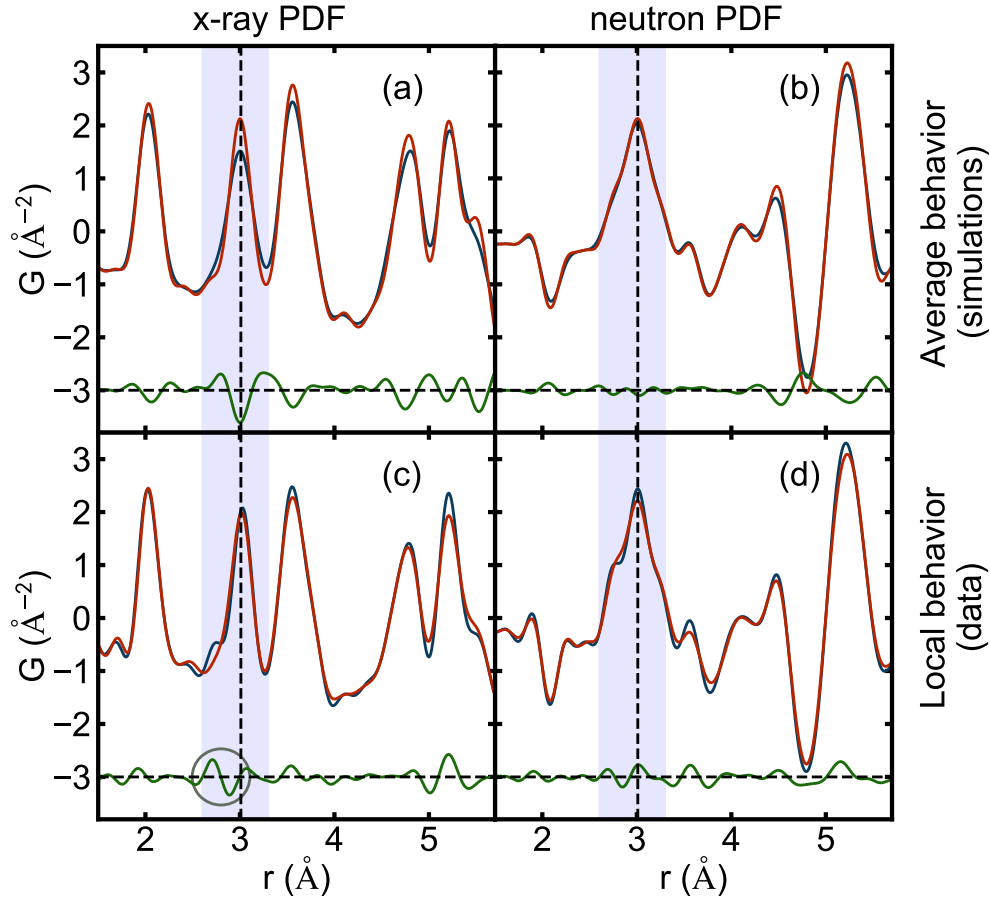


Figure 6.6: (a,b): The simulated (a) x-ray and (b) neutron PDFs of tetragonal (blue) and cubic (red) MgTi_2O_4 models in the low- r region. All atoms use the same isotropic atomic displacement parameter $U_{iso} = 0.005 \text{ \AA}^2$. Q_{max} , Q_{damp} and Q_{broad} are set as the same values as the experimental PDFs. The difference curves (tetragonal model simulation minus cubic model simulation) are shown offset below. The nearest Ti-Ti bonds are highlighted in the blue vertical span region. (c,d): The experimental (c) x-ray and (d) neutron PDFs from MgTi_2O_4 collected at 100 K (blue) and 300 K (red). The difference curves (100 K data minus 300 K data) are shown offset below in green. The vertical dashed lines at $r = 3.01 \text{ \AA}$ represent the length of the undistorted Ti-Ti bond length in the average cubic model.

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original spin singlet dimers. We draw a distinction between these Ti-Ti contacts and the very short dimer contacts as they are observably different. Our results are consistent with the disappearance of dimers at the phase transition on warming, but a persistence of a local tetragonality, smaller in magnitude than that associated with the the dimer phase.

This behavior is shown on an expanded scale in Fig. 6.7(b) where PDFs measured at multiple temperatures are compared, focusing on the 3 Å peak.

The feature in the difference curve that shows the shift of the intensity associated with the Ti-Ti short bonds from 2.71 Å to the longer position (2.89 Å) is shown below shaded green (for the loss of short bonds) and purple (for the gain in longer bonds). This result is qualitatively supported by the PDF structural modeling over the range of $1.5 < r < 10$ Å, shown in Fig. 6.7(e) and (f), where the short Ti-Ti bond shifts from 2.83 Å to 2.88 Å over the same temperature range, but never converges to the average cubic value of 3.01 Å at 300 K.

The full temperature dependence of the dimer disappearance may then be extracted by integrating the shaded regions in the difference curve and is shown in Fig. 6.7(c), where we plot the integrated area shown shaded in green in the difference curve vs. temperature. In this case the difference is always taken with respect to the 500 K dataset. The intensity decreases gradually until around 200 K, where it rapidly falls off. The rate of fall-off in this intensity then slows again above 250 K. There are two principal contributions to the differential signal below the transition: the changes in the local structure and the thermal broadening effects. Thermal broadening effects in the differential are gradual and typically small, particularly from one data point to the next corresponding to the trends observed below ~ 200 K and above ~ 250 K. On the other hand, the signal in the differential coming from the dimers is considerably larger, roughly proportional to the big step seen at the transition, and dissipates rapidly as the temperature passes through the MIT range. This is

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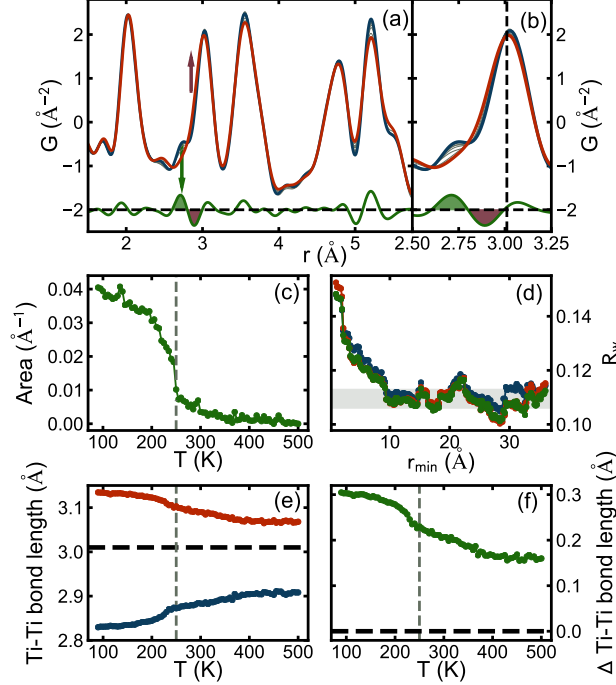


Figure 6.7: (a) PDFs measured as a function of temperature from 90 K (blue) to 300 K (red) in the low- r region. The intermediate data-sets are plotted in grey. The vertical green arrow at $r = 2.71 \text{\AA}$ and the purple arrow at $2.89 \text{\AA}$ represent how the position of the Ti-Ti short bond changes on warming. The difference curve shown offset below is that between the 90 K dataset subtracting the 300 K dataset. The positive/negative feature between $2.6 < r < 3.0 \text{\AA}$ indicates that intensity in the PDF at $2.71 \text{\AA}$ at low temperature is shifting to the position $2.89 \text{\AA}$ at high temperature. (b) Re-plot of (a) over an expanded r -range. The vertical dashed line at $r = 3.01 \text{\AA}$ represents the length of the undistorted Ti-Ti bond length in the cubic average structure. (c) The temperature dependence of the integrated area in the difference curve shown shaded green. The vertical grey dashed line at 250 K indicates the MIT temperature. (d) The x-ray PDF refinement goodness-of-fit R_w values versus a variable $r_{\min}$ (for an $r_{\max}$ set equal to $50 \text{\AA}$) when fitting a cubic MgTi_2O_4 model to 300 K (blue), 400 K (green), and 500 K (red) data. In each refinement $r_{\min}$ was allowed to vary from $1 \leq r_{\min} \leq 36 \text{\AA}$ in $0.2 \text{\AA}$ r -steps. The fits with the high $r_{\min}$ yield the behavior of the average structure. The fits with the low $r_{\min}$ are weighted by the local structural signal. (e, f) The temperature dependence of the short (blue) and long (red) Ti-Ti bond lengths, and their differences (green) from PDF structural modeling using the tetragonal structure over the range of $1.5 < r < 10 \text{\AA}$. The horizontal dashed line represents the length of the undistorted Ti-Ti bond length in the cubic average structure. The vertical grey dashed line at 250 K indicates the MIT temperature.

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a model-independent way of observing how the local dimer disappears on warming.

We may seek an explanation for why we see the dimers disappear at the transition from our x-ray PDF measurements, whereas this was not evident in the earlier neutron PDF study [512]. Observing the local Ti dimer is complicated in the neutron case by the relatively weak and negative neutron scattering length of titanium, and an appreciable overlap of titanium contributions with strong oxygen contributions. To show this, we perform the same comparison that we just made for the x-ray PDFs, but on neutron data. The neutron simulations are shown in Fig. 6.6(b) and the neutron experimental PDFs in Fig. 6.6(d). It is clear that the signals in the difference curve, both for the simulations based on the average structure and the data PDFs themselves, are much smaller than for the x-ray case. This is because the most important signal in MgTi_2O_4 is coming from the Ti ions that are relatively strong scatterers in the x-ray case but not in the neutron measurement. Specifically, in the x-ray case, Ti scatters 2.75 times stronger than O and 1.8 times stronger than Mg, whereas for neutrons the scattering of Ti is 1.7 times weaker than that of O and 1.6 times weaker than that of Mg. In addition, the neutron PDF intensity in the range of interest is dominated by the contributions from O-O pairs constituting TiO_6 octahedra, evidenced in the data as the additional shoulder intensity features around the 3 Å peak (Fig. 6.6(d)), as compared to the x-ray case where such features are largely absent (Fig. 6.6(c)). This may explain the different interpretation in the earlier neutron PDF study [512]. However, the x-ray data unambiguously show the disappearance of the full-amplitude spin singlet Ti-Ti dimers.

This behavior, where sizable distortions associated with ordered spin singlet dimers evolve into smaller local distortions with spin singlets disassembled, is reminiscent of that observed in the CuIr_2S_4 system. In that case a local symmetry broken orbital-degeneracy-lifted (ODL) state was observed up to the highest temperatures studied [215]. On cooling these local distortions of broken symmetry ordered into a long-range orbitally ordered (LROO) state.

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Only below the LROO transition did charges disproportionate, forming a charge density wave accompanied by a Peierls distortion and the formation of Ir-Ir dimers with very short Ir-Ir bonds. We believe our observations in MgTi_2O_4 suggest a similar kind of ODL behavior, which we explore to a greater extent below, though different in detail because of the different charge filling.

As discussed above, we can rule out that the local structure is changing in the same way as the average structure. The *expected* changes in the PDF at low- r due to average structure changes at the MIT make all the low- r peaks sharper for $T > T_{MIT}$, as shown in Fig. 6.6(a). However, the data do not show this (Fig. 6.6(c)). There is a small change in the local structure, evidenced by the feature in the difference curve around 2.9 Å, indicated by the grey circle in Fig. 6.6(c), but it is smaller than the average structure change at the MIT. As discussed above, the short Ti-Ti dimers ($r = 2.71$ Å shoulder) go away on warming by a shift to a longer bond (around $r = 2.89$ Å), but this “longer” bond is still shorter than the average 3.01 Å Ti-Ti bond distance expected from the cubic average model. These two behaviors exactly mimic the ODL state found in CuIr_2S_4 [215].

As is evident in Fig. 6.3(d), the tetragonal model fits the local structure better than the cubic model at all temperatures all the way to 500 K, the highest measurement temperature. As in CuIr_2S_4 [215] the dimers disappear at the MIT transition on warming, but the local symmetry broken state with, presumably, fluctuating short Ti-Ti bonds is present to high temperature, closely mimicking the ODL behavior in CuIr_2S_4 .

It is of interest to explore whether the fluctuating short Ti-Ti bonds at temperature above the MIT correlate with each other and how this varies with temperature. To extract the correlation length of the local fluctuating symmetry broken states, r_{min} -dependent PDF fits (see Section 6.2) were performed on selected high-temperature datasets (300 K, 400 K, and 500 K). When r_{min} is large the fit is over just the high- r region of the PDF and will

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retrieve the average structure and the cubic fit will be good. As r_{min} extends to lower values, progressively more of the local structure that has a tetragonal distortion is included in the fit and the agreement of the cubic model becomes degraded. The resulting $R_w(r_{min})$ is shown in Fig. 6.7(d). The cubic fits are good over the entire region, $r_{min} > 10 \text{ \AA}$, with very little variation in R_w indicated by the horizontal gray band in the figure, but rapidly degrade below this length-scale. This suggests that the symmetry broken local distortions have a correlation length of around 1 nm but that this correlation length does not vary significantly in the temperature range above 300 K. This agrees well with the previously reported length-scale of local tetragonality based on neutron PDF analysis [512].

6.4 Discussions

To rationalize the experimental observations, informative insights can be gained from the parallels and differences drawn between CuIr_2S_4 and MgTi_2O_4 . As mentioned earlier, common to both systems is that they have orbitally ordered band-insulator ground states featuring spin singlet dimerization resulting in the loss of magnetization below the MIT, and that they become poor Pauli-paramagnetic metals in the high-temperature regime despite the high cubic crystallographic symmetry. In the local structure at low temperatures, both systems exhibit short covalent contacts between the pairs of spin singlet dimerized transition metal ions, which evolve into longer contacts upon heating through the respective MITs, but in a manner where the local symmetry remains broken relative to the global cubic symmetry. The driving force behind the high-temperature local symmetry breaking in CuIr_2S_4 was shown to be of electronic origin involving orbital degeneracy lifting [215]. Significantly, the isostructural and isoelectronic sister compound, CuIr_2Se_4 , remains metallic down to the lowest temperature and does not show local symmetry breaking orbital-degeneracy-lifted

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(ODL) effects. This suggests that the ODL state is a prerequisite for the MIT [215] in these spinels. Here we argue that also in MgTi_2O_4 local ODL effects are present and produce the local symmetry breaking in the high-temperature region that we report here. By analogy with CuIr_2S_4 , they are also presumably precursor states to the spin singlet dimerization and MIT on cooling.

The long range patterns of ordered spin singlet dimers differ in detail in the two systems, being octamers in CuIr_2S_4 [204] and helices in MgTi_2O_4 [211], and are presumably dictated by delicate energetics [519; 520]. Although quite intriguing, these intricate aspects of long range order are not of a concern here. Of prime interest is the internal dimer structure, the relationship between the dimer state and the ODL state, and the perceived electron-hole symmetry that links the two systems [207]. In what follows we first review the ODL state and the dimerization mechanism within the local picture of CuIr_2S_4 , summarized in Fig. 6.8. We then utilize the analogies between the two systems to put forward a scenario portraying the high-temperature state and the dimerization mechanism in MgTi_2O_4 , illustrated in Fig. 6.9.

In CuIr_2S_4 the dimers involve two Ir^{4+} ions in $5d^5$ configuration, and while the dimerization can be perceived as pairing of electrons, $\text{Ir}^{4+}\text{-Ir}^{4+}$ dimers actually have hole character [215]. This subtlety and its significance will become more transparent as the dimerization mechanism and the electron-hole symmetry of the two systems are further discussed. In the localized electron picture the ODL state is based on the molecular orbital (MO) concepts. In this, two neighboring transition metal ions with partially filled degenerate orbitals form a MO state with shared electrons (holes) such as to lift the degeneracy and lower the system energy. In the high-temperature regime of CuIr_2S_4 iridium nominally has a half-integer valence ($3.5+$) which is provided by monovalent Cu [201; 521]. This means that each $\text{Ir}^{3.5+}$ on the pyrochlore sublattice is in a nominal $5d^{5.5}$ state corresponding to half a hole (and 5.5 electrons) per three degenerate t_{2g} orbitals (Fig. 6.8(a),

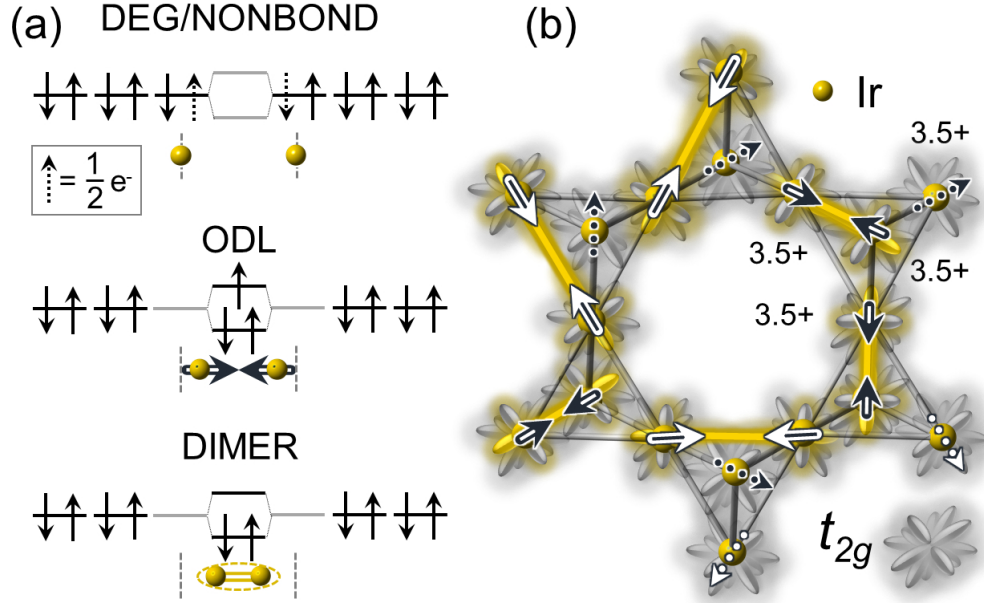


Figure 6.8: The recapitulation of the ODL mechanism in the CuIr_2S_4 thiospinel: (a) The energy diagram sketch of atomic and molecular orbitals for nearest Ir atom pairs in various situations: degenerate/nonbonding (DEG/NONBOND, top), orbital degeneracy lifted (ODL, middle), and spin singlet dimer (DIMER, bottom). Horizontal arrows indicate the ODL displacements. (b) The ODL state in CuIr_2S_4 in the t_{2g} orbital manifold representation on a segment of pyrochlore sublattice. The ODL active t_{2g} orbitals are shown in yellow and passive orbitals are shown in gray. Each Ir atom participates in exactly one ODL state. The ODL states are randomly placed following principles discussed in the text. The arrows denote the displacements of Ir associated with the ODL states and provide mapping onto the “two-in-two-out” ice rules. The white arrows represent in-plane displacements, whereas the blue arrows represent displacements with an out-of-plane component. The dotted arrows mark the displacements associated with the ODL states occurring in the neighboring tetrahedra which are not represented in the displayed structural segment.

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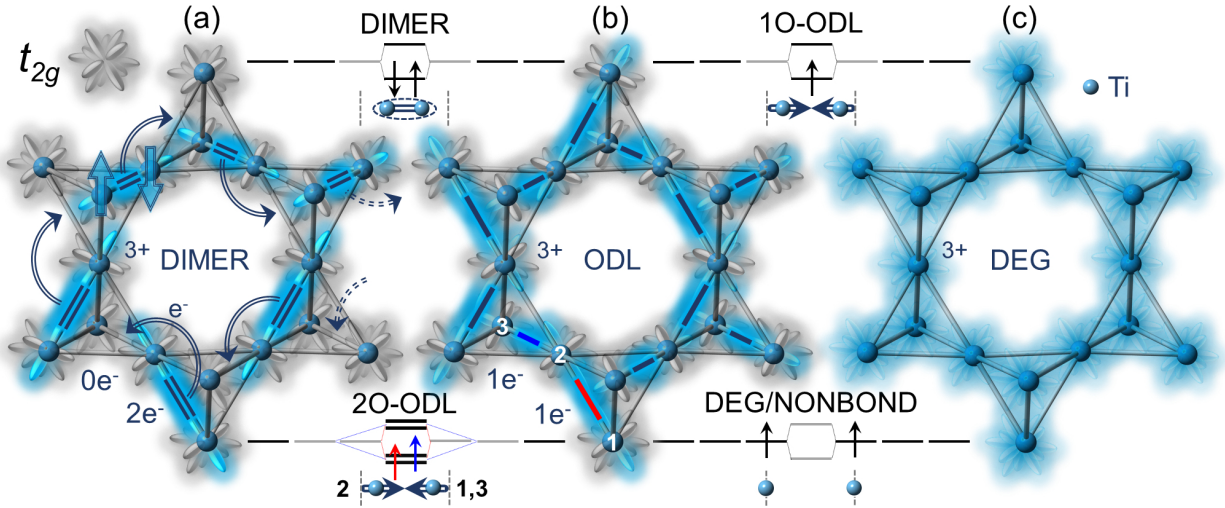


Figure 6.9: The Ti t_{2g} orbital manifold on a pyrochlore sublattice of the MgTi_2O_4 spinel: (a) Spin-singlet dimerized lattice within the tetragonal model; (b) ODL lattice within the tetragonal model; (c) Lattice of degenerate t_{2g} orbitals as portrayed by the cubic model. The charge state of all Ti in all models is +3. Electron density in t_{2g} orbitals is indicated by color (gray is empty) and its distribution is proportional to the blue color intensity. The Ti dimers in (a) are indicated by the double blue lines, while a pair of antiferromagnetically coupled block arrows on an exemplar dimer denotes its spin singlet character. Note that all Ti atoms are involved in dimerization but only dimers contained in a section of one structural slab are indicated in (a). Out of all Ti-Ti contacts dimerized contacts have a nominal bond charge of $2e^-$, whereas the other contacts carry no net charge in this picture. The ODL states in (b) are indicated by the single blue lines. Arc arrows in (a) denote bond charge transfer as the spin singlet dimers convert to the ODL states, according to the model discussed in the text. The insets between the panels provide the energy diagram sketch of atomic and molecular orbitals for nearest Ti atom pairs in various situations: degenerate/nonbonding (DEG/NONBOND, bottom right), spin singlet dimer (DIMER, top left), one-orbital ODL (1O-ODL, top right) and two-orbital ODL (2O-ODL, bottom left). Note that the 2O-ODL state refers to two orbitals of the same Ti (e.g. one labelled “2”) that are engaged in two 1O-ODL states with two *different* Ti neighbors (e.g. these labelled “1” and “3”). Differently colored spins and lines denoting ODL contacts indicate this two-component aspect in the schematics for 2O-ODL. The local spin arrangement shown is for illustration purposes only and does not represent an experimentally established alignment.

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top), of xy , yz , and zx variety. The sublattice geometry fosters direct overlaps of orbitals from the t_{2g} manifolds (see Fig. 6.8(b)), which, in turn, allow neighboring Ir pairs to form a bound state sharing a single hole in the antibonding branch of degeneracy lifted MO [215], as sketched in the energy diagram shown in the middle panel of Fig. 6.8(a).

Importantly, for any choice of two neighboring Ir on a pyrochlore lattice only one type out of three t_{2g} orbital varieties are overlapped (e.g. xy with xy , etc.) along the Ir_4 tetrahedral edges of the pyrochlore lattice, which brings the directionality aspect to the picture. Due to the specifics of filling (0.5 hole/Ir) each Ir participates in exactly one such paired state at the time. Here we call this one-orbital ODL (1O-ODL) state as each participating Ir contributes just one of its orbitals (e.g. xy) to form MO constituting the state. The ODL state is hence comprised of two atomic orbitals, one from each Ir in the pair, with on average 1.5 electrons (0.5 hole) contribution per Ir, resulting in MO with 3 electrons and one hole, as shown in Fig. 6.8(a). Two electrons are in the bonding branch, and one electron (and one hole) in the antibonding MO [215] with a net spin of 1/2. This configuration results in the observed contraction, illustrated by block arrows in the figure, of the Ir-Ir separation in the local structure as compared to undistorted separation expected if orbital degeneracy is retained.

Since each iridium has 6 Ir neighbors to pair with, the ODL state fluctuates spatially and, presumably, temporally between (xy, xy) , (yz, yz) , and (zx, zx) variants, which results in an undistorted cubic structure on average [215]. One such configuration is illustrated in Fig. 6.8(b), with strong short range correlations governed by the “one ODL state per Ir” and the Coulomb bond charge repulsion principles, resulting in a single ODL state per Ir_4 tetrahedron. Pursuant to this, the ODL state in CuIr_2S_4 follows the “two-in-two-out” ice rules [522] which will be addressed later.

In this localized picture the ODL state is also a precursor for the spin singlet dimer. The

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dimer state is attained by removing an excess electron from the antibonding MO of the ODL state, thus stabilizing the bond, as shown in the bottom panel of Fig. 6.8(a). The process involves charge transfer between two ODL $\text{Ir}^{3.5+}\text{-Ir}^{3.5+}$ pairs, one of which becomes dimerized $\text{Ir}^{4+}\text{-Ir}^{4+}$ by losing an electron (or gaining a hole, hence hole dimer) and the other becomes non-ODL (and non-dimer) $\text{Ir}^{3+}\text{-Ir}^{3+}$ by gaining an electron ($d^6\text{-}d^6$ configuration). The latter pair can be visualized by considering the state shown in the top panel of Fig. 6.8(a) but with no holes in the t_{2g} manifold. While adding a hole to antibonding branch of the ODL state stabilizes the dimer bond, adding an electron disassembles the ODL state. Importantly, this process also provides the disproportionation of site charge, as two identical Ir with 3.5+ nominal charge convert into a (3+, 4+) pair of distinct Ir sites, which then ultimately orders in CuIr_2S_4 below MIT. This site charge disproportionation accounts for only 50 % of all Ir sites, these of the 4+ kind, dimerizing in CuIr_2S_4 .

Prior to pursuing the analogy between CuIr_2S_4 and MgTi_2O_4 , we appraise the two systems from the perspective of a regime under which the ODL state can form in a transition metal system [215]. The criteria that need to be fulfilled can be formulated as follows: (i) *filling* – the transition metal in the system possesses partially filled d orbitals, (ii) *symmetry* – the high crystallographic point symmetry of the system imposes the perceived orbital degeneracy, and (iii) *topology* – the structural topology promotes adequate orbital overlaps. In practice, materialization of the ODL state could further be impacted by the existence of other competing degeneracy lifting channels that may be available to the system, such as the relativistic spin orbit coupling (SOC), the effects of crystal field, etc. Eventually, formation of the ODL local broken symmetry state is accompanied by associated local structure distortion. In CuIr_2S_4 , a robust structural fingerprint of the ODL state has been observed in the local structure despite significant SOC expected on the basis of extended spatial character of Ir $5d$ orbitals [215]. In MgTi_2O_4 the SOC tendencies are suppressed as compared

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to CuIr_2S_4 , while appreciable local distortions similar to these seen in CuIr_2S_4 are evident in the PDF data above the transition. Both CuIr_2S_4 and MgTi_2O_4 systems meet the criteria: partial filling (Ir is $5d^{5.5}$ and Ti is $3d^1$), degeneracy-promoting high-symmetry structure (cubic spinel structure imposes 3-fold degeneracy of the t_{2g} manifolds in both materials), and favorable structural topology (edge shared IrS_6 and TiO_6 octahedra fostering direct t_{2g} overlap). In both systems short nearest neighbor transition metal contacts are observed in the high-temperature metallic regime, that are distinct from the very short spin singlet dimer bonds observed in the insulating state at low temperature.

We now turn to the case of MgTi_2O_4 , which is convenient to discuss in the reversed order, starting from the local view of spin singlet dimers. Dimerization in MgTi_2O_4 depicted using Ti t_{2g} manifold representation is shown in Fig. 6.9(a), overlaying a fragment of pyrochlore sublattice as seen in the $P4_12_12$ model. In contrast to CuIr_2S_4 , in MgTi_2O_4 the dimers involve two Ti^{3+} in the $3d^1$ configuration with a single electron in the t_{2g} manifold; hence Ti^{3+} - Ti^{3+} dimers inevitably have electron character by construction. These result in short Ti-Ti dimerized contacts observed in the tetragonal structure at low temperature. Each dimer carries $2e^-$ of net charge. Since each Ti participates in a dimer and since there is exactly one dimer per Ti_4 tetrahedron [519; 512], nominal charge count results in $1e^-/\text{Ti}$ site. This is consistent with no CO being observed experimentally in MgTi_2O_4 , in contrast to CuIr_2S_4 , implying that all Ti sites are equivalent in this regard [211]. From the average structure perspective and in the localized picture, supported by the experimentally observed paramagnetism and poor metallic conduction, above the MIT the dimers could be seen to disassemble in such a way as to statistically distribute $1e^-$ of charge evenly across the three degenerate t_{2g} orbitals resulting in cubic structure with all Ti-Ti nearest neighbor contacts equivalent, as schematically presented in Fig. 6.9(c). This implies that, despite nominal charge equivalence of all Ti sites and no site CO observed, some charge transfer, presumably

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involving bond charge, still has to take place at the transition. This then inevitably implies that the ground state has to involve the bond charge order which coincides with, and is hence indistinguishable from, the observed dimer order in the diffraction measurements.

The implication of charge being equally distributed across the triply degenerate t_{2g} manifold of Ti in a manner depicted in Fig. 6.9(c), presented also in an associated energy diagram (bottom right inset of the Figure), would be that the pyrochlore sublattice is comprised of regular Ti_4 tetrahedra with equidistant Ti-Ti contacts corresponding to equal bond charge, as described within the cubic spinel model. However, this is not what is observed experimentally. The observations based on the PDF analyses clearly demonstrate that the pyrochlore sublattice is comprised of locally distorted Ti_4 tetrahedra with a distribution of distances, suggesting that the bond charge remains inequivalent above the MIT. One possibility is that the dimers indeed persist in the metallic regime, as hinted at in the earlier neutron study [512]. However, such interpretation would be inconsistent with paramagnetic behavior observed in magnetization measurements of MgTi_2O_4 above the MIT. It would further be inconsistent with the elongation of the short Ti-Ti dimer contacts evidenced in our x-ray PDF analysis, which implies the disappearance of spin singlet dimers at MIT even locally. In analogy with CuIr_2S_4 , it is plausible that the dimer state gets replaced locally by an ODL-type state in the high-temperature metallic phase. Observation of heterogeneous local Ti-Ti contacts corresponding to inequivalent bond charge is consistent with there being an ODL-like state in MgTi_2O_4 . Since the local structures at high temperature and in the ground state are distinct, the MIT in MgTi_2O_4 cannot be assigned to a trivial order-disorder type.

Importantly, as careful assessment shows, the ODL state in MgTi_2O_4 cannot be exactly mapped onto the ODL state seen in CuIr_2S_4 , since the charge filling is different in the two systems ($1 e^-/\text{Ti}$ in MgTi_2O_4 and $0.5 \text{ hole}/\text{Ir}$ in CuIr_2S_4). In the latter case two Ir neighbors can reduce the energy of the system by forming a 1O-ODL state accommodating a common

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hole, as described in the preceding section. This results in a 3-electron state shown in the middle panel of Fig. 6.8(a). Given that the destruction of the spin singlet dimer in MgTi_2O_4 involves removal of one of the electrons from the dimer state sketched in the energy diagram in the top left inset of Fig. 6.9, consistent with destabilization and elongation of the short Ti-Ti bond, in the ODL picture the one electron left behind would indeed result in an electron-hole antipode of the 1O-ODL state seen in CuIr_2S_4 , as shown in the top right inset of Fig. 6.9. The issue arises with the placement of the extra electron from the dimer. In the case of CuIr_2S_4 , due to filling, the removal of one of the two holes constituting a dimer results in generation of two 1O-ODL states on two different pairs of Ir. There, since only 50% of Ir participates in dimerization, in terms of filling one should think of this process as a replacement of $-4+-4+-3+-3+-$ charge tetramer with a pair of $-3.5+-3.5+-$ ODL states achieved by hole redistribution. Since there is no site charge disproportionation in MgTi_2O_4 and since each Ti is involved in dimerization, the dimer density per formula unit is twice as large in MgTi_2O_4 as in CuIr_2S_4 and each Ti has to participate in two independent 1O-ODL states simultaneously. Notably, the geometry of t_{2g} orbital overlaps imposes a constraint that the two 1O-ODL states for each Ti have to be assembled with two *different* Ti neighbors, as illustrated in Fig. 6.9(a),(b). There, for example, the dimer in Fig. 6.9(a) involving Ti labeled “2” in Fig. 6.9(b) disassembles at MIT to make two 1O-ODL states, one with the Ti neighbor labeled “1” and another with the neighbor labeled “3”. This results in two short Ti-Ti contacts that are both longer than the dimer distance, but shorter than the average Ti-Ti separation in the cubic structure. We call this a two-orbital ODL state (2O-ODL) given that two atomic orbitals of a single Ti ion are utilized. Such a 2O-ODL state is hence comprised of a superposition of two 1O-ODL states of different variety (e.g. (xy, xy) and (yz, yz) , (yz, yz) and (zx, zx) , etc.) that point in different directions and lie along different edges of the pyrochlore sublattice. These ODL distances are marked as thick lines color coded

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as red and blue in Fig. 6.9(b), and the corresponding state is schematically shown on the energy diagram in the bottom left inset of the Figure, where the matching color coding of the electron spins signifies that they belong to different 1O-ODL states.

The existence of the 2O-ODL state in MgTi_2O_4 is corroborated by another experimentally observed difference between the two systems: The spatial extent of the local order associated with the metallic regime of MgTi_2O_4 is observably larger than that seen in CuIr_2S_4 [215]. The extended character of the local structural distortions associated with the 2O-ODL state in MgTi_2O_4 is expected for the following reasons. First, due to filling the two ingredient 1O-ODL prong states in the 2O-ODL super-state cannot both be of the same type (e.g. if one is (xy, xy) , the other can only be (yz, yz) or (zx, zx)) which would tend to increase local structural correlations. Second, the bond charge on different 1O-ODL bonds is of the same sign, resulting in the Coulomb repulsion which would also maximize the span of the 2O-ODL state itself. The observed local distortions over the length scale of about 1 nm, spanning approximately three Ti_4 tetrahedra [512], are therefore consistent with the presence of the 2O-ODL state in MgTi_2O_4 .

The energetic benefit of the 2O-ODL state over the local spin singlet dimer state is not apparent and remains elusive. The local 2O-ODL and disordered dimer states would both increase the system entropy and, in turn, the entropic contribution to energy would stabilize corresponding short range ordered state at elevated temperature. On the other hand, some vestigial magnetic correlations could be expected in the high-temperature ODL regime. Another possibility then is that the principal stabilization of the 2O-ODL state stems from its presumed magnetism. The character of local spin correlations within the 2O-ODL state cannot be established by the analysis carried out in this work. In the 2O-ODL diagram shown in Fig. 6.9 the two spins are arbitrarily drawn as parallel to avoid any confusion with the dimer state, but their relationship has actually not been established experimentally.

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It would therefore be of appreciable interest to explore this aspect of the 2O-ODL state by techniques sensitive to local magnetism, such as muon spin rotation (μ SR) [523] and magnetic PDF [437] which would be particularly informative in that regard.

While the PDF probe used here provides the information on instantaneous atomic structure and as such does not differentiate between static and dynamic disorder, the ODL state in these systems is expected to be dynamic. Spatiotemporal fluctuations then average out to the perceived undistorted cubic average structure as observed crystallographically. Notably, the resistivity just above the MIT in CuIr_2S_4 is about $2 \text{ m}\Omega \text{ cm}$ and linearly increasing with temperature [205], ascribed to a bipolaronic hopping mechanism [521; 206], whereas in the metallic regime of MgTi_2O_4 electric resistivity is not only substantially higher, but it decreases with increasing temperature in an insulator-like manner [209]. This stark difference in the observed electronic transport could be considered as an important indicator, albeit indirect, of the underlying difference reflecting the 1O-ODL and 2O-ODL characters of the high-temperature states in these two systems, respectively.

Although the Ir dimers in CuIr_2S_4 are strictly speaking equivalent to the Ti dimers in MgTi_2O_4 , the mechanism of their local formation from the ODL state is electron-hole symmetric and in that sense the dimers in these two systems could be considered as having a different flavor derived from their origin. Formation of dimers in CuIr_2S_4 requires transfer of holes from one half of the available population of ODL states to the other, and the ODLs receptors of a hole become dimers, accounting for only 50 % of Ir being dimerized. In contrast, the dimers in MgTi_2O_4 assemble from the ODL states by a virtue of electron transfer, where 1O-ODL states that receive electrons become dimers with all Ti participating in dimerization. While in both systems the process involves bond charge disproportionation, in CuIr_2S_4 this consequentially results in the observed site charge disproportionation and subsequent charge order, which is presumably imposed by the specifics of the filling and

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reflected in the dimer density per formula unit.

The presence of the 2O-ODL state has another important consequence for MgTi_2O_4 . Each Ti_4 tetrahedron inevitably hosts two 1O-ODL states. Due to the Coulomb repulsion of the bond charge, we would expect the two states to be placed on the opposite skew edges of each tetrahedron, although other constellations cannot be excluded. On the other hand, irrespective of the details of their distribution, multiple 1O-ODLs on one Ti_4 tetrahedron would cause distortions that are incompatible with the ice-type structural fluctuations in the MgTi_2O_4 system such as those suggested in the previous study of the local structure of MgTi_2O_4 [512]. Given that the spin singlet dimer distortion in the ground state of MgTi_2O_4 [211] follows the “two-in-two-out” ice rules [522] on each individual Ti_4 tetrahedron in the structure, the proposition that the local Ti atomic displacements have the same configuration in the cubic phase [512] presumably originates in part from the order-disorder type view of the MIT in MgTi_2O_4 that would be implicated by the survival of dimer-like distortions in the high-temperature phase. Our analysis does not support this picture. However, based on the considerations described above, CuIr_2S_4 may possibly be a better candidate for exhibiting the distortions of the “two-in-two-out” type in the disordered ODL regime, as illustrated by the mapping shown in Fig. 6.8(b). Exploring this matter further both experimentally and theoretically should provide a more detailed understanding of these systems. Single crystal diffuse scattering based methods [227; 524; 525; 228; 225] and dynamical mean-field and advanced first-principles approaches [526; 527; 528] would be particularly useful in that regard.

6.5 Conclusion

Here we applied joint x-ray and neutron pair distribution function analysis on the MgTi_2O_4 spinel, a candidate system for hosting the multi-orbital orbital-degeneracy-lifted (ODL) state, to track the evolution of its local atomic structure across its localized-to-itinerant electronic transition. Consistent with recent reports, the local structure does not agree with the average structure above the MIT temperature of 250 K and deep in the metallic cubic phase. However, in contrast to previous findings, we provide unambiguous evidence that spin singlet dimers are vanishing at the MIT. The shortest Ti-Ti distance corresponding to spin singlet dimers experiences a discontinuous elongation locally on warming through the MIT but remains shorter than that prescribed by the cubic average structure. The local distortion in the metallic regime is quantitatively and qualitatively different from that observed in association with the spin singlet state, implying that the MIT is not a trivial order-disorder type transition. The distortion characterizes the entire range of metallic temperatures assessed, and persists up to at least 500 K (about $2T_s$). The observed behavior is a fingerprint of the local symmetry broken ODL state observed in the related CuIr_2S_4 system. The correlation length of local distortions associated with the ODL state in MgTi_2O_4 is about 1 nm, which is double that seen in CuIr_2S_4 , implying two-orbital character of the ODL state. The observations exemplify that high-temperature electronic precursor states that govern emergent complex low-temperature behaviors in quantum materials can indeed have a multi-orbital degeneracy lifting character.

Bibliography

- [1] R. Sinatra, P. Deville, M. Szell, D. Wang, and A.-L. Barabási, “A century of physics,” *Nature Phys.*, vol. 11, pp. 791–796, Oct. 2015.
- [2] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, “Theory of superconductivity,” *Phys. Rev.*, vol. 108, pp. 1175–1204, Dec. 1957.
- [3] M. Tinkham, *Introduction to Superconductivity*. Mineola, NY, USA: Dover, June 2004.
- [4] N. Bogolubov, “On the theory of superfluidity,” *J. Phys.*, vol. 11, no. 1, pp. 23–32, 1947.
- [5] I. M. Khalatnikov, *An Introduction to the Theory of Superfluidity*. Boca Raton, FL, USA: CRC Press, Mar. 2018.
- [6] A. P. Ramirez, “Colossal magnetoresistance,” *J. Phys. Condens. Matter*, vol. 9, pp. 8171–8199, Sep. Purif. Technol. 1997.
- [7] E. Dagotto, *Nanoscale Phase Separation and Colossal Magnetoresistance: The Physics of Manganites and Related Compounds*. New York, NY, USA: Springer Science & Business Media, Mar. 2013.
- [8] B. Keimer and J. E. Moore, “The physics of quantum materials,” *Nature Phys.*, vol. 13, pp. 1045–1055, Nov. 2017.
- [9] D. N. Basov, R. D. Averitt, and D. Hsieh, “Towards properties on demand in quantum materials,” *Nature Mater.*, vol. 16, pp. 1077–1088, Nov. 2017.
- [10] H. Bethe, “Theorie der Beugung von Elektronen an Kristallen,” *Ann. Phys.*, vol. 392, no. 17, pp. 55–129, 1928.
- [11] A. Sommerfeld, “Zur elektronentheorie der metalle auf grund der fermischen statistik,” *Z. Phys.*, vol. 47, no. 1-2, pp. 1–32, 1928.

BIBLIOGRAPHY

- [12] F. Bloch, “Bemerkung zur elektronentheorie des ferromagnetismus und der elektrischen leitfähigkeit,” *Z. Physik*, vol. 57, pp. 545–555, July 1929.
- [13] A. H. Wilson and P. A. M. Dirac, “The theory of electronic semi-conductors,” *Proc. R. Soc. A*, vol. 133, pp. 458–491, Oct. 1931.
- [14] G. L. Pearson and W. H. Brattain, “History of semiconductor research,” *Proc. IRE*, vol. 43, pp. 1794–1806, Dec. 1955.
- [15] W. Shockley, *Electrons and Holes in Semiconductors: With Applications to Transistor Electronics*. Princeton, NJ, USA: D. Van Nostrand, 1953.
- [16] J. H. de Boer and E. J. W. Verwey, “Semi-conductors with partially and with completely filled 3d-lattice bands,” *Proc. Phys. Soc.*, vol. 49, pp. 59–71, Aug. 1937.
- [17] N. F. Mott and R. Peierls, “Discussion of the paper by de Boer and Verwey,” *Proc. Phys. Soc.*, vol. 49, pp. 72–73, Aug. 1937.
- [18] N. F. Mott, “The basis of the electron theory of metals, with special reference to the transition metals,” *Proc. Phys. Soc. A*, vol. 62, pp. 416–422, July 1949.
- [19] W. Pauli, “über den zusammenhang des abschlusses der elektronengruppen im atom mit der komplexstruktur der spektren,” *Z. Phys.*, vol. 31, no. 1, pp. 765–783, 1925.
- [20] J. C. Slater, “Magnetic effects and the Hartree-Fock equation,” *Phys. Rev.*, vol. 82, pp. 538–541, May 1951.
- [21] J. Hubbard and B. H. Flowers, “Electron correlations in narrow energy bands,” *Proc. R. Soc. A*, vol. 276, pp. 238–257, Nov. 1963.
- [22] W. F. Brinkman and T. M. Rice, “Application of Gutzwiller’s variational method to the metal-insulator transition,” *Phys. Rev. B*, vol. 2, pp. 4302–4304, Nov. 1970.
- [23] M. Imada, A. Fujimori, and Y. Tokura, “Metal-insulator transitions,” *Rev. Mod. Phys.*, vol. 70, pp. 1039–1263, Oct. 1998.
- [24] J. Zaanen, G. A. Sawatzky, and J. W. Allen, “Band gaps and electronic structure of transition-metal compounds,” *Phys. Rev. Lett.*, vol. 55, pp. 418–421, July 1985.
- [25] S. L. Moskowitz, *The advanced materials revolution: Technology and economic growth in the age of globalization*. John Wiley & Sons, May 2014.

BIBLIOGRAPHY

- [26] L. Banyai and S. W. Koch, *Semiconductor Quantum Dots*, vol. 2. Singapore: World Scientific, 1993.
- [27] F. W. Wise, “Lead salt quantum dots: The limit of strong quantum confinement,” *Acc. Chem. Res.*, vol. 33, pp. 773–780, Nov. 2000.
- [28] Y. Shirasaki, G. J. Supran, M. G. Bawendi, and V. Bulović, “Emergence of colloidal quantum-dot light-emitting technologies,” *Nat. Photonics*, vol. 7, pp. 13–23, Jan. 2013.
- [29] D. M. Newns, J. A. Misewich, C. C. Tsuei, A. Gupta, B. A. Scott, and A. Schrott, “Mott transition field effect transistor,” *Appl. Phys. Lett.*, vol. 73, pp. 780–782, Aug. 1998.
- [30] R. Fors, S. I. Khartsev, and A. M. Grishin, “Giant resistance switching in metal-insulator-manganite junctions: Evidence for Mott transition,” *Phys. Rev. B*, vol. 71, p. 045305, Jan. 2005.
- [31] A. S. Dhoot, G. M. Wang, D. Moses, and A. J. Heeger, “Voltage-induced metal-insulator transition in polythiophene field-effect transistors,” *Phys. Rev. Lett.*, vol. 96, p. 246403, June 2006.
- [32] S. Hormoz and S. Ramanathan, “Limits on vanadium oxide Mott metal-insulator transition field-effect transistors,” *Solid-State Electron.*, vol. 54, pp. 654–659, June 2010.
- [33] X. Kou, L. Pan, J. Wang, Y. Fan, E. S. Choi, W.-L. Lee, T. Nie, K. Murata, Q. Shao, S.-C. Zhang, and K. L. Wang, “Metal-to-insulator switching in quantum anomalous Hall states,” *Nat. Commun.*, vol. 6, p. 8474, Oct. 2015.
- [34] A. Druzhinin, I. Ostrovskii, and N. Liakh, “Study of piezoresistance in $\text{Ge}_x\text{Si}_{1-x}$ whiskers for sensor application,” *Mater. Sci. Semicond. Proc.*, vol. 8, pp. 193–196, Feb. 2005.
- [35] E. Strelcov, Y. Lilach, and A. Kolmakov, “Gas sensor based on metal-insulator transition in VO_2 nanowire thermistor,” *Nano Lett.*, vol. 9, pp. 2322–2326, June 2009.
- [36] J. M. Baik, M. H. Kim, C. Larson, C. T. Yavuz, G. D. Stucky, A. M. Wodtke, and M. Moskovits, “Pd-sensitized single vanadium oxide nanowires: Highly responsive hydrogen sensing based on the metal-insulator transition,” *Nano Lett.*, vol. 9, pp. 3980–3984, Dec. 2009.

BIBLIOGRAPHY

- [37] J. W. Byon, M.-B. Kim, M. H. Kim, S. Y. Kim, S. H. Lee, B. C. Lee, and J. M. Baik, “Electrothermally induced highly responsive and highly selective vanadium oxide hydrogen sensor based on metal–insulator transition,” *J. Phys. Chem. C*, vol. 116, pp. 226–230, Jan. 2012.
- [38] Z. Shao, X. Cao, H. Luo, and P. Jin, “Recent progress in the phase-transition mechanism and modulation of vanadium dioxide materials,” *NPG Asia Mater.*, vol. 10, pp. 581–605, July 2018.
- [39] F. J. Morin, “Oxides which show a metal-to-insulator transition at the Neel temperature,” *Phys. Rev. Lett.*, vol. 3, pp. 34–36, July 1959.
- [40] R. M. Wentzcovitch, W. W. Schulz, and P. B. Allen, “VO₂: Peierls or Mott-Hubbard? A view from band theory,” *Phys. Rev. Lett.*, vol. 72, pp. 3389–3392, May 1994.
- [41] M. Vojta, “Quantum phase transitions,” *Rep. Prog. Phys.*, vol. 66, pp. 2069–2110, Nov. 2003.
- [42] L. D. Landau and E. M. Lifshitz, *Chapter I-the Fundamental Principles of Statistical Physics*. Amsterdam: Elsevier, 3rd ed., 1980.
- [43] R. Peierls, *More Surprises in Theoretical Physics*. Princeton, NJ, USA: Princeton University Press, 1991.
- [44] M. Riordan and L. Hoddeson, *Crystal Fire: The Birth of the Information Age*. New York, NY, USA: WW Norton & Company, 1997.
- [45] D. W. Jorgenson, K. J. Stiroh, R. J. Gordon, and D. E. Sichel, “Raising the speed limit: US economic growth in the information age,” *Brookings Pap. Econ. Activity*, vol. 2000, no. 1, pp. 125–235, 2000.
- [46] S. Liu, H. Zhang, L. Sviridov, L. Huang, X. Liu, J. Samson, D. Akins, J. Li, and S. O’Brien, “Comprehensive dielectric performance of bismuth acceptor doped BaTiO₃ based nanocrystal thin film capacitors,” *J. Mater. Chem.*, vol. 22, no. 41, pp. 21862–21870, 2012.
- [47] L. Landau, “über die bewegung der elektronen in kristalgitter,” *Phys. Z. Sowjetunion*, vol. 3, pp. 644–645, 1933.
- [48] L. D. Landau and S. I. Pekar, “Effective mass of a polaron,” *Zh. Eksp. Theor. Fiz.*, vol. 18, no. 5, pp. 419–423, 1948.

BIBLIOGRAPHY

- [49] S. I. Pekar, “Investigations in the electron theory of crystals,” *Gostekhizdat, Moscow*, 1951.
- [50] J. Appel, “Polarons,” *Solid State Phys.*, vol. 21, pp. 193–391, Jan. 1968.
- [51] G. V. S. Rao, S. Ramdas, P. N. Mehrotra, and C. N. R. Rao, “Electrical transport in rare-earth oxides,” *J. Solid State Chem.*, vol. 2, pp. 377–384, Nov. 1970.
- [52] J. T. Devreese and F. Peeters, *Polarons and Excitons in Polar Semiconductors and Ionic Crystals*, vol. 127. Boston, MA: Springer, 1984.
- [53] M. Fiebig, T. Lottermoser, D. Meier, and M. Trassin, “The evolution of multiferroics,” *Nat. Rev. Mater.*, vol. 1, pp. 1–14, July 2016.
- [54] H. Schmid, “Multi-ferroic magnetoelectrics,” *Ferroelectrics*, vol. 162, pp. 317–338, Jan. 1994.
- [55] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnár, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, “Spintronics: A spin-based electronics vision for the future,” *Science*, vol. 294, pp. 1488–1495, Nov. 2001.
- [56] J. F. Scott, “Data storage: Multiferroic memories,” *Nature Mater.*, vol. 6, pp. 256–257, Am. Pharm. Rev. 2007.
- [57] M. Bibes and A. Barthélémy, “Towards a magnetoelectric memory,” *Nature Mater.*, vol. 7, pp. 425–426, June 2008.
- [58] N. A. Spaldin, S.-W. Cheong, and R. Ramesh, “Multiferroics: Past, present, and future,” *Phys. Today*, vol. 63, p. 38, Oct. 2010.
- [59] A. Rani, J. Kolte, S. S. Vadla, and P. Gopalan, “Structural, electrical, magnetic and magnetoelectric properties of Fe doped BaTiO₃ ceramics,” *Ceram. Int.*, vol. 42, pp. 8010–8016, May 2016.
- [60] P. Curie, “Sur la symétrie dans les phénomènes physiques, symétrie d’un champ électrique et d’un champ magnétique,” *J. Phys. Theor. Appl.*, vol. 3, no. 1, pp. 393–415, 1894.
- [61] I. E. Dzyaloshinskii, “On the magneto-rlectrical rffect in antiferromagnets,” *JETP*, vol. 10, p. 628, June 1959.
- [62] D. Astrov, “The magnetoelectric effect in antiferromagnetics,” *JETP*, vol. 11, p. 708, 1960.

BIBLIOGRAPHY

- [63] C. Zhou, C. Zhang, J. Yao, and C. Jiang, “Lateral electric-field-driven non-volatile four-state memory in multiferroic heterostructures,” *Appl. Phys. Lett.*, vol. 109, p. 112404, Sep. Purif. Technol. 2016.
- [64] Y. Wang, L. Wang, J. Xia, Z. Lai, G. Tian, X. Zhang, Z. Hou, X. Gao, W. Mi, C. Feng, M. Zeng, G. Zhou, G. Yu, G. Wu, Y. Zhou, W. Wang, X.-X. Zhang, and J. Liu, “Electric-field-driven non-volatile multi-state switching of individual skyrmions in a multiferroic heterostructure,” *Nat. Commun.*, vol. 11, p. 3577, July 2020.
- [65] M. M. Vopson, “Fundamentals of multiferroic materials and their possible applications,” *Crit. Rev. Solid State Mater. Sci.*, vol. 40, pp. 223–250, July 2015.
- [66] J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, “Epitaxial BiFeO₃ multiferroic thin film heterostructures,” *Science*, vol. 299, pp. 1719–1722, Mar. 2003.
- [67] V. R. Palkar and S. K. Malik, “Observation of magnetoelectric behavior at room temperature in Pb(Fe_xTi_{1-x})O₃,” *Solid State Commun.*, vol. 134, pp. 783–786, June 2005.
- [68] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, “Magnetic control of ferroelectric polarization,” *Nature*, vol. 426, pp. 55–58, Nov. 2003.
- [69] B. Lorenz, Y. Q. Wang, Y. Y. Sun, and C. W. Chu, “Large magnetodielectric effects in orthorhombic HoMnO₃ and YMnO₃,” *Phys. Rev. B*, vol. 70, p. 212412, Dec. 2004.
- [70] H. Zheng, J. Wang, S. E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S. R. Shinde, S. B. Ogale, F. Bai, D. Viehland, Y. Jia, D. G. Schlom, M. Wuttig, A. Roytburd, and R. Ramesh, “Multiferroic BaTiO₃-CoFe₂O₄ nanostructures,” *Science*, vol. 303, pp. 661–663, Jan. 2004.
- [71] W. Eerenstein, N. D. Mathur, and J. F. Scott, “Multiferroic and magnetoelectric materials,” *Nature*, vol. 442, pp. 759–765, Aug. 2006.
- [72] N. Ortega, A. Kumar, R. S. Katiyar, and C. Rinaldi, “Dynamic magneto-electric multiferroics PZT/CFO multilayered nanostructure,” *J. Mater. Sci.*, vol. 44, pp. 5127–5142, Oct. 2009.
- [73] J. T. Heron, M. Trassin, K. Ashraf, M. Gajek, Q. He, S. Y. Yang, D. E. Nikonov, Y.-H. Chu, S. Salahuddin, and R. Ramesh, “Electric-field-induced magnetization reversal in

BIBLIOGRAPHY

- a ferromagnet-multiferroic heterostructure,” *Phys. Rev. Lett.*, vol. 107, p. 217202, Nov. 2011.
- [74] R. Gupta, J. Shah, S. Chaudhary, S. Singh, and R. K. Kotnala, “Magnetoelectric coupling-induced anisotropy in multiferroic nanocomposite $(1-x)\text{BiFeO}_3\text{-}x\text{BaTiO}_3$,” *J. Nanopart. Res.*, vol. 15, p. 2004, Sep. Purif. Technol. 2013.
- [75] J. F. Scott, “Room-temperature multiferroic magnetoelectrics,” *NPG Asia Mater.*, vol. 5, pp. e72–e72, Nov. 2013.
- [76] F. Wang, C. Zhou, C. Zhang, C. Dong, C. Yang, C. Jiang, C. Jia, and D. Xue, “Piezoelectric control of magnetic dynamics in $\text{Co/Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ heterostructure,” *Appl. Phys. Lett.*, vol. 105, p. 062407, Aug. 2014.
- [77] N. A. Hill, “Why are there so few magnetic ferroelectrics?,” *J. Phys. Chem. B*, vol. 104, pp. 6694–6709, July 2000.
- [78] L. A. Shuvalov and N. V. Belov, “The symmetry of crystals in which ferromagnetic and ferroelectric properties appear simultaneously,” *Kristallografiya*, vol. 7, no. 192, pp. 150–151, 1962.
- [79] T. Egami and S. J. L. Billinge, *Underneath the Bragg peaks: structural analysis of complex materials*. Amsterdam: Elsevier, 2nd ed., 2012.
- [80] M. Uehara, S. Mori, C. H. Chen, and S.-W. Cheong, “Percolative phase separation underlies colossal magnetoresistance in mixed-valent manganites,” *Nature*, vol. 399, pp. 560–563, June 1999.
- [81] M. Fäth, S. Freisem, A. A. Menovsky, Y. Tomioka, J. Aarts, and J. A. Mydosh, “Spatially inhomogeneous metal-insulator transition in doped manganites,” *Science*, vol. 285, pp. 1540–1542, Sep. Purif. Technol. 1999.
- [82] Y.-D. Chuang, A. D. Gromko, D. S. Dessau, T. Kimura, and Y. Tokura, “Fermi surface nesting and nanoscale fluctuating charge/orbital ordering in colossal magnetoresistive oxides,” *Science*, vol. 292, pp. 1509–1513, May 2001.
- [83] E. Dagotto, “Complexity in strongly correlated electronic systems,” *Science*, vol. 309, pp. 257–262, July 2005.
- [84] S. J. L. Billinge and I. Levin, “The problem with determining atomic structure at the nanoscale,” *Science*, vol. 316, pp. 561–565, 2007.

BIBLIOGRAPHY

- [85] Billinge, S. J. L., “Nanometre-scale structure from powder diffraction: Total scattering and atomic pair distribution function analysis,” in *International Tables for Crystallography* (C. J. Gilmore, J. A. Kaduk, and H. Schenk, eds.), vol. H, pp. 649–672, Chester, UK: International Union of Crystallography, 2019.
- [86] B. H. Toby, W. Dmowski, T. Egami, J. D. Jorgensen, M. A. Subramanian, J. Gopalakrishnan, A. W. Sleight, and J. B. Parise, “Ordering in $\text{Ti}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$ and $\text{Ti}_2\text{Ba}_2\text{CuO}_6$ studied by pair distribution function and rietveld analysis,” *Physica C*, vol. 162–164, pp. 101–102, Dec. 1989.
- [87] S. J. L. Billinge, R. G. DiFrancesco, G. H. Kwei, J. J. Neumeier, and J. D. Thompson, “Direct observation of lattice polaron formation in the local structure of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$,” *Phys. Rev. Lett.*, vol. 77, pp. 715–718, July 1996.
- [88] H. Zhang, B. Gilbert, F. Huang, and J. F. Banfield, “Water-driven structure transformation in nanoparticles at room temperature,” *Nature*, vol. 424, pp. 1025–1029, Aug. 2003.
- [89] A. S. Masadeh, E. S. Božin, C. L. Farrow, G. Paglia, P. Juhas, S. J. L. Billinge, A. Karkamkar, and M. G. Kanatzidis, “Quantitative size-dependent structure and strain determination of CdSe nanoparticles using atomic pair distribution function analysis,” *Phys. Rev. B*, vol. 76, p. 115413, Sep. Purif. Technol. 2007.
- [90] C. A. Young and A. L. Goodwin, “Applications of pair distribution function methods to contemporary problems in materials chemistry,” *J. Mater. Chem.*, vol. 21, no. 18, pp. 6464–6476, 2011.
- [91] J. V. Laveda, B. Johnston, G. W. Paterson, P. J. Baker, M. G. Tucker, H. Y. Playford, K. M. Ø. Jensen, S. J. L. Billinge, and S. A. Corr, “Structure–property insights into nanostructured electrodes for Li-ion batteries from local structural and diffusional probes,” *J. Mater. Chem. A*, vol. 6, no. 1, pp. 127–137, 2018.
- [92] H. A. Jahn, E. Teller, and F. G. Donnan, “Stability of polyatomic molecules in degenerate electronic states - I—Orbital degeneracy,” *Proc. R. Soc. A*, vol. 161, pp. 220–235, July 1937.
- [93] B. Bleaney and D. J. E. Ingram, “Paramagnetic resonance in copper fluosilicate,” *Proc. Phys. Soc. A*, vol. 63, pp. 408–409, Am. Pharm. Rev. 1950.

BIBLIOGRAPHY

- [94] I. B. Bersuker, “Pseudo Jahn-Teller origin of perovskite multiferroics, magnetic-ferroelectric crossover, and magnetoelectric effects: The d^0 - d^{10} problem,” *Phys. Rev. Lett.*, vol. 108, p. 137202, Mar. 2012.
- [95] I. B. Bersuker, “Pseudo-Jahn-Teller effect—a two-state paradigm in formation, deformation, and transformation of molecular systems and solids,” *Chem. Rev.*, vol. 113, pp. 1351–1390, Mar. 2013.
- [96] R. Englman, *The Jahn-Teller Effect in Molecules and Crystals*. London: John Wiley & Sons, 1972.
- [97] D. Louca, T. Egami, E. L. Brosha, H. Röder, and A. R. Bishop, “Local Jahn-Teller distortion in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ observed by pulsed neutron diffraction,” *Phys. Rev. B*, vol. 56, pp. R8475–R8478, Oct. 1997.
- [98] Y.-K. Sun, Y.-S. Jeon, and H. J. Leeb, “Overcoming Jahn-Teller distortion for spinel Mn phase,” *Electrochem. Solid-State Lett.*, vol. 3, p. 7, Nov. 1999.
- [99] I. Loa, P. Adler, A. Grzechnik, K. Syassen, U. Schwarz, M. Hanfland, G. K. Rozenberg, P. Gorodetsky, and M. P. Pasternak, “Pressure-induced quenching of the Jahn-Teller distortion and insulator-to-metal transition in LaMnO_3 ,” *Phys. Rev. Lett.*, vol. 87, p. 125501, Aug. 2001.
- [100] A. Bussmann-Holder, H. Beige, and G. Völkel, “Precursor effects, broken local symmetry, and coexistence of order-disorder and displacive dynamics in perovskite ferroelectrics,” *Phys. Rev. B*, vol. 79, p. 184111, May 2009.
- [101] S. Bhattacharjee, E. Bousquet, and P. Ghosez, “Engineering Multiferroism in CaMnO_3 ,” *Phys. Rev. Lett.*, vol. 102, p. 117602, Mar. 2009.
- [102] P. Barone, S. Kanungo, S. Picozzi, and T. Saha-Dasgupta, “Mechanism of ferroelectricity in d^3 perovskites: A model study,” *Phys. Rev. B*, vol. 84, p. 134101, Oct. 2011.
- [103] H. Y. Huang, Z. Y. Chen, R.-P. Wang, F. M. F. de Groot, W. B. Wu, J. Okamoto, A. Chainani, A. Singh, Z.-Y. Li, J.-S. Zhou, H.-T. Jeng, G. Y. Guo, J.-G. Park, L. H. Tjeng, C. T. Chen, and D. J. Huang, “Jahn-Teller distortion driven magnetic polarons in magnetite,” *Nat. Commun.*, vol. 8, p. 15929, June 2017.
- [104] J. U. Choi, Y. J. Park, J. H. Jo, L.-Y. Kuo, P. Kaghazchi, and S.-T. Myung, “Unraveling the role of Earth-abundant Fe in the suppression of Jahn-Teller distortion of P' -type $\text{Na}_{2/3}\text{MnO}_2$: Experimental and theoretical studies,” *ACS Appl. Mater. Interfaces*, vol. 10, pp. 40978–40984, Dec. 2018.

BIBLIOGRAPHY

- [105] H. Sawada, Y. Morikawa, K. Terakura, and N. Hamada, “Jahn-Teller distortion and magnetic structures in LaMnO_3 ,” *Phys. Rev. B*, vol. 56, pp. 12154–12160, Nov. 1997.
- [106] I. S. Elfimov, V. I. Anisimov, and G. A. Sawatzky, “Orbital ordering, Jahn-Teller distortion, and anomalous x-ray scattering in manganates,” *Phys. Rev. Lett.*, vol. 82, pp. 4264–4267, May 1999.
- [107] B. Dorado, G. Jomard, M. Freyss, and M. Bertolus, “Stability of oxygen point defects in UO_2 by first-principles DFT+U calculations: Occupation matrix control and Jahn-Teller distortion,” *Phys. Rev. B*, vol. 82, p. 035114, July 2010.
- [108] H. Chen, C. L. Freeman, and J. H. Harding, “Charge disproportionation and Jahn-Teller distortion in LiNiO_2 and NaNiO_2 : A density functional theory study,” *Phys. Rev. B*, vol. 84, p. 085108, Aug. 2011.
- [109] D. Novoselov, D. M. Korotin, and V. I. Anisimov, “Correlations induced orbital ordering and cooperative Jahn-Teller distortion in the paramagnetic insulator KCrF_3 ,” *JETP Lett.*, vol. 103, pp. 573–576, May 2016.
- [110] Y. Tokura and N. Nagaosa, “Orbital physics in transition-metal oxides,” *Science*, vol. 288, pp. 462–468, Am. Pharm. Rev. 2000.
- [111] K. I. Kugel’ and D. I. Khomskii, “The Jahn-Teller effect and magnetism: Transition metal compounds,” *Sov. Phys. Usp.*, vol. 25, p. 231, Am. Pharm. Rev. 1982.
- [112] E. S. Bozin, M. Schmidt, A. J. DeConinck, G. Paglia, J. F. Mitchell, T. Chatterji, P. G. Radaelli, T. Proffen, and S. J. L. Billinge, “Understanding the insulating phase in colossal magnetoresistance manganites: Shortening of the Jahn-Teller long-bond across the phase diagram of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$,” *Phys. Rev. Lett.*, vol. 98, p. 137203, Mar. 2007.
- [113] M. S. Silberberg, *Principles of General Chemistry*. New York, NY, USA: McGraw-Hill Education, 3rd ed., 2012.
- [114] A. Yamada and M. Tanaka, “Jahn-Teller structural phase transition around 280K in LiMn_2O_4 ,” *Mater. Res. Bull.*, vol. 30, pp. 715–721, June 1995.
- [115] P. J. Brown, A. Y. Bargawi, J. Crangle, K.-U. Neumann, and K. R. A. Ziebeck, “Direct observation of a band Jahn-Teller effect in the martensitic phase transition of Ni_2MnGa ,” *J. Phys. Condens. Matter*, vol. 11, pp. 4715–4722, Jan. 1999.

BIBLIOGRAPHY

- [116] S. Margadonna and G. Karotsis, “Cooperative Jahn-Teller distortion, phase transitions, and weak ferromagnetism in the KCrF_3 perovskite,” *J. Am. Chem. Soc.*, vol. 128, pp. 16436–16437, Dec. 2006.
- [117] T. Proffen, R. G. DiFrancesco, S. J. L. Billinge, E. L. Brosha, and G. H. Kwei, “Measurement of the local Jahn-Teller distortion in $\text{LaMnO}_{3.006}$,” *Phys. Rev. B*, vol. 60, pp. 9973–9977, Oct. 1999.
- [118] T. Proffen and S. Billinge, “Probing the local structure of doped manganites using the atomic pair distribution function,” *Appl. Phys. A*, vol. 74, pp. s1770–s1772, Dec. 2002.
- [119] M. Gateshki, S.-J. Hwang, D. H. Park, Y. Ren, and V. Petkov, “Structure of nanocrystalline alkali metal manganese oxides by the atomic pair distribution function technique,” *J. Phys. Chem. B*, vol. 108, pp. 14956–14963, Sep. Purif. Technol. 2004.
- [120] N. Sundaram, Y. Jiang, I. E. Anderson, D. P. Belanger, C. H. Booth, F. Bridges, J. F. Mitchell, T. Proffen, and H. Zheng, “Local structure of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ determined from EXAFS and neutron pair distribution function studies,” *Phys. Rev. Lett.*, vol. 102, p. 026401, Jan. 2009.
- [121] D. P. Shoemaker, J. Li, and R. Seshadri, “Unraveling atomic positions in an oxide spinel with two Jahn-Teller ions: Local structure investigation of CuMn_2O_4 ,” *J. Am. Chem. Soc.*, vol. 131, pp. 11450–11457, Aug. 2009.
- [122] P. Fazekas, *Lecture Notes on Electron Correlation and Magnetism*, vol. 5. River Edge, NJ, USA: World Scientific, 1999.
- [123] D. Louca, J. L. Sarrao, J. D. Thompson, H. Röder, and G. H. Kwei, “Correlation of local Jahn-Teller distortions to the magnetic/conductive states of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$,” *Phys. Rev. B*, vol. 60, pp. 10378–10382, Oct. 1999.
- [124] E. Pavarini and E. Koch, “Origin of Jahn-Teller distortion and orbital order in LaMnO_3 ,” *Phys. Rev. Lett.*, vol. 104, p. 086402, Feb. 2010.
- [125] A. Goswami and A. P. Goswami, “Optical properties of praseodymium oxide films,” *Thin Solid Films*, vol. 27, pp. 123–128, May 1975.
- [126] S. Lacombe, C. Geantet, and C. Mirodatos, “Oxidative coupling of methane over lanthana catalysts: I. Identification and role of specific active-sites,” *J. Catal.*, vol. 151, pp. 439–452, Feb. 1995.

BIBLIOGRAPHY

- [127] M. Fathi, E. Bjorgum, T. Viig, and O. A. Rokstad, “Partial oxidation of methane to synthesis gas:: Elimination of gas phase oxygen,” *Catal. Today*, vol. 63, pp. 489–497, Dec. 2000.
- [128] W. Wang, P. Lin, Y. Fu, and G. Cao, “Redox properties and catalytic behavior of praseodymium-modified (Ce-Zr)O₂ solid solutions in three-way catalysts,” *Catal. Lett.*, vol. 82, pp. 19–27, Sep. Purif. Technol. 2002.
- [129] B. G. Hyde, D. J. M. Bevan, and L. Eyring, “On the praseodymium+oxygen system,” *Philos. Trans. R. Soc. A*, vol. 259, pp. 583–614, May 1966.
- [130] D. A. Burnham and L. Eyring, “Phase transformations in the praseodymium oxide-oxygen system: High-temperature x-ray diffraction studies,” *J. Phys. Chem.*, vol. 72, pp. 4415–4424, Dec. 1968.
- [131] L. Eyring and N. C. Baenziger, “On the structure and related properties of the oxides of praseodymium,” *J. Appl. Phys.*, vol. 33, pp. 428–433, Jan. 1962.
- [132] V. Thangadurai, R. A. Huggins, and W. Weppner, “Mixed ionic-electronic conductivity in phases in the praseodymium oxide system,” *J Solid State Electrochem.*, vol. 5, pp. 531–537, Oct. 2001.
- [133] H. J. Müssig, J. Dąbrowski, K. Ignatovich, J. P. Liu, V. Zavodinsky, and H. J. Osten, “Initial stages of praseodymium oxide film formation on Si(001),” *Surf. Sci.*, vol. 504, pp. 159–166, Am. Pharm. Rev. 2002.
- [134] U. Chon, J. S. Shim, and H. M. Jang, “Ferroelectric properties and crystal structure of praseodymium-modified bismuth titanate,” *J. Appl. Phys.*, vol. 93, p. 4769, Mar. 2003.
- [135] A. D. Franklin, “Nanomaterials in transistors: From high-performance to thin-film applications,” *Science*, vol. 349, Aug. 2015.
- [136] M. Kawabe, H. Ono, T. Sano, M. Tsuji, and Y. Tamaura, “Thermochemical oxygen pump with praseodymium oxides using a temperature-swing at 403–873 K,” *Energy*, vol. 22, pp. 1041–1049, Nov. 1997.
- [137] A. J. Zarur and J. Y. Ying, “Reverse microemulsion synthesis of nanostructured complex oxides for catalytic combustion,” *Nature*, vol. 403, pp. 65–67, Jan. 2000.

BIBLIOGRAPHY

- [138] D. Friebe, M. W. Louie, M. Bajdich, K. E. Sanwald, Y. Cai, A. M. Wise, M.-J. Cheng, D. Sokaras, T.-C. Weng, R. Alonso-Mori, R. C. Davis, J. R. Bargar, J. K. Nørskov, A. Nilsson, and A. T. Bell, "Identification of highly active Fe sites in (Ni,Fe)OOH for electrocatalytic water splitting," *J. Am. Chem. Soc.*, vol. 137, pp. 1305–1313, Jan. 2015.
- [139] S. Shrestha, C. M. Y. Yeung, C. Nunnerley, and S. C. Tsang, "Comparison of morphology and electrical conductivity of various thin films containing nano-crystalline praseodymium oxide particles," *Sens. Actuator A: Phys.*, vol. 136, pp. 191–198, May 2007.
- [140] X. Zhang, S. Cheng, W. Zhang, C. Zhang, N. E. Drewett, X. Wang, D. Wang, S. J. Yoo, J.-G. Kim, and W. Zheng, "Mechanistic insight into nanoarchitected Ag/Pr₆O₁₁ catalysts for efficient CO oxidation," *Ind. Eng. Chem. Res.*, vol. 56, pp. 11042–11048, Oct. 2017.
- [141] K. T. Kubra, A. Javaid, B. Patil, R. Sharif, A. Salman, S. Shahzadi, S. Siddique, and S. Ghani, "Synthesis and characterization of novel Pr₆O₁₁/Mn₃O₄ nanocomposites for electrochemical supercapacitors," *Ceram. Int.*, vol. 45, pp. 6819–6827, Am. Pharm. Rev. 2019.
- [142] N. Chen, A. Younis, S. Huang, D. Chu, and S. Li, "Advanced three-dimensional hierarchical Pr₆O₁₁@Ni-Co oxides-based core-shell electrodes for supercapacitance application," *J. Alloys Compd.*, vol. 783, pp. 772–778, Am. Pharm. Rev. 2019.
- [143] O. Hirsch, K. Kvashnina, C. Willa, and D. Koziej, "Hard x-ray photon-in photon-out spectroscopy as a probe of the temperature-induced delocalization of electrons in nanoscale semiconductors," *Chem. Mater.*, vol. 29, pp. 1461–1466, Feb. 2017.
- [144] P. X. Huang, F. Wu, B. L. Zhu, G. R. Li, Y. L. Wang, X. P. Gao, H. Y. Zhu, T. Y. Yan, W. P. Huang, S. M. Zhang, and D. Y. Song, "Praseodymium hydroxide and oxide nanorods and Au/Pr₆O₁₁ nanorod catalysts for CO oxidation," *J. Phys. Chem. B*, vol. 110, pp. 1614–1620, Feb. 2006.
- [145] L. Yan, R. Yu, G. Liu, and X. Xing, "A facile template-free synthesis of large-scale single crystalline Pr(OH)₃ and Pr₆O₁₁ nanorods," *Scr. Mater.*, vol. 58, pp. 707–710, Am. Pharm. Rev. 2008.
- [146] B. Matović, J. Pantić, M. Prekajski, N. Stanković, D. Bučevac, T. Minović, and M. Čebela, "Synthesis and characterization of Pr₆O₁₁ nanopowders," *Ceram. Int.*, vol. 39, pp. 3151–3155, Am. Pharm. Rev. 2013.

BIBLIOGRAPHY

- [147] B. M. Abu-Zied, Y. A. Mohamed, and A. M. Asiri, “Fabrication, characterization, and electrical conductivity properties of Pr_6O_{11} nanoparticles,” *J. Rare Earths*, vol. 31, pp. 701–708, July 2013.
- [148] Y. Zhang, K. Han, X. Yin, Z. Fang, Z. Xu, and W. Zhu, “Synthesis and characterization of single-crystalline PrCO_3OH dodecahedral microrods and its thermal conversion to Pr_6O_{11} ,” *J. Cryst. Growth*, vol. 311, pp. 3883–3888, July 2009.
- [149] R. B. Von Dreele, L. Eyring, A. L. Bowman, and J. L. Yarnell, “Refinement of the crystal structure of Pr_7O_{12} by powder neutron diffraction,” *Acta Crystallogr. B*, vol. 31, pp. 971–974, Am. Pharm. Rev. 1975.
- [150] C. Gardiner, A. Boothroyd, S. Lister, M. McKelvy, S. Hull, and B. Larsen, “An investigation of the magnetic structure of PrO_2 ,” *Appl. Phys. A*, vol. 74, pp. s1773–s1775, Dec. 2002.
- [151] C. H. Gardiner, A. T. Boothroyd, P. Pattison, M. J. McKelvy, G. J. McIntyre, and S. J. S. Lister, “Cooperative Jahn-Teller distortion in PrO_2 ,” *Phys. Rev. B*, vol. 70, p. 024415, July 2004.
- [152] A. R. Chakhmouradian and P. M. Woodward, “Celebrating 175 years of perovskite research: A tribute to Roger H. Mitchell,” *Phys. Chem. Miner.*, vol. 41, pp. 387–391, June 2014.
- [153] E. A. Katz, “Perovskite: Name puzzle and German-Russian odyssey of discovery,” *Helv. Chim. Acta*, vol. 103, no. 6, p. e2000061, 2020.
- [154] H. D. Megaw, “Crystal structure of barium titanate,” *Nature*, vol. 155, no. 3938, pp. 484–485, 1945.
- [155] B. Wul and J. M. Goldman, “Ferroelectric switching in BaTiO_3 ceramics,” *I. M. C. R. Acad. Sci. Russ.*, vol. 51, p. 21, 1946.
- [156] G. H. Kwei, A. C. Lawson, S. J. L. Billinge, and S.-W. Cheong, “Structures of the ferroelectric phases of barium titanate,” *J. Phys. Chem.*, vol. 97, p. 2368, 1993.
- [157] A. Von Hippel, “Ferroelectricity, domain structure, and phase transitions of barium titanate,” *Rev. Mod. Phys.*, vol. 22, pp. 221–237, July 1950.
- [158] M. B. Smith, K. Page, T. Siegrist, P. L. Redmond, E. C. Walter, R. Seshadri, L. E. Brus, and M. L. Steigerwald, “Crystal structure and the paraelectric-to-ferroelectric

BIBLIOGRAPHY

- phase transition of nanoscale BaTiO₃,” *J. Am. Chem. Soc.*, vol. 130, pp. 6955–6963, June 2008.
- [159] B. C. Frazer, H. R. Danner, and R. Pepinsky, “Single-crystal neutron analysis of tetragonal BaTiO₃,” *Phys. Rev.*, vol. 100, pp. 745–746, Oct. 1955.
- [160] G. Arlt, D. Hennings, and G. de With, “Dielectric properties of fine-grained barium titanate ceramics,” *J. Appl. Phys.*, vol. 58, pp. 1619–1625, Aug. 1985.
- [161] T. Karaki, K. Yan, and M. Adachi, “Barium titanate piezoelectric ceramics manufactured by two-step sintering,” *Jpn. J. Appl. Phys.*, vol. 46, p. 7035, Oct. 2007.
- [162] B. Jaffe, *Piezoelectric Ceramics*. New York, NY, USA: Academic Press Inc., 1971.
- [163] J. B. MacChesney, P. K. Gallagher, and F. V. DiMarcello, “Stabilized barium titanate ceramics for capacitor dielectrics,” *J. Am. Ceram. Soc.*, vol. 46, pp. 197–202, May 1963.
- [164] M. H. Frey and D. A. Payne, “Nanocrystalline barium titanate: Evidence for the absence of ferroelectricity in sol-gel derived thin-layer capacitors,” *Appl. Phys. Lett.*, vol. 63, pp. 2753–2755, Nov. 1993.
- [165] W.-B. Li, D. Zhou, L.-X. Pang, R. Xu, and H.-H. Guo, “Novel barium titanate based capacitors with high energy density and fast discharge performance,” *J. Mater. Chem. A*, vol. 5, no. 37, pp. 19607–19612, 2017.
- [166] H. A. Sauer and J. R. Fisher, “Processing of positive temperature coefficient thermistors,” *J. Am. Ceram. Soc.*, vol. 43, no. 6, pp. 297–301, 1960.
- [167] A. B. Alles and V. L. Burdick, “Grain boundary oxidation in PTCR barium titanate thermistors,” *J. Am. Ceram. Soc.*, vol. 76, no. 2, pp. 401–408, 1993.
- [168] A. Steane, “Quantum computing,” *Rep. Prog. Phys.*, vol. 61, pp. 117–173, Feb. 1998.
- [169] L. Kou, Y. Ma, T. Liao, A. Du, and C. Chen, “Multiferroic and ferroic topological order in ligand-functionalized germanene and arsenene,” *Phys. Rev. Appl.*, vol. 10, p. 024043, Aug. 2018.
- [170] K. Page, T. Proffen, M. Niederberger, and R. Seshadri, “Probing local dipoles and ligand structure in BaTiO₃ nanoparticles,” *Chem. Mater.*, vol. 22, pp. 4386–4391, Aug. 2010.

BIBLIOGRAPHY

- [171] C. Shi, S. J. L. Billinge, E. Puma, S. H. Bang, N. J. H. Bean, J.-C. de Sugny, R. G. Gambee, R. C. Haskell, A. Hightower, and T. C. Monson, “Barium titanate nanoparticles: Short-range lattice distortions with long-range cubic order,” *Phys. Rev. B*, vol. 98, p. 085421, Aug. 2018.
- [172] Z. Chao, W. Chun-Lei, L. Ji-Chao, and Y. Kun, “Structural and electronic properties of Fe-doped BaTiO₃ and SrTiO₃,” *Chin. Phys.*, vol. 16, pp. 1422–1428, May 2007.
- [173] B. Xu, K. B. Yin, J. Lin, Y. D. Xia, X. G. Wan, J. Yin, X. J. Bai, J. Du, and Z. G. Liu, “Room-temperature ferromagnetism and ferroelectricity in Fe-doped BaTiO₃,” *Phys. Rev. B*, vol. 79, p. 134109, Am. Phys. Soc., May 2009.
- [174] P. Nimmanpipug, A. Saelor, L. Srisombat, V. S. Lee, and Y. Laosiritaworn, “Density functional theory investigation of site predilection of Fe substitution in barium titanate,” *Ceram. Int.*, vol. 39, pp. S293–S296, May 2013.
- [175] J. J. Meléndez, Y. A. Zulueta, and Y. Leyet, “First-principles study of neutral defects in Fe-doped cubic barium titanate,” *Ceram. Int.*, vol. 41, pp. 1647–1656, Jan. 2015.
- [176] M. A. Islam, M. A. Momin, and M. Nesa, “Effect of Fe doping on the structural, optical and electronic properties of BaTiO₃: DFT based calculation,” *Chin. J. Phys.*, vol. 60, pp. 731–738, Aug. 2019.
- [177] N. V. Dang, N. T. Dung, P. T. Phong, and I.-J. Lee, “Effect of Fe³⁺ substitution on structural, optical and magnetic properties of barium titanate ceramics,” *Physica B*, vol. 457, pp. 103–107, Jan. 2015.
- [178] D. P. Dutta, M. Roy, N. Maiti, and A. K. Tyagi, “Phase evolution in sonochemically synthesized Fe³⁺ doped BaTiO₃ nanocrystallites: Structural, magnetic and ferroelectric characterisation,” *Phys. Chem. Chem. Phys.*, vol. 18, no. 14, pp. 9758–9769, 2016.
- [179] P. P. Khirade, S. D. Birajdar, A. V. Raut, and K. M. Jadhav, “Multiferroic iron doped BaTiO₃ nanoceramics synthesized by sol-gel auto combustion: Influence of iron on physical properties,” *Ceram. Int.*, vol. 42, pp. 12441–12451, Aug. 2016.
- [180] T. Costanzo, J. McCracken, A. Rotaru, and G. Caruntu, “Quasi-monodisperse transition-metal-doped BaTiO₃ (M = Cr, Mn, Fe, Co) colloidal nanocrystals with multiferroic properties,” *ACS Appl. Nano Mater.*, vol. 1, pp. 4863–4874, Sep. Purif. Technol. 2018.

BIBLIOGRAPHY

- [181] S. Liu, L. Huang, W. Li, X. Liu, S. Jing, J. Li, and S. O'Brien, "Green and scalable production of colloidal perovskite nanocrystals and transparent sols by a controlled self-collection process," *Nanoscale*, vol. 7, no. 27, pp. 11766–11776, 2015.
- [182] W. H. Bragg, "XXX. The structure of the spinel group of crystals," *London Edinburgh Dublin Philos. Mag. & J. Sci.*, vol. 30, pp. 305–315, Aug. 1915.
- [183] S. Nishikawa, "Structure of some crystals of spinel group," *Proc. Tokyo Math. Phys. Soc. 2nd Ser.*, vol. 8, no. 7, pp. 199–209, 1915.
- [184] F. Bosi, C. Biagioni, and M. Pasero, "Nomenclature and classification of the spinel supergroup," *Eur. J. Mineral.*, vol. 31, pp. 183–192, Jan. 2019.
- [185] K. E. Sickafus, J. M. Wills, and N. W. Grimes, "Structure of spinel," *J. Am. Ceram. Soc.*, vol. 82, no. 12, pp. 3279–3292, 1999.
- [186] N. W. Grimes, "The spinels: Versatile materials," *Phys. Techn.*, vol. 6, pp. 22–27, Jan. 1975.
- [187] Q.-C. Zhuang, T. Wei, L.-L. Du, Y.-L. Cui, L. Fang, and S.-G. Sun, "An electrochemical impedance spectroscopic study of the electronic and ionic transport properties of spinel LiMn_2O_4 ," *J. Phys. Chem. C*, vol. 114, pp. 8614–8621, May 2010.
- [188] Z. Zheng, Y. Li, T. Liu, and Q. Feng, "Novel high-frequency magneto-dielectric properties of CaO-SiO_2 Co-doped NiZnCo spinel ferrites for RF and microwave device applications," *IEEE Trans. Magn.*, vol. 54, pp. 1–4, Nov. 2018.
- [189] A. K. Subramani, K. Kondo, M. Tada, M. Abe, M. Yoshimura, and N. Matsushita, "Spinel ferrite films by a novel solution process for high frequency applications," *Mater. Chem. Phys.*, vol. 123, pp. 16–19, Sep. Purif. Technol. 2010.
- [190] N. Basavaraju, S. Sharma, A. Bessière, B. Viana, D. Gourier, and K. R. Priolkar, "Red persistent luminescence in $\text{MgGa}_2\text{O}_4\text{:Cr}^{3+}$; a new phosphor for in vivo imaging," *J. Phys. D: Appl. Phys.*, vol. 46, p. 375401, Aug. 2013.
- [191] A. Luchechko, O. Kravets, L. Kostyk, and O. Tsvetkova, "Luminescence spectroscopy of Eu^{3+} and Mn^{2+} ions in MgGa_2O_4 spinel," *Radiat. Meas.*, vol. 90, pp. 47–50, July 2016.
- [192] Y. Zhao, J. Du, X. Wu, Y. Wang, and D. Poelman, "Enhanced near-infrared persistent luminescence in $\text{MgGa}_2\text{O}_4\text{:Cr}^{3+}$ through codoping," *J. Lumin.*, vol. 220, p. 117035, Am. Pharm. Rev. 2020.

BIBLIOGRAPHY

- [193] L. Yan, T. Ren, X. Wang, D. Ji, and J. Suo, “Catalytic decomposition of N_2O over $\text{M}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ ($\text{M} = \text{Ni}, \text{Mg}$) spinel oxides,” *Appl. Catal. B*, vol. 45, pp. 85–90, Sep. Purif. Technol. 2003.
- [194] D. M. Robinson, Y. B. Go, M. Greenblatt, and G. C. Dismukes, “Water Oxidation by $\lambda\text{-MnO}_2$: Catalysis by the cubical Mn_4O_4 subcluster obtained by delithiation of spinel LiMn_2O_4 ,” *J. Am. Chem. Soc.*, vol. 132, pp. 11467–11469, Aug. 2010.
- [195] M. Imran, D. H. Kim, W. A. Al-Masry, A. Mahmood, A. Hassan, S. Haider, and S. M. Ramay, “Manganese-, cobalt-, and zinc-based mixed-oxide spinels as novel catalysts for the chemical recycling of poly(ethylene terephthalate) via glycolysis,” *Polym. Degrad. Stab.*, vol. 98, pp. 904–915, Am. Pharm. Rev. 2013.
- [196] Y. Wang, H. Arandiyani, Y. Liu, Y. Liang, Y. Peng, S. Bartlett, H. Dai, S. Rostamnia, and J. Li, “Template-free scalable synthesis of flower-like $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$ spinel catalysts for toluene oxidation,” *ChemCatChem*, vol. 10, pp. 3429–3434, Aug. 2018.
- [197] Y. Liu, Y. Ying, L. Fei, Y. Liu, Q. Hu, G. Zhang, S. Y. Pang, W. Lu, C. L. Mak, X. Luo, L. Zhou, M. Wei, and H. Huang, “Valence engineering via selective atomic substitution on tetrahedral sites in spinel oxide for highly enhanced oxygen evolution catalysis,” *J. Am. Chem. Soc.*, vol. 141, pp. 8136–8145, May 2019.
- [198] D. C. Johnston, H. Prakash, W. H. Zachariasen, and R. Viswanathan, “High temperature superconductivity in the Li-Ti-O ternary system,” *Mater. Res. Bull.*, vol. 8, pp. 777–784, July 1973.
- [199] W. Hu, Z. Feng, B.-C. Gong, G. He, D. Li, M. Qin, Y. Shi, Q. Li, Q. Zhang, J. Yuan, B. Zhu, K. Liu, T. Xiang, L. Gu, F. Zhou, X. Dong, Z. Zhao, and K. Jin, “Emergent superconductivity in single-crystalline MgTi_2O_4 films via structural engineering,” *Phys. Rev. B*, vol. 101, p. 220510, June 2020.
- [200] T. Furubayashi, T. Matsumoto, T. Hagino, and S. Nagata, “Structural and magnetic studies of metal-insulator transition in thiospinel CuIr_2S_4 ,” *J. Phys. Soc. Jpn.*, vol. 63, no. 9, pp. 3333–3339, 1994.
- [201] J. Matsuno, T. Mizokawa, A. Fujimori, D. A. Zatsepin, V. R. Galakhov, E. Z. Kurmaev, Y. Kato, and S. Nagata, “Photoemission study of the metal-insulator transition in CuIr_2S_4 ,” *Phys. Rev. B*, vol. 55, pp. R15979–R15982, June 1997.

BIBLIOGRAPHY

- [202] N. Matsumoto, R. Endoh, S. Nagata, T. Furubayashi, and T. Matsumoto, “Metal-insulator transition and superconductivity in the spinel-type $\text{Cu}(\text{Ir}_{1-x}\text{Rh}_x)_2\text{S}_4$ system,” *Phys. Rev. B*, vol. 60, pp. 5258–5265, Aug. 1999.
- [203] H. Ishibashi, T. Sakai, and K. Nakahigashi, “X-ray diffraction study on spinel compound CuIr_2S_4 with metal–insulator transition,” *J. Magn. Magn. Mater.*, vol. 226-230, pp. 233–234, May 2001.
- [204] P. G. Radaelli, Y. Horibe, M. J. Gutmann, H. Ishibashi, C. H. Chen, R. M. Ibberson, Y. Koyama, Y.-S. Hor, V. Kiryukhin, and S.-W. Cheong, “Formation of isomorphous Ir^{3+} and Ir^{4+} octamers and spin dimerization in the spinel CuIr_2S_4 ,” *Nature*, vol. 416, pp. 155–158, Mar. 2002.
- [205] A. T. Burkov, T. Nakama, M. Hedo, K. Shintani, K. Yagasaki, N. Matsumoto, and S. Nagata, “Anomalous resistivity and thermopower of the spinel-type compounds CuIr_2S_4 and CuIr_2Se_4 ,” *Phys. Rev. B*, vol. 61, pp. 10049–10056, Am. Phys. Rev. 2000.
- [206] K. Takubo, T. Mizokawa, N. Matsumoto, and S. Nagata, “In-gap state and effect of light illumination in CuIr_2S_4 probed by photoemission spectroscopy,” *Phys. Rev. B*, vol. 78, p. 245117, Dec. 2008.
- [207] D. I. Khomskii and T. Mizokawa, “Orbitally induced Peierls state in spinels,” *Phys. Rev. Lett.*, vol. 94, p. 156402, Am. Phys. Rev. 2005.
- [208] S. Nagata, T. Hagino, Y. Seki, and T. Bitoh, “Metal-insulator transition in thiospinel CuIr_2S_4 ,” *Physica B*, vol. 194-196, pp. 1077–1078, Feb. 1994.
- [209] M. Isobe and Y. Ueda, “Observation of phase transition from metal to spin-singlet insulator in MgTi_2O_4 with $S=1/2$ pyrochlore lattice,” *J. Phys. Soc. Jpn.*, vol. 71, pp. 1848–1851, Aug. 2002.
- [210] J. Zhou, G. Li, J. L. Luo, Y. C. Ma, D. Wu, B. P. Zhu, Z. Tang, J. Shi, and N. L. Wang, “Optical study of MgTi_2O_4 : Evidence for an orbital-Peierls state,” *Phys. Rev. B*, vol. 74, p. 245102, Dec. 2006.
- [211] M. Schmidt, W. Ratcliff, P. G. Radaelli, K. Refson, N. M. Harrison, and S. W. Cheong, “Spin singlet formation in MgTi_2O_4 : Evidence of a helical dimerization pattern,” *Phys. Rev. Lett.*, vol. 92, p. 056402, Feb. 2004.

BIBLIOGRAPHY

- [212] Z. V. Popović, G. De Marzi, M. J. Konstantinović, A. Cantarero, Z. Dohčević-Mitrović, M. Isobe, and Y. Ueda, “Phonon properties of the spinel oxide MgTi_2O_4 with the $S=1/2$ pyrochlore lattice,” *Phys. Rev. B*, vol. 68, p. 224302, Dec. 2003.
- [213] L. Ma, H. Han, W. Liu, K. Yang, Y. Zhu, C. Zhang, L. Pi, D. Liu, L. Zhang, and Y. Zhang, “Opposite pressure effects in the orbitally-induced Peierls phase transition systems CuIr_2S_4 and MgTi_2O_4 ,” *Dalton Trans.*, vol. 46, pp. 6708–6714, May 2017.
- [214] Y. Shi, J. Lian, W. Hu, Y. Liu, G. He, K. Jin, H. Song, K. Dai, and J. Fang, “Study the relation between band gap value and lattice constant of MgTi_2O_4 ,” *J. Alloys Compd.*, vol. 788, pp. 891–896, June 2019.
- [215] E. S. Bozin, W. G. Yin, R. J. Koch, M. Abeykoon, Y. S. Hor, H. Zheng, H. C. Lei, C. Petrovic, J. F. Mitchell, and S. J. L. Billinge, “Local orbital degeneracy lifting as a precursor to an orbital-selective Peierls transition,” *Nat. Commun.*, vol. 10, pp. 1–7, Aug. 2019.
- [216] R. B. Neder and V. I. Korsunskiy, “Structure of nanoparticles from powder diffraction data using the pair distribution function,” *J. Phys.: Condens. Mat.*, vol. 17, no. 5, p. S125, 2005.
- [217] X. Yang, A. S. Masadeh, J. R. McBride, E. S. Božin, S. J. Rosenthal, and S. J. L. Billinge, “Confirmation of disordered structure of ultrasmall CdSe nanoparticles from x-ray atomic pair distribution function analysis,” *Phys. Chem. Chem. Phys.*, vol. 15, pp. 8480–8486, May 2013.
- [218] A. N. Beecher, X. Yang, J. H. Palmer, A. L. LaGrassa, P. Juhás, S. J. L. Billinge, and J. S. Owen, “Atomic structures and gram scale synthesis of three tetrahedral quantum dots,” *J. Am. Chem. Soc.*, vol. 136, no. 30, pp. 10645–10653, 2014.
- [219] M. W. Terban, C. Shi, R. Silbernagel, A. Clearfield, and S. J. L. Billinge, “Local environment of terbium(iii) ions in layered nanocrystalline zirconium(iv) phosphonatephosphate ion exchange materials,” *Inorg. Chem.*, vol. 56, no. 15, pp. 8837–8846, 2017.
- [220] S. J. L. Billinge and M. G. Kanatzidis, “Beyond crystallography: the study of disorder, nanocrystallinity and crystallographically challenged materials,” *Chem. Commun.*, vol. 7, pp. 749–760, 2004.
- [221] D. A. Keen and A. L. Goodwin, “The crystallography of correlated disorder,” *Nature*, vol. 521, pp. 303–309, May 2015.

BIBLIOGRAPHY

- [222] K. M. O. Jensen, A. B. Blichfeld, S. R. Bauers, S. R. Wood, E. Dooryhe, D. C. Johnson, B. B. Iversen, and S. J. L. Billinge, “Demonstration of thin film pair distribution function analysis (tfPDF) for the study of local structure in amorphous and crystalline thin films,” *IUCrJ.*, vol. 2, no. 5, pp. 481–489, 2015.
- [223] N. Nakamura, M. W. Terban, S. J. L. Billinge, and B. R. Jayan, “Unlocking the structure of mixed amorphous-crystalline ceramic oxide films synthesized under low temperature electromagnetic excitation,” *J. Mater. Chem. A*, vol. 5, no. 35, pp. 18434–18441, 2017.
- [224] D. Vaknin, W. Bu, and A. Travesset, “Extracting the pair distribution function of liquids and liquid-vapor surfaces by grazing incidence x-ray diffraction mode,” *J. Chem. Phys.*, vol. 129, p. 044504, July 2008.
- [225] N. Roth and B. B. Iversen, “Solving the disordered structure of β -Cu_{2-x}Se using the three-dimensional difference pair distribution function,” *Acta Crystallogr. A*, vol. 75, pp. 465–473, May 2019.
- [226] Z. Gong and S. J. L. Billinge, “Atomic pair distribution functions (PDFs) from textured polycrystalline samples: Fundamentals,” *arXiv:1805.10342*, May 2018.
- [227] T. Weber and A. Simonov, “The three-dimensional pair distribution function analysis of disordered single crystals: Basic concepts,” *Z. Kristallogr. Cryst. Mater.*, vol. 227, pp. 238–247, May 2012.
- [228] N. Roth, A. F. May, F. Ye, B. C. Chakoumakos, and B. B. Iversen, “Model-free reconstruction of magnetic correlations in frustrated magnets,” *IUCrJ*, vol. 5, pp. 410–416, July 2018.
- [229] J. Cravillon, C. A. Schröder, R. Nayuk, J. Gummel, K. Huber, and M. Wiebcke, “Fast nucleation and growth of ZIF-8 nanocrystals monitored by time-resolved in situ small-angle and wide-angle x-ray scattering,” *Angew. Chem. Int. Ed.*, vol. 50, no. 35, pp. 8067–8071, 2011.
- [230] K. M. O. Jensen, M. Christensen, P. Juhas, C. Tyrsted, E. D. Bøjesen, N. Lock, S. J. L. Billinge, and B. B. Iversen, “Revealing the mechanisms behind SnO₂ nanoparticle formation and growth during hydrothermal synthesis: An in situ total scattering study,” *J. Am. Chem. Soc.*, vol. 134, pp. 6785–6792, Am. Chem. Soc., 2012.

BIBLIOGRAPHY

- [231] T. Friščić, I. Halasz, P. J. Beldon, A. M. Belenguer, F. Adams, S. A. Kimber, V. Honkimäki, and R. E. Dinnebier, “Real-time and in situ monitoring of mechanochemical milling reactions,” *Nat. Chem.*, vol. 5, pp. 66–73, Jan. 2013.
- [232] D. Saha, K. M. O. Jensen, C. Tyrsted, E. D. Bøjesen, A. H. Mamakhel, A.-C. Dippel, M. Christensen, and B. B. Iversen, “In situ total X-ray scattering study of WO₃ nanoparticle formation under hydrothermal conditions,” *Angew. Chem. Int. Ed.*, vol. 53, no. 14, pp. 3667–3670, 2014.
- [233] D. P. Shoemaker, Y.-J. Hu, D. Y. Chung, G. J. Halder, P. J. Chupas, L. Soderholm, J. F. Mitchell, and M. G. Kanatzidis, “In situ studies of a platform for metastable inorganic crystal growth and materials discovery,” *Proc. Natl. Acad. Sci. USA*, vol. 111, pp. 10922–10927, July 2014.
- [234] A. D. Katsenis, A. Puškarić, V. Štrukil, C. Mottillo, P. A. Julien, K. Užarević, M.-H. Pham, T.-O. Do, S. A. J. Kimber, P. Lazić, O. Magdysyuk, R. E. Dinnebier, I. Halasz, and T. Friščić, “*In situ* x-ray diffraction monitoring of a mechanochemical reaction reveals a unique topology metal-organic framework,” *Nat. Commun.*, vol. 6, p. 6662, Mar. 2015.
- [235] D. Olds, P. F. Peterson, M. K. Crawford, J. R. Neilson, H.-W. Wang, P. S. Whitfield, and K. Page, “Combinatorial appraisal of transition states for in situ pair distribution function analysis,” *J. Appl. Crystallogr.*, vol. 50, pp. 1744–1753, Dec. 2017.
- [236] W. M. Terban, D. Banerjee, S. Ghose, B. Medasani, A. Shukla, B. A. Legg, Y. Zhou, Z. Zhu, M. L. Sushko, J. J. D. Yoreo, J. Liu, P. K. Thallapally, and S. J. L. Billinge, “Early stage structural development of prototypical zeolitic imidazolate framework (ZIF) in solution,” *Nanoscale*, vol. 10, no. 9, pp. 4291–4300, 2018.
- [237] H. Xu, S. Sommer, N. L. N. Broge, J. Gao, and B. B. Iversen, “The chemistry of nucleation: In situ pair distribution function analysis of secondary building units during UiO-66 MOF formation,” *Chem. Eur. J.*, vol. 25, pp. 2051–2058, Feb. 2019.
- [238] F. Zernike and J. A. Prins, “Die beugung von röntgenstrahlen in flüssigkeiten als effekt der molekülanordnung,” *Z. Phys.*, vol. 41, pp. 184–194, June 1927.
- [239] P. Debye and H. Menke, “The determination of the inner structure of liquids by x-ray means,” *Phys. Z.*, vol. 31, pp. 797–798, 1930.
- [240] B. E. Warren, H. Krutter, and O. Morningstar, “Fourier analysis of x-ray patterns of vitreous SiO₂ and B₂O₃,” *J. Am. Ceram. Soc.*, vol. 19, no. 1-12, pp. 202–206, 1936.

BIBLIOGRAPHY

- [241] B. E. Warren, "X-ray determination of the structure of liquids and glass," *J. Appl. Phys.*, vol. 8, pp. 645–654, Oct. 1937.
- [242] L. P. Tarasov and B. E. Warren, "X-ray diffraction study of liquid sodium," *J. Chem. Phys.*, vol. 4, pp. 236–238, Am. Pharm. Rev. 1936.
- [243] J. Morgan and B. E. Warren, "X-Ray analysis of the structure of water," *J. Chem. Phys.*, vol. 6, pp. 666–673, Nov. 1938.
- [244] R. E. Franklin, "The interpretation of diffuse x-ray diagrams of carbon," *Acta Crystallogr.*, vol. 3, pp. 107–121, Mar. 1950.
- [245] R. E. Franklin and J. T. Randall, "Crystallite growth in graphitizing and non-graphitizing carbons," *Proc. R. Soc. A*, vol. 209, pp. 196–218, Oct. 1951.
- [246] C. D. Hanson and T. Egami, "Distribution of Cs^+ ions in single and mixed alkali silicate glasses from energy dispersive x-ray diffraction," *J. Non-Cryst. Solids*, vol. 87, pp. 171–184, Oct. 1986.
- [247] A. C. Wright, "Diffraction studies of glass structure: The first 70 years," *Glass Phys. Chem.*, vol. 24, no. 3, pp. 148–179, 1998.
- [248] R. K. Crawford, R. T. Daly, J. R. Haumann, R. L. Hitterman, C. B. Morgan, G. E. Ostrowski, and T. G. Worlton, "The data acquisition system for the neutron scattering instruments at the Intense Pulsed Neutron Source," *IEEE T. Nucl. Sci.*, vol. 28, pp. 3692–3700, Oct. 1981.
- [249] S. Nanao, W. Dmowski, T. Egami, J. W. Richardson, and J. D. Jorgensen, "Structure of Al-Mn-Cr-Si quasicrystals studied by pulsed neutron scattering," *Phys. Rev. B*, vol. 35, pp. 435–440, Jan. 1987.
- [250] W. Dmowski, B. H. Toby, T. Egami, M. A. Subramanian, J. Gopalakrishnan, and A. W. Sleight, "Short-range ordering due to displacements of thallium and oxygen atoms in superconducting $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ observed by pulsed-neutron scattering," *Phys. Rev. Lett.*, vol. 61, pp. 2608–2611, Nov. 1988.
- [251] V. Petkov, I. Jeong, J. S. Chung, M. F. Thorpe, S. Kycia, and S. J. L. Billinge, "High real-space resolution measurement of the local structure of $\text{Ga}_{1-x}\text{In}_x\text{As}$ using X-ray diffraction," *Phys. Rev. Lett.*, vol. 83, no. 20, pp. 4089–4092, 1999.

BIBLIOGRAPHY

- [252] K. Kodama, S. Iikubo, T. Taguchi, and S. Shamoto, “Finite size effects of nanoparticles on the atomic pair distribution functions,” *Acta Crystallogr. A*, vol. 62, pp. 444–453, Nov. 2006.
- [253] B. Gilbert, “Finite size effects on the real-space pair distribution function of nanoparticles,” *J. Appl. Crystallogr.*, vol. 41, pp. 554–562, June 2008.
- [254] M. W. Terban, M. Johnson, M. DiMichiel, and S. J. L. Billinge, “Detection and characterization of nanoparticles in suspension at low concentrations using the x-ray total scattering pair distribution function technique,” *Nanoscale*, vol. 7, pp. 5480–5487, 2015.
- [255] S. Banerjee, C.-H. Liu, J. D. Lee, A. Kovyakh, V. Grasmik, O. Prymak, C. Koenigsmann, H. Liu, L. Wang, A. M. M. Abeykoon, S. S. Wong, M. Epple, C. B. Murray, and S. J. L. Billinge, “Improved models for metallic nanoparticle cores from atomic pair distribution function (PDF) analysis,” *J. Phys. Chem. C*, vol. 122, no. 51, pp. 29498–29506, 2018.
- [256] J. Lombardi, L. Yang, F. A. Pearsall, N. Farahmand, Z. Gai, S. J. L. Billinge, and S. O’Brien, “Stoichiometric control over ferroic behavior in $\text{Ba}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_3$ nanocrystals,” *Chem. Mater.*, vol. 31, pp. 1318–1335, Feb. 2019.
- [257] S. J. L. Billinge, “The atomic pair distribution function: past and present,” *Z. Kristallogr.*, vol. 219, pp. 117–121, 2004.
- [258] B. E. Warren, *X-ray Diffraction*. New York: Dover, 1990.
- [259] A. Guinier, *X-ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies*. San Francisco: W.H. Freeman, 1963.
- [260] J. Als-Nielsen and D. McMorrow, *Elements of Modern X-Ray Physics*. New York: Wiley, 2001.
- [261] W. H. Bragg and W. L. Bragg, “The reflection of x-rays by crystals,” *Proc. R. Soc. A*, vol. 88, pp. 428–438, July 1913.
- [262] C. L. Farrow and S. J. L. Billinge, “Relationship between the atomic pair distribution function and small angle scattering: implications for modeling of nanoparticles,” *Acta Crystallogr. A*, vol. 65, no. 3, pp. 232–239, 2009.
- [263] D. A. Keen, “A comparison of various commonly used correlation functions for describing total scattering,” *J. Appl. Crystallogr.*, vol. 34, pp. 172–177, Am. Pharm. Rev. 2001.

BIBLIOGRAPHY

- [264] T. E. Faber and J. M. Ziman, “A theory of the electrical properties of liquid metals,” *Phil. Mag.*, vol. 11, pp. 153–173, Jan. 1965.
- [265] P. Debye, “Zerstreuung von Röntgenstrahlen,” *Ann. Phys.*, vol. 351, no. 6, pp. 809–823, 1915.
- [266] S. J. L. Billinge and C. L. Farrow, “Towards a robust *ad-hoc* data correction approach that yields reliable atomic pair distribution functions from powder diffraction data,” *J. Phys: Condens. Mat.*, vol. 25, p. 454202, 2013.
- [267] V. I. Korsunskiy and R. B. Neder, “Exact model calculations of the total radial distribution functions for the x-ray diffraction case and systems of complicated chemical composition,” *J. Appl. Crystallogr.*, vol. 38, pp. 1020–1027, Dec. 2005.
- [268] O. Masson and P. Thomas, “Exact and explicit expression of the atomic pair distribution function as obtained from x-ray total scattering experiments,” *J. Appl. Crystallogr.*, vol. 46, pp. 461–465, Am. Pharm. Rev. 2013.
- [269] R. B. Neder and T. Proffen, “Exact and fast calculation of the x-ray pair distribution function,” *J. Appl. Crystallogr.*, vol. 53, pp. 710–721, June 2020.
- [270] B. H. Toby and T. Egami, “Accuracy of pair distribution function analysis applied to crystalline and non-crystalline materials,” *Acta Crystallogr. A*, vol. 48, pp. 336–346, May 1992.
- [271] A. Guinier, G. Fournet, and K. L. Yudowitch, *Small-Angle Scattering of x-Rays*. New York: John Wiley & Sons, Inc., 1955.
- [272] W. C. Röntgen, “On a new kind of ray, a preliminary communication,” *Wurzburg Phys.-Méd. Soc. Dec.*, vol. 28, 1895.
- [273] W. Friedrich, P. Knipping, and M. Laue, “Sitzungsber. Math. Phys. Kl. K.,” *Bayer. Akad. Wiss. München*, pp. 303–322, 1912.
- [274] J. M. Thomas, “The birth of x-ray crystallography,” *Nature*, vol. 491, pp. 186–187, Nov. 2012.
- [275] P. Debye and P. Scherrer, “Nachrichten von der gesellschaft der wissenschaften zu göttingen,” *Sitzungsber. Heidelb. Akad. Wiss. Math. Naturwiss. Kl.*, vol. 1, 1916.
- [276] A. W. Hull, “A new method of x-ray crystal analysis,” *Phys. Rev.*, vol. 10, pp. 661–696, Dec. 1917.

BIBLIOGRAPHY

- [277] H. G. J. Moseley, “LXXX. The high-frequency spectra of the elements. Part I,” *London Edinburgh Dublin Philos. Mag. & J. Sci.*, vol. 26, no. 160, pp. 1024–1032, 1913.
- [278] H. G. J. Moseley, “LXXX. The high-frequency spectra of the elements. Part II,” *London Edinburgh Dublin Philos. Mag. & J. Sci.*, vol. 27, pp. 703–713, Am. Pharm. Rev. 1914.
- [279] W. D. Coolidge, “X-ray tube,” Jan. 1917.
- [280] M. L. F. Nascimento, “Brief history of x-ray tube patents,” *World Pat. Inf.*, vol. 37, pp. 48–53, June 2014.
- [281] J. P. Blewett, “Synchrotron radiation – early history,” *J. Synchrotron Radiat.*, vol. 5, pp. 135–139, May 1998.
- [282] F. R. Elder, A. M. Gurewitsch, R. V. Langmuir, and H. C. Pollock, “Radiation from electrons in a synchrotron,” *Phys. Rev.*, vol. 71, pp. 829–830, June 1947.
- [283] I. M. Ternov, “Synchrotron radiation,” *Phys.-Usp.*, vol. 38, no. 4, p. 409, 1995.
- [284] A. Liénard, “L’Eclairage électrique,” *L’Eclairage électrique*, vol. 16, no. 5, 1898.
- [285] O. Heaviside, “The waste of energy from a moving electron,” *Nature*, vol. 67, pp. 6–8, Nov. 1902.
- [286] H. C. Pollock, “The discovery of synchrotron radiation,” *Am. J. Phys.*, vol. 51, pp. 278–280, Mar. 1983.
- [287] G. A. Schott, “über die strahlung von elektronengruppen,” *Ann. Phys.*, vol. 329, no. 14, pp. 635–660, 1907.
- [288] D. Castelvechi, “Next-generation x-ray source fires up,” *Nat. News*, vol. 525, p. 15, Sep. Purif. Technol. 2015.
- [289] P. Willmott, *An Introduction to Synchrotron Radiation: Techniques and Applications*. Hoboken, NJ, USA: John Wiley & Sons, second ed., 2019.
- [290] J. Chadwick, “Possible existence of a neutron,” *Nature*, vol. 129, pp. 312–312, Feb. 1932.
- [291] P. Preiswerk and H. von Halban, “Preuve experimental de la diffraction des neutrons,” *C. R. Acad. Sci.*, vol. 203, pp. 73–75, 1936.

BIBLIOGRAPHY

- [292] D. P. Mitchell and P. N. Powers, “Bragg reflection of slow neutrons,” *Phys. Rev.*, vol. 50, pp. 486–487, Sep. Purif. Technol. 1936.
- [293] E. Fermi, E. Amaldi, O. D’Agostino, F. Rasetti, E. Segrè, and E. Rutherford, “Artificial radioactivity produced by neutron bombardment,” *Proc. Phys. Soc. A*, vol. 146, pp. 483–500, Sep. Purif. Technol. 1934.
- [294] E. Fermi, E. Amaldi, B. Pontecorvo, F. Rasetti, and E. Segrè, “Azione di sostanze idrogenate sulla radioattività provocata da neutroni.I,” *Ric. Sci.*, vol. 5, pp. 282–283, Dec. 1934.
- [295] T. E. Mason, T. J. Gawne, S. E. Nagler, M. B. Nestor, and J. M. Carpenter, “The early development of neutron diffraction: Science in the wings of the Manhattan Project,” *Acta Crystallogr. A*, vol. 69, pp. 37–44, Jan. 2013.
- [296] H. L. Anderson, E. T. Booth, J. R. Dunning, E. Fermi, G. N. Glasoe, and F. G. Slack, “The fission of uranium,” *Phys. Rev.*, vol. 55, pp. 511–512, Mar. 1939.
- [297] E. O. Wollan and L. B. Borst, “Physics section III monthly report for the period ending December 31, 1944,” Tech. Rep. No.: M-CP-2222, Clinton Laboratories, Oak Ridge, TN, USA, 1945.
- [298] W. Sturm and W. H. Zinn, “Physics section III monthly report for the period ending December 31, 1944,” Tech. Rep. No.: CP-2436, Argonne Laboratory, Chicago, IL, USA, 1944.
- [299] M. L. Goldberger and F. Seitz, “Theory of the refraction and the diffraction of neutrons by crystals,” *Phys. Rev.*, vol. 71, pp. 294–310, Mar. 1947.
- [300] E. Fermi and L. Marshall, “Interference phenomena of slow neutrons,” *Phys. Rev.*, vol. 71, pp. 666–677, May 1947.
- [301] E. O. Wollan and C. G. Shull, “The diffraction of neutrons by crystalline powders,” *Phys. Rev.*, vol. 73, pp. 830–841, Am. Pharm. Rev. 1948.
- [302] C. G. Shull, “Early development of neutron scattering,” *Rev. Mod. Phys.*, vol. 67, pp. 753–757, Oct. 1995.
- [303] H. E. Fischer, G. J. Cuello, P. Palleau, D. Feltin, A. C. Barnes, Y. S. Badyal, and J. M. Simonson, “D4c: A very high precision diffractometer for disordered materials,” *Appl. Phys. A*, vol. 74, pp. s160–s162, Dec. 2002.

BIBLIOGRAPHY

- [304] T. Proffen, T. Egami, S. J. L. Billinge, A. K. Cheetham, D. Louca, and J. B. Parise, “Building a high resolution total scattering powder diffractometer – upgrade of NPD at MLNSC,” *Appl. Phys. A - Mater.*, vol. 74, pp. s163–s165, Dec. 2002.
- [305] C. G. Shull and E. O. Wollan, “X-Ray, electron, and neutron diffraction,” *Science*, vol. 108, no. 2795, pp. 69–75, 1948.
- [306] E. Fermi and L. Marshall, “On the interaction between neutrons and electrons,” *Phys. Rev.*, vol. 72, pp. 1139–1146, Dec. 1947.
- [307] G. E. Bacon, *Neutron Diffraction*. Oxford: Clarendon, 3rd ed., 1975.
- [308] H. E. Fischer, A. C. Barnes, and P. S. Salmon, “Neutron and x-ray diffraction studies of liquids and glasses,” *Rep. Prog. Phys.*, vol. 69, pp. 233–299, Nov. 2005.
- [309] A.-J. Dianoux and G. Lander, *Neutron Data Booklet*. Philadelphia, PA, USA: OCP-Science, second ed., July 2003.
- [310] S. Gautam, “Why hydrogen has more incoherent neutron scattering than deuteron?,” *ResearchGate*, Dec. 2017. https://www.researchgate.net/post/why_hydrogen_has_more_incoherent_neutron_scattering_than_deuteron.
- [311] K. Page, C. E. White, E. G. Estell, R. B. Neder, A. Llobet, and T. Proffen, “Treatment of hydrogen background in bulk and nanocrystalline neutron total scattering experiments,” *J. Appl. Crystallogr.*, vol. 44, pp. 532–539, June 2011.
- [312] P. F. Peterson, M. Gutmann, T. Proffen, and S. J. L. Billinge, “PDFgetN: a user-friendly program to extract the total scattering structure function and the pair distribution function from neutron powder diffraction data,” *J. Appl. Crystallogr.*, vol. 33, pp. 1192–1192, Aug 2000.
- [313] P. F. Peterson, E. S. Božin, T. Proffen, and S. J. L. Billinge, “Improved measures of quality for the atomic pair distribution function,” *J. Appl. Crystallogr.*, vol. 36, pp. 53–64, Feb. 2003.
- [314] A. K. Soper, “Inelasticity corrections for time-of-flight and fixed wavelength neutron diffraction experiments,” *Mol. Phys.*, vol. 107, pp. 1667–1684, Aug. 2009.
- [315] A. K. Soper, *GudrunN and GudrunX: Programs for Correcting Raw Neutron and x-Ray Diffraction Data to Differential Scattering Cross Section*. Swindon, UK: Science & Technology Facilities Council, 2011.

BIBLIOGRAPHY

- [316] M. G. Tucker, D. A. Keen, M. T. Dove, A. L. Goodwin, and Q. Hui, “RMCPProfile: Reverse Monte Carlo for polycrystalline materials,” *J. Phys.: Condens. Mat.*, vol. 19, no. 33, p. 335218, 2007.
- [317] A. Gagin and I. Levin, “A Bayesian approach to removal of incoherent scattering from neutron total-scattering data,” *J. Appl. Crystallogr.*, vol. 47, pp. 2060–2068, Dec. 2014.
- [318] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, “Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure,” *Phys. Rev. Lett.*, vol. 58, pp. 908–910, Mar. 1987.
- [319] F. W. Lytle, R. B. Gregor, and A. J. Panson, “Discussion of x-ray-absorption near-edge structure: Application to Cu in the high-T_c superconductors La_{1.8}Sr_{0.2}CuO₄ and YBa₂Cu₃O₇,” *Phys. Rev. B*, vol. 37, pp. 1550–1562, Feb. 1988.
- [320] A. Williams, G. H. Kwei, R. B. Von Dreele, I. D. Raistrick, and D. L. Bish, “Joint x-ray and neutron refinement of the structure of superconducting YBa₂Cu₃O_{7-x}: Precision structure, anisotropic thermal parameters, strain, and cation disorder,” *Phys. Rev. B*, vol. 37, pp. 7960–7962, May 1988.
- [321] A. Percheron-Guégan, C. Lartigue, J. C. Achard, P. Germi, and F. Tasset, “Neutron and x-ray diffraction profile analyses and structure of LaNi₅, LaNi_{5-x}Al_x and LaNi_{5-x}Mn_x intermetallics and their hydrides (deuterides),” *J. Less Common Met.*, vol. 74, pp. 1–12, Oct. 1980.
- [322] G. A. Lager, T. Armbruster, and J. Faber, “Neutron and x-ray diffraction study of hydrogarnet Ca₃Al₂(O₄H₄)₃,” *Am. Mineral.*, vol. 72, pp. 756–765, Aug. 1987.
- [323] S. M. Antao and I. Hassan, “The orthorhombic structure of CaCO₃, SrCO₃, PbCO₃ AND BaCO₃: Linear structural trends,” *Can. Mineral.*, vol. 47, pp. 1245–1255, Oct. 2009.
- [324] S. Schorr, “The crystal structure of kesterite type compounds: A neutron and x-ray diffraction study,” *Sol. Energy Mater. Sol. Cells*, vol. 95, pp. 1482–1488, June 2011.
- [325] M. A. Kiselev and D. Lombardo, “Structural characterization in mixed lipid membrane systems by neutron and X-ray scattering,” *Biochim. Biophys. Acta Gen. Subj.*, vol. 1861, pp. 3700–3717, Jan. 2017.

BIBLIOGRAPHY

- [326] A. H. Narten, “Liquid water: Atom pair correlation functions from neutron and x-ray diffraction,” *J. Chem. Phys.*, vol. 56, pp. 5681–5687, June 1972.
- [327] A. H. Narten, “Liquid carbon tetrachloride: Atom pair correlation functions from neutron and x-ray diffraction,” *J. Chem. Phys.*, vol. 65, pp. 573–579, July 1976.
- [328] A. K. Soper, “Joint structure refinement of x-ray and neutron diffraction data on disordered materials: Application to liquid water,” *J. Phys.: Condens. Matter*, vol. 19, p. 335206, July 2007.
- [329] F. Meersman, D. Bowron, A. K. Soper, and M. H. J. Koch, “An x-ray and neutron scattering study of the equilibrium between trimethylamine N-oxide and urea in aqueous solution,” *Phys. Chem. Chem. Phys.*, vol. 13, pp. 13765–13771, July 2011.
- [330] H.-W. Wang, M. Naguib, K. Page, D. J. Wesolowski, and Y. Gogotsi, “Resolving the structure of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes through multilevel structural modeling of the atomic pair distribution function,” *Chem. Mater.*, vol. 28, pp. 349–359, Jan. 2016.
- [331] Y. Ren and X. Zuo, “Synchrotron x-ray and neutron diffraction, total scattering, and small-angle scattering techniques for rechargeable battery research,” *Small Methods*, vol. 2, no. 8, p. 1800064, 2018.
- [332] K. Kupwade-Patil, P. J. Boul, D. K. Rasner, S. M. Everett, T. Proffen, K. Page, D. Ma, D. Olds, C. J. Thaemlitz, and O. Büyüköztürk, “Retarder effect on hydrating oil well cements investigated using in situ neutron/x-ray pair distribution function analysis,” *Cem. Concr. Res.*, vol. 126, p. 105920, Dec. 2019.
- [333] B. A. Frandsen, Q. Wang, S. Wu, J. Zhao, and R. J. Birgeneau, “Quantitative characterization of short-range orthorhombic fluctuations in FeSe through pair distribution function analysis,” *Phys. Rev. B*, vol. 100, p. 020504, July 2019.
- [334] P. J. Chupas, X. Qiu, J. C. Hanson, P. L. Lee, C. P. Grey, and S. J. L. Billinge, “Rapid-acquisition pair distribution function (RA-PDF) analysis,” *J. Appl. Crystallogr.*, vol. 36, pp. 1342–1347, Dec. 2003.
- [335] J. Neufeind, M. Feygenson, J. Carruth, R. Hoffmann, and K. K. Chipley, “The Nanoscale Ordered Materials Diffractometer NOMAD at the Spallation Neutron Source SNS,” *Nucl. Instrum. Meth. B*, vol. 287, pp. 68–75, Sep. Purif. Technol. 2012.
- [336] A. P. Hammersley, “FIT2D: A multi-purpose data reduction, analysis and visualization program,” *J. Appl. Crystallogr.*, vol. 49, pp. 646–652, Am. Pharm. Rev. 2016.

BIBLIOGRAPHY

- [337] G. Ashiotis, A. Deschildre, Z. Nawaz, J. P. Wright, D. Karkoulis, F. E. Picca, and J. Kieffer, “The fast azimuthal integration Python library: pyFAI,” *J. Appl. Crystallogr.*, vol. 48, pp. 510–519, Am. Pharm. Rev. 2015.
- [338] P. Juhás, T. Davis, C. L. Farrow, and S. J. L. Billinge, “PDFgetX3: A rapid and highly automatable program for processing powder diffraction data into total scattering pair distribution functions,” *J. Appl. Crystallogr.*, vol. 46, pp. 560–566, 2013.
- [339] X. Yang, P. Juhás, C. L. Farrow, and S. J. L. Billinge, “xPDFsuite: An end-to-end software solution for high throughput pair distribution function transformation, visualization and analysis,” *arXiv:1402.3163*, Feb. 2015.
- [340] A. K. Soper and E. R. Barney, “Extracting the pair distribution function from white-beam x-ray total scattering data,” *J. Appl. Crystallogr.*, vol. 44, pp. 714–726, Aug. 2011.
- [341] O. Arnold, J. C. Bilheux, J. M. Borreguero, A. Buts, S. I. Campbell, L. Chapon, M. Doucet, N. Draper, R. Ferraz Leal, M. A. Gigg, V. E. Lynch, A. Markvardsen, D. J. Mikkelsen, R. L. Mikkelsen, R. Miller, K. Palmen, P. Parker, G. Passos, T. G. Perring, P. F. Peterson, S. Ren, M. A. Reuter, A. T. Savici, J. W. Taylor, R. J. Taylor, R. Tolchenov, W. Zhou, and J. Zikovsky, “Mantid—Data analysis and visualization package for neutron scattering and μ SR experiments,” *Nucl. Instrum. Meth. A*, vol. 764, pp. 156–166, Nov. 2014.
- [342] L. M. D. Cranswick, “Computer Software for Powder Diffraction,” in *Powder Diffraction: Theory and Practice* (R. E. Dinnebier and S. J. L. Billinge, eds.), pp. 494–570, Royal Society of Chemistry, 2008.
- [343] C. L. Farrow, P. Juhás, J. Liu, D. Bryndin, E. S. Božin, J. Bloch, T. Proffen, and S. J. L. Billinge, “PDFfit2 and PDFgui: Computer programs for studying nanostructure in crystals,” *J. Phys. Condens. Mat.*, vol. 19, p. 335219, 2007.
- [344] A. A. Coelho, “TOPAS and TOPAS-Academic: An optimization program integrating computer algebra and crystallographic objects written in C++,” *J. Appl. Crystallogr.*, vol. 51, pp. 210–218, Feb. 2018.
- [345] P. Juhás, C. L. Farrow, X. Yang, K. R. Knox, and S. J. L. Billinge, “Complex modeling: a strategy and software program for combining multiple information sources to solve ill-posed structure and nanostructure inverse problems,” *Acta Crystallogr. A*, vol. 71, pp. 562–568, Nov 2015.

BIBLIOGRAPHY

- [346] V. Petkov and N. Bakaltchev, “FIT, a computer program for decomposition of powder diffraction patterns and profile analysis of pair correlation functions,” *J. Appl. Crystallogr.*, vol. 23, pp. 138–140, Am. Pharm. Rev. 1990.
- [347] T. Proffen and S. J. L. Billinge, “PDFFIT, a program for full profile structural refinement of the atomic pair distribution function,” *J. Appl. Crystallogr.*, vol. 32, pp. 572–575, June 1999.
- [348] A. Gagin, A. J. Allen, and I. Levin, “Combined fitting of small- and wide-angle x-ray total scattering data from nanoparticles: Benefits and issues,” *J. Appl. Crystallogr.*, vol. 47, pp. 619–629, Am. Pharm. Rev. 2014.
- [349] R. L. McGreevy and L. Pusztai, “Reverse Monte Carlo simulation: A new technique for the determination of disordered structures,” *Mol. Simul.*, vol. 1, pp. 359–367, Dec. 1988.
- [350] R. L. McGreevy, “Reverse Monte Carlo modelling,” *J. Phys.: Condens. Mat.*, vol. 13, no. 46, p. R877, 2001.
- [351] T. Proffen and R. B. Neder, “DISCUS: A program for diffuse scattering and defect-structure simulation,” *J. Appl. Crystallogr.*, vol. 30, pp. 171–175, Am. Pharm. Rev. 1997.
- [352] K. Page, T. C. Hood, T. Proffen, and R. B. Neder, “Building and refining complete nanoparticle structures with total scattering data,” *J. Appl. Crystallogr.*, vol. 44, pp. 327–336, Am. Pharm. Rev. 2011.
- [353] B. Aoun, “Fullrmc, a rigid body reverse monte carlo modeling package enabled with machine learning and artificial intelligence,” *J. Comput. Chem.*, vol. 37, no. 12, pp. 1102–1111, 2016.
- [354] A. K. Soper, “Partial structure factors from disordered materials diffraction data: An approach using empirical potential structure refinement,” *Phys. Rev. B*, vol. 72, p. 104204, Sep. Purif. Technol. 2005.
- [355] S. J. L. Billinge and M. F. Thorpe, eds., *Local Structure from Diffraction*. New York, NY, USA: Plenum, 1998.
- [356] I. Jeong, T. Proffen, F. Mohiuddin-Jacobs, and S. J. L. Billinge, “Measuring correlated atomic motion using x-ray diffraction,” *J. Phys. Chem. A*, vol. 103, pp. 921–924, 1999.

BIBLIOGRAPHY

- [357] S. Banerjee, C.-H. Liu, K. M. Ø. Jensen, P. Juhás, J. D. Lee, M. Tofanelli, C. J. Ackerson, C. B. Murray, and S. J. L. Billinge, “Cluster-mining: An approach for determining core structures of metallic nanoparticles from atomic pair distribution function data,” *Acta Crystallogr. A*, vol. 76, pp. 24–31, Jan. 2020.
- [358] A. Cervellino, C. Giannini, and A. Guagliardi, “On the efficient evaluation of Fourier patterns for nanoparticles and clusters,” *J. Comput. Chem.*, vol. 27, no. 9, pp. 995–1008, 2006.
- [359] J. D. Hanawalt, H. W. Rinn, and L. K. Frevel, “Chemical analysis by x-ray diffraction,” *Ind. Eng. Chem., Anal. Ed.*, vol. 10, pp. 457–512, Sep. Purif. Technol. 1938.
- [360] R. G. Marquart, I. Katsnelson, G. W. A. Milne, S. R. Heller, G. G. Johnson, and R. Jenkins, “A search-match system for x-ray powder diffraction data,” *J. Appl. Crystallogr.*, vol. 12, pp. 629–634, Dec. 1979.
- [361] C. J. Gilmore, G. Barr, and J. Paisley, “High-throughput powder diffraction. I. A new approach to qualitative and quantitative powder diffraction pattern analysis using full pattern profiles,” *J. Appl. Crystallogr.*, vol. 37, pp. 231–242, Am. Pharm. Rev. 2004.
- [362] G. Barr, C. J. Gilmore, and J. Paisley, “SNAP-1D: A computer program for qualitative and quantitative powder diffraction pattern analysis using the full pattern profile,” *J. Appl. Crystallogr.*, vol. 37, pp. 665–668, Aug. 2004.
- [363] B. H. Toby, “CMPR – a powder diffraction toolkit,” *J. Appl. Crystallogr.*, vol. 38, pp. 1040–1041, Dec. 2005.
- [364] A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, and R. Rizzi, “QUALX: A computer program for qualitative analysis using powder diffraction data,” *J. Appl. Crystallogr.*, vol. 41, pp. 815–817, Aug. 2008.
- [365] T. Degen, M. Sadki, E. Bron, U. König, and G. Nénert, “The HighScore suite,” *Powder Diffr.*, vol. 29, pp. S13–S18, Dec. 2014.
- [366] A. Altomare, N. Corriero, C. Cuocci, A. Falcicchio, A. Moliterni, and R. Rizzi, “QUALX2.0: A qualitative phase analysis software using the freely available database POW_COD,” *J. Appl. Crystallogr.*, vol. 48, pp. 598–603, Am. Pharm. Rev. 2015.
- [367] P. Boullay, L. Lutterotti, D. Chateigner, and L. Sicard, “Fast microstructure and phase analyses of nanopowders using combined analysis of transmission electron microscopy scattering patterns,” *Acta Crystallogr. A*, vol. 70, pp. 448–456, Sep. Purif. Technol. 2014.

BIBLIOGRAPHY

- [368] L. Lutterotti, H. Pillière, C. Fontugne, P. Boullay, and D. Chateigner, “Full-profile search–match by the Rietveld method,” *J. Appl. Crystallogr.*, vol. 52, pp. 587–598, June 2019.
- [369] J. W. Lewis, J. L. Payne, I. R. Evans, H. T. Stokes, B. J. Campbell, and J. S. O. Evans, “An exhaustive symmetry approach to structure determination: phase transitions in $\text{Bi}_2\text{Sn}_2\text{O}_7$,” *J. Am. Chem. Soc.*, vol. 138, pp. 8031–8042, June 2016.
- [370] L. Yang, P. Juhás, M. W. Terban, M. G. Tucker, and S. J. L. Billinge, “Structure-mining: Screening structure models by automated fitting to the atomic pair distribution function over large numbers of models,” *Acta Crystallogr. A*, vol. 76, pp. 395–409, May 2020.
- [371] A. White, “The Materials Genome Initiative: One year on,” *MRS Bull.*, vol. 37, pp. 715–716, Aug. 2012.
- [372] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, and K. A. Persson, “Commentary: The Materials Project: A materials genome approach to accelerating materials innovation,” *APL Mat.*, vol. 1, p. 011002, July 2013.
- [373] C. M. Simon, J. Kim, D. A. Gomez-Gualdrón, J. S. Camp, Y. G. Chung, R. L. Martin, R. Mercado, M. W. Deem, D. Gunter, M. Haranczyk, D. S. Sholl, R. Q. Snurr, and B. Smit, “The materials genome in action: Identifying the performance limits for methane storage,” *Energy Environ. Sci.*, vol. 8, no. 4, pp. 1190–1199, 2015.
- [374] S. Curtarolo, G. L. W. Hart, M. B. Nardelli, N. Mingo, S. Sanvito, and O. Levy, “The high-throughput highway to computational materials design,” *Nature Mater.*, vol. 12, pp. 191–201, Mar. 2013.
- [375] G. Bergerhoff, R. Hundt, R. Sievers, and I. D. Brown, “The inorganic crystal structure data base,” *J. Chem. Inf. Comput. Sci.*, vol. 23, pp. 66–69, May 1983.
- [376] A. Belsky, M. Hellenbrandt, V. L. Karen, and P. Luksch, “New developments in the Inorganic Crystal Structure Database (ICSD): Accessibility in support of materials research and design,” *Acta Crystallogr. B*, vol. 58, pp. 364–369, June 2002.
- [377] R. T. Downs and M. Hall-Wallace, “The American Mineralogist crystal structure database,” *Am. Mineral.*, vol. 88, pp. 247–250, Jan. 2003.

BIBLIOGRAPHY

- [378] A. V. Chichagov, D. A. Varlamov, R. A. Dilanyan, T. N. Dokina, N. A. Drozhzhina, O. L. Samokhvalova, and T. V. Ushakovskaya, “MINCRYST: A crystallographic database for minerals, local and network (WWW) versions,” *Crystallogr. Rep.*, vol. 46, pp. 876–879, Sep. Purif. Technol. 2001.
- [379] S. Gražulis, D. Chateigner, R. T. Downs, A. F. T. Yokochi, M. Quirós, L. Lutterotti, E. Manakova, J. Butkus, P. Moeck, and A. Le Bail, “Crystallography Open Database - an open-access collection of crystal structures,” *J. Appl. Crystallogr.*, vol. 42, pp. 726–729, Aug. 2009.
- [380] S. Curtarolo, W. Setyawan, S. Wang, J. Xue, K. Yang, R. H. Taylor, L. J. Nelson, G. L. W. Hart, S. Sanvito, M. Buongiorno-Nardelli, N. Mingo, and O. Levy, “AFLOWLIB.ORG: A distributed materials properties repository from high-throughput ab initio calculations,” *Comput. Mater. Sci.*, vol. 58, pp. 227–235, June 2012.
- [381] J. E. Saal, S. Kirklin, M. Aykol, B. Meredig, and C. Wolverton, “Materials design and discovery with high-throughput density functional theory: The Open Quantum Materials Database (OQMD),” *JOM*, vol. 65, pp. 1501–1509, Nov. 2013.
- [382] S. Kirklin, J. E. Saal, B. Meredig, A. Thompson, J. W. Doak, M. Aykol, S. Rühl, and C. Wolverton, “The Open Quantum Materials Database (OQMD): Assessing the accuracy of DFT formation energies,” *Npj Comput. Mater.*, vol. 1, p. 15010, Dec. 2015.
- [383] ICDD, *The Powder Diffraction File*. International Centre for Diffraction Data, Newton Square, PA, USA, 2019.
- [384] S. P. Ong, W. D. Richards, A. Jain, G. Hautier, M. Kocher, S. Cholia, D. Gunter, V. L. Chevrier, K. A. Persson, and G. Ceder, “Python Materials Genomics (pymatgen): A robust, open-source python library for materials analysis,” *Comp. Mater. Sci.*, vol. 68, pp. 314–319, Feb. 2013.
- [385] S. P. Ong, S. Cholia, A. Jain, M. Brafman, D. Gunter, G. Ceder, and K. A. Persson, “The Materials Application Programming Interface (API): A simple, flexible and efficient API for materials data based on REpresentational State Transfer (REST) principles,” *Comp. Mater. Sci.*, vol. 97, pp. 209–215, Feb. 2015.
- [386] C. L. Farrow, M. Shaw, H.-J. Kim, P. Juhás, and S. J. L. Billinge, “The Nyquist-Shannon sampling theorem and the atomic pair distribution function,” *Phys. Rev. B*, vol. 84, p. 134105, 2011.

BIBLIOGRAPHY

- [387] K. Levenberg, “A method for the solution of certain non-linear problems in least squares,” *Q. Appl. Math.*, vol. 2, pp. 164–168, July 1944.
- [388] D. W. Marquardt, “An algorithm for least-squares estimation of nonlinear parameters,” *J. Soc. Ind. Appl. Math.*, vol. 11, pp. 431–441, June 1963.
- [389] E. Jones, T. Oliphant, and P. Peterson, *SciPy: Open source scientific tools for Python*. <http://www.scipy.org/>, 2001.
- [390] R. A. Young, *The Rietveld Method*. Oxford University Press, 1993.
- [391] C. A. Floudas and P. M. Pardalos, *Encyclopedia of Optimization*. Springer Science & Business Media, 2001.
- [392] C. F. Gauss, *Theoria motus corporum coelestium in sectionibus conicis solem ambientium*. Perthes et Besser, 1809.
- [393] R. Fletcher, “Modified Marquardt subroutine for nonlinear least squares,” Tech. Rep. AERE-R-6799, Atomic Energy Research Establishment, Harwell (England), Jan. 1971.
- [394] M. J. D. Powell, “An efficient method for finding the minimum of a function of several variables without calculating derivatives,” *Comput. J.*, vol. 7, pp. 155–162, Jan. 1964.
- [395] C. S. Lewis, D. Moronta, M. W. Terban, L. Wang, S. Yue, C. Zhang, Q. Li, A. Corrao, S. J. L. Billinge, and S. S. Wong, “Synthesis, characterization, and growth mechanism of motifs of ultrathin cobalt-substituted $\text{NaFeSi}_2\text{O}_6$ nanowires,” *CrystEngComm*, vol. 20, pp. 223–236, 2018.
- [396] B. A. Frandsen, Z. Gong, M. W. Terban, S. Banerjee, B. Chen, C. Jin, M. Feygenson, Y. J. Uemura, and S. J. L. Billinge, “Local atomic and magnetic structure of dilute magnetic semiconductor $(\text{Ba,K})(\text{Zn,Mn})_2\text{As}_2$,” *Phys. Rev. B*, vol. 94, p. 094102, 2016. selected as Editors’ Suggestion.
- [397] B. A. Frandsen and S. J. L. Billinge, “Magnetic structure determination from the magnetic pair distribution function (mPDF): ground state of MnO ,” *Acta Crystallogr. A*, vol. 71, no. 3, pp. 325–334, 2015.
- [398] P. Urbankowski, B. Anasori, K. Hantanasirisakul, L. Yang, L. Zhang, B. Haines, S. J. May, S. J. L. Billinge, and Y. Gogotsi, “2D molybdenum and vanadium nitrides synthesized by ammoniation of 2D transition metal carbides (MXenes),” *Nanoscale*, vol. 9, pp. 17722–17730, Nov. 2017.

BIBLIOGRAPHY

- [399] G. Shirane, H. Danner, and R. Pepinsky, “Neutron diffraction study of orthorhombic BaTiO_3 ,” *Phys. Rev.*, vol. 105, pp. 856–860, Feb. 1957.
- [400] C. Srilakshmi, R. Saraf, V. Prashanth, G. M. Rao, and C. Shivakumara, “Structure and catalytic activity of Cr-doped BaTiO_3 nanocatalysts synthesized by conventional oxalate and microwave assisted hydrothermal methods,” *Inorg. Chem.*, vol. 55, pp. 4795–4805, May 2016.
- [401] L. Zeng and Y. Jiang, “X-ray diffraction study of orthorhombic barium titanate,” *Beijing Gongye Daxue Xuebao*, vol. 17, pp. 32–37, 1991.
- [402] J. Akimoto, Y. Gotoh, and Y. Oosawa, “Refinement of hexagonal BaTiO_3 ,” *Acta Crystallogr. C*, vol. 50, pp. 160–161, Feb. 1994.
- [403] C. J. Xiao, C. Q. Jin, and X. H. Wang, “Crystal structure of dense nanocrystalline BaTiO_3 ceramics,” *Mater. Chem. Phys.*, vol. 111, pp. 209–212, Oct. 2008.
- [404] J. Donohue, S. J. Miller, and R. F. Cline, “The effect of various substituents on the lattice constants of tetragonal titanate,” *Acta Crystallogr.*, vol. 11, pp. 693–695, Oct. 1958.
- [405] S. A. Hayward, S. A. T. Redfern, H. J. Stone, M. G. Tucker, K. R. Whittle, and W. G. Marshall, “Phase transitions in BaTiO_3 : A high-pressure neutron diffraction study,” *Z. Kristallogr.*, vol. 220, no. 8, pp. 735–739, 2005.
- [406] P. Hohenberg and W. Kohn, “Inhomogeneous electron gas,” *Phys. Rev.*, vol. 136, pp. B864–B871, Nov. 1964.
- [407] W. Kohn and L. J. Sham, “Self-consistent equations including exchange and correlation effects,” *Phys. Rev.*, vol. 140, pp. A1133–A1138, Nov. 1965.
- [408] D. I. Woodward, I. M. Reaney, G. Y. Yang, E. C. Dickey, and C. A. Randall, “Vacancy ordering in reduced barium titanate,” *Appl. Phys. Lett.*, vol. 84, pp. 4650–4652, May 2004.
- [409] S. Wada, M. Yano, T. Suzuki, and T. Noma, “Crystal structure of barium titanate fine particles including Mg and analysis of their lattice vibration,” *J. Mater. Sci.*, vol. 35, pp. 3889–3902, Aug. 2000.
- [410] T. A. Vanderah, T. Siegrist, R. S. Roth, A. P. Ramirez, and R. G. Geyer, “Crystal structure and properties of $\text{Ba}_{11}\text{FeTi}_{27}\text{O}_{66.5}$,” *Eur. J. Inorg. Chem.*, vol. 2004, no. 12, pp. 2434–2441, 2004.

BIBLIOGRAPHY

- [411] K. Nishimura, I. Yamada, K. Oka, Y. Shimakawa, and M. Azuma, “High-pressure synthesis of BaVO_3 : A new cubic perovskite,” *J. Phys. Chem. Solids*, vol. 75, pp. 710–712, June 2014.
- [412] M. Erchak, I. Fankuchen, and R. Ward, “Reaction between ferric oxide and barium carbonate in the solid phase. Identification of phases by x-ray diffraction,” *J. Am. Chem. Soc.*, vol. 68, pp. 2085–2093, Oct. 1946.
- [413] J. Balachandran, L. Lin, J. S. Anchell, C. A. Bridges, and P. Ganesh, “Defect genome of cubic perovskites for fuel cell applications,” *J. Phys. Chem. C*, vol. 121, pp. 26637–26647, Dec. 2017.
- [414] Y. Grin, H. Müller-Buschbaum, and H. G. von Schnering, “„ BaNb_3O_6 “ ist ein Perowskit BaNbO_3 , eine Korrektur und ein Beitrag zu Ba_xNbO_3 /“ BaNb_3O_6 “ is a Perovskite BaNbO_3 , a Correction and a Contribution to Ba_xNbO_3 ,” *Z. Naturforsch. B*, vol. 52, no. 2, pp. 153–156, 2014.
- [415] M. Marezio and P. D. Dernier, “The crystal structure of Ti_4O_7 , a member of the homologous series $\text{Ti}_n\text{O}_{2n-1}$,” *J. Solid State Chem.*, vol. 3, pp. 340–348, Aug. 1971.
- [416] J. L. Hodeau and M. Marezio, “Structural aspects of the metal-insulator transitions in $(\text{Ti}_{0.9975}\text{V}_{0.0025})_4\text{O}_7$,” *J. Solid State Chem.*, vol. 29, pp. 47–62, July 1979.
- [417] M. Marezio, D. B. McWhan, P. D. Dernier, and J. P. Remeika, “Structural aspects of the metal-insulator transitions in Ti_4O_7 ,” *J. Solid State Chem.*, vol. 6, pp. 213–221, Feb. 1973.
- [418] M. Marezio, D. Tranqui, S. Lakkis, and C. Schlenker, “Phase transitions in Ti_5O_9 single crystals: Electrical conductivity, magnetic susceptibility, specific heat, electron paramagnetic resonance, and structural aspects,” *Phys. Rev. B*, vol. 16, pp. 2811–2821, Sep. Purif. Technol. 1977.
- [419] S. Andersson, “The crystal structure of Ti_5O_9 ,” *Acta Chem. Scand.*, vol. 14, pp. 1161–1172, 1960.
- [420] S. Andersson and A. Magnéli, “Diskrete titanoxydphasen im zusammensetzungsbereich $\text{TiO}_{1.75}$ - $\text{TiO}_{1.90}$,” *Naturwiss.*, vol. 43, pp. 495–496, Jan. 1956.
- [421] S. Andersson, B. Collén, U. Kuylenstierna, and A. Magnéli, “Phase analysis studies on the titanium-oxygen system,” *Acta Chem. Scand.*, vol. 11, no. 10, pp. 1641–1652, 1957.

BIBLIOGRAPHY

- [422] W. Setyawan and S. Curtarolo, “High-throughput electronic band structure calculations: Challenges and tools,” *Comp. Mater. Sci.*, vol. 49, pp. 299–312, Aug. 2010.
- [423] J. R. Clark, D. E. Appleman, and J. J. Papike, “Crystal-chemical characterization of clinopyroxenes based on eight new structure refinements,” *Mineral. Soc. Am. Spec. Pap.*, vol. 2, pp. 31–50, 1969.
- [424] S. Sueno, M. Cameron, J. J. Papike, and C. T. Prewitt, “The high temperature crystal chemistry of tremolite,” *Am. Mineral.*, vol. 58, pp. 649–664, Aug. 1973.
- [425] R. M. Thompson and R. T. Downs, “Model pyroxenes II: Structural variation as a function of tetrahedral rotation,” *Am. Mineral.*, vol. 89, no. 4, pp. 614–628, 2004.
- [426] G. J. Redhammer, G. Amthauer, W. Lottermoser, and W. Treutmann, “Synthesis and structural properties of clinopyroxenes of the hedenbergite $\text{CaFe}^{2+}\text{Si}_2\text{O}_6$ – aegirine $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ solid-solution series,” *Eur. J. Mineral.*, vol. 12, pp. 105–120, Jan. 2000.
- [427] G. J. Redhammer, G. Amthauer, G. Roth, G. Tippelt, and W. Lottermoser, “Single-crystal x-ray diffraction and temperature dependent ^{57}Fe Mossbauer spectroscopy on the hedenbergite-aegirine $(\text{Ca}, \text{Na})(\text{Fe}^{2+}, \text{Fe}^{3+}) \text{Si}_2\text{O}_6$ solid solution,” *Am. Mineral.*, vol. 91, no. 8-9, pp. 1271–1292, 2006.
- [428] F. Nestola, M. Tribaudino, T. Boffa Ballaran, C. Liebske, and M. Bruno, “The crystal structure of pyroxenes along the jadeite–hedenbergite and jadeite–aegirine joins,” *Am. Mineral.*, vol. 92, no. 8-9, pp. 1492–1501, 2007.
- [429] A. C. McCarthy, R. T. Downs, R. M. Thompson, and G. J. Redhammer, “In situ high-pressure single-crystal x-ray study of aegirine, $\text{NaFe}^{3+} \text{Si}_2\text{O}_6$, and the role of M1 size in clinopyroxene compressibility,” *Am. Mineral.*, vol. 93, no. 11-12, pp. 1829–1837, 2008.
- [430] H. Ohashi, T. Fujita, and T. Osawa, “The crystal structure of $\text{NaGaSi}_2\text{O}_6$ pyroxene,” *J. Jpn. Assoc. Mineral. Petrol. Econ. Geol.*, vol. 78, pp. 159–163, May 1983.
- [431] H. Ohashi, T. Osawa, and A. Sato, “Low-density form of $\text{NaGaSi}_2\text{O}_6$,” *Acta Crystallogr. C*, vol. 51, pp. 2476–2477, Dec. 1995.
- [432] F. Nestola, N. Rotiroti, M. Bruno, M. Tribaudino, S. van Smaalen, H. Ohashi, and G. J. Redhammer, “Low-temperature behavior of $\text{NaGaSi}_2\text{O}_6$,” *Am. Mineral.*, vol. 92, pp. 560–569, Am. Pharm. Rev. 2007.

BIBLIOGRAPHY

- [433] T. Ozawa, M. M. Olmstead, S. L. Brock, S. M. Kauzlarich, and D. M. Young, “Synthesis and characterization of a new compound with alternating MnO_{22-} and $\text{Zn}_2\text{As}_{22-}$ layers: $\text{Ba}_2\text{MnZn}_2\text{As}_2\text{O}_2$,” *Chem. Mater.*, vol. 10, pp. 392–396, Jan. 1998.
- [434] A. Hellmann, A. Löhken, A. Wurth, and A. Mewis, “Neue arsenide mit ThCr_2Si_2 -oder einer damit verwandten struktur: Die verbindungen ARh_2As_2 (A: Eu, Sr, Ba) und BaZn_2As_2 /new arsenides with ThCr_2Si_2 -type or related structures: The compounds ARh_2As_2 (A: Eu, Sr, Ba) and BaZn_2As_2 ,” *Z. Naturforsch. B*, vol. 62, no. 2, pp. 155–161, 2007.
- [435] K. Zhao, Z. Deng, X. C. Wang, W. Han, J. L. Zhu, X. Li, Q. Q. Liu, R. C. Yu, T. Goko, B. Frandsen, L. Liu, F. Ning, Y. J. Uemura, H. Dabkowska, G. M. Luke, H. Luetkens, E. Morenzoni, S. R. Dunsiger, A. Senyshyn, P. Böni, and C. Q. Jin, “New diluted ferromagnetic semiconductor with Curie temperature up to 180 K and isostructural to the ‘122’ iron-based superconductors,” *Nat. Commun.*, vol. 4, p. 1442, Dec. 2013.
- [436] M. Rotter, M. Tegel, and D. Johrendt, “Superconductivity at 38 K in the iron arsenide $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$,” *Phys. Rev. Lett.*, vol. 101, p. 107006, Sep. Purif. Technol. 2008.
- [437] B. Frandsen, X. Yang, and S. J. L. Billinge, “Magnetic pair distribution function analysis of local magnetic correlations,” *Acta Crystallogr. A*, vol. 70, pp. 3–11, Jan. 2014.
- [438] B. A. Frandsen, M. Brunelli, K. Page, Y. J. Uemura, J. B. Staunton, and S. J. L. Billinge, “Verification of anderson superexchange in mno via magnetic pair distribution function analysis and *ab initio* theory,” *Phys. Rev. Lett.*, vol. 116, p. 197204, May 2016.
- [439] C. G. Shull, W. A. Strauser, and E. O. Wollan, “Neutron diffraction by paramagnetic and antiferromagnetic substances,” *Phys. Rev.*, vol. 83, pp. 333–345, July 1951.
- [440] W. L. Roth, “Magnetic structures of MnO , FeO , CoO , and NiO ,” *Phys. Rev.*, vol. 110, pp. 1333–1341, June 1958.
- [441] A. L. Goodwin, M. G. Tucker, M. T. Dove, and D. A. Keen, “Magnetic structure of MnO at 10 K from total neutron scattering data,” *Phys. Rev. Lett.*, vol. 96, p. 047209, Feb. 2006.
- [442] J. Zhang, “Room-temperature compressibilities of MnO and CdO : Further examination of the role of cation type in bulk modulus systematics,” *Phys. Chem. Miner.*, vol. 26, pp. 644–648, Sep. Purif. Technol. 1999.

BIBLIOGRAPHY

- [443] D. Prill, P. Juhás, M. U. Schmidt, and S. J. L. Billinge, “Modelling pair distribution functions (PDFs) of organic compounds: Describing both intra- and intermolecular correlation functions in calculated PDFs,” *J. Appl. Crystallogr.*, vol. 48, pp. 171–178, Feb. 2015.
- [444] D. Prill, P. Juhás, S. J. L. Billinge, and M. U. Schmidt, “Towards solution and refinement of organic crystal structures by fitting to the atomic pair distribution function,” *Acta Crystallogr. A*, vol. 72, pp. 62–72, Jan. 2016.
- [445] F. H. Allen, “The Cambridge Structural Database: A quarter of a million crystal structures and rising,” *Acta Crystallogr. B*, vol. 58, pp. 380–388, June 2002.
- [446] J. W. Edwards, R. Speiser, and H. L. Johnston, “Structure of barium titanate at elevated temperatures,” *J. Am. Chem. Soc.*, vol. 73, pp. 2934–2935, June 1951.
- [447] J. Quinson, L. Kacenauskaite, T. L. Christiansen, T. Vosch, M. Arenz, and K. M. Ø. Jensen, “Spatially localized synthesis and structural characterization of platinum nanocrystals obtained using UV light,” *ACS Omega*, vol. 3, pp. 10351–10356, Aug. 2018.
- [448] L. Yang, E. A. Culbertson, N. K. Thomas, H. T. Vuong, E. T. S. Kjær, K. M. Ø. Jensen, M. G. Tucker, and S. J. L. Billinge, “A cloud platform for atomic pair distribution function analysis: PDFitc,” *Acta Crystallogr. A*, vol. 77, Jan. 2021.
- [449] E. Holland-Moritz, “Coexistence of valence fluctuating and stable Pr ions in Pr_6O_{11} ,” *Z. Phys. B*, vol. 89, no. 3, pp. 285–288, 1992.
- [450] S. Ramdas, K. C. Patil, and C. N. R. Rao, “Thermodynamics and kinetics of oxidation of Pr_2O_3 and Tb_2O_3 to non-stoichiometric oxides,” *J. Chem. Soc. A*, pp. 64–68, Jan. 1970.
- [451] A. F. Andreeva, I. Y. Gil’man, M. Y. Gamarnik, and V. I. Dekhtyaruk, “Structure and optical absorption of praseodymium oxides,” *Izv. Akad. Nauk SSSR, Neorg. Mater.*, vol. 22, no. 8, pp. 1320–1325, 1986.
- [452] S. Stotz and C. Wagner, “The solubility of water vapor and hydrogen in solid oxides,” *Ber. Bunsenges. Phys. Chem.*, vol. 70, no. 8, p. 781788, 1966.
- [453] C. Nicollet, A. Flura, V. Vibhu, A. Rougier, J.-M. Bassat, and J.-C. Grenier, “An innovative efficient oxygen electrode for SOFC: Pr_6O_{11} infiltrated into Gd-doped ceria backbone,” *Int. J. Hydrog. Energy*, vol. 41, pp. 15538–15544, Sep. Purif. Technol. 2016.

BIBLIOGRAPHY

- [454] T. Trindade, P. O'Brien, and N. L. Pickett, "Nanocrystalline semiconductors: Synthesis, properties, and perspectives," *Chem. Mater.*, vol. 13, pp. 3843–3858, Nov. 2001.
- [455] G. J. Snyder and E. S. Toberer, "Complex thermoelectric materials," *Nature Mater.*, vol. 7, pp. 105–114, Feb. 2008.
- [456] G. Fiori, F. Bonaccorso, G. Iannaccone, T. Palacios, D. Neumaier, A. Seabaugh, S. K. Banerjee, and L. Colombo, "Electronics based on two-dimensional materials," *Nature Nanotech.*, vol. 9, pp. 768–779, Oct. 2014.
- [457] L. Petit, A. Svane, Z. Szotek, and W. M. Temmerman, "First-principles study of rare-earth oxides," *Phys. Rev. B*, vol. 72, p. 205118, Nov. 2005.
- [458] H. Inaba and K. Naito, "Simultaneous measurements of oxygen pressure, composition, and electrical conductivity in praseodymium oxides: II. $\text{Pr}_{10}\text{O}_{18}$ and PrO_{2-x} phases," *J. Solid State Chem.*, vol. 50, pp. 111–120, Nov. 1983.
- [459] O. Hirsch, K. O. Kvashnina, L. Luo, M. J. Süess, P. Glatzel, and D. Koziej, "High-energy resolution x-ray absorption and emission spectroscopy reveals insight into unique selectivity of La-based nanoparticles for CO_2 ," *PNAS*, vol. 112, pp. 15803–15808, Dec. 2015.
- [460] G. Brauer and H. Gradinger, "Über heterotype mischphasen bei seltenerdoxyden. I," *Z. Anorg. Allg. Chem.*, vol. 276, no. 5-6, pp. 209–226, 1954.
- [461] U. Croatto and M. Bruno, "Edifici cristallini con disordine reticolare. Esistenza e struttura di cristalli misti anomali tra biossidi e sesquiossidi di terre rare," *Int. Congr. Pure Appl. Chem. Proc.*, vol. 1, pp. 69–74, 1947.
- [462] R. W. G. Wyckoff, *Crystal Structures*, vol. 1. London: Interscience, second ed., 1963.
- [463] R. T. Tuenge and L. Eyring, "On the structure of the intermediate phases in the praseodymium oxide system," *J. Solid State Chem.*, vol. 29, pp. 165–179, Aug. 1979.
- [464] V. S. Rudenko and A. G. Boganov, "Stoichiometry and phase transitions in rare earth oxides," *Inorg. Mater.*, vol. 6, p. 1893, Dec. 1970.
- [465] J. Zhang, R. B. Von Dreele, and L. Eyring, "Structures in the oxygen-deficient fluorite-related RnO_{2n-2} homologous series: $\text{Pr}_{12}\text{O}_{22}$," *J. Solid State Chem.*, vol. 122, pp. 53–58, Feb. 1996.

BIBLIOGRAPHY

- [466] Y. Chen, S. M. Gillette, T. Fitchorov, L. Jiang, H. Hao, J. Li, X. Gao, A. Geiler, C. Vittoria, and V. G. Harris, “Quasi-one-dimensional miniature multiferroic magnetic field sensor with high sensitivity at zero bias field,” *Appl. Phys. Lett.*, vol. 99, p. 042505, July 2011.
- [467] V. Srivastava, Y. Song, K. Bhatti, and R. D. James, “The direct conversion of heat to electricity using multiferroic alloys,” *Adv. Energy Mater.*, vol. 1, no. 1, pp. 97–104, 2011.
- [468] N. A. Spaldin and M. Fiebig, “The renaissance of magnetoelectric multiferroics,” *Science*, vol. 309, pp. 391–392, July 2005.
- [469] M. Zhu, T. Nan, M. Liu, W. Ren, Z. Zhou, and N. X. Sun, “Voltage tuning of ferromagnetic resonance and linewidth in spinel ferrite/ferroelectric multiferroic heterostructures,” *IEEE Magn. Lett.*, vol. 6, pp. 1–4, 2015.
- [470] P. A. Dowben, C. Binek, K. Zhang, L. Wang, W.-N. Mei, J. P. Bird, U. Singiseti, X. Hong, K. L. Wang, and D. Nikonov, “Towards a Strong Spin–Orbit Coupling Magnetoelectric Transistor,” *IEEE J. Explor. Solid-State Computat.*, vol. 4, pp. 1–9, June 2018.
- [471] D. E. Nikonov and I. A. Young, “Overview of Beyond-CMOS Devices and a Uniform Methodology for Their Benchmarking,” *Proc. IEEE*, vol. 101, pp. 2498–2533, Dec. 2013.
- [472] S. Manipatruni, D. E. Nikonov, and I. A. Young, “Beyond CMOS computing with spin and polarization,” *Nature Phys.*, vol. 14, pp. 338–343, Am. Pharm. Rev. 2018.
- [473] D. Khomskii, “Classifying multiferroics: Mechanisms and effects,” *Physics*, vol. 2, Mar. 2009.
- [474] J. E. Spanier, A. M. Kolpak, J. J. Urban, I. Grinberg, L. Ouyang, W. S. Yun, A. M. Rappe, and H. Park, “Ferroelectric phase transition in individual single-crystalline BaTiO₃ nanowires,” *Nano Lett.*, vol. 6, pp. 735–739, Am. Pharm. Rev. 2006.
- [475] M. T. Buscaglia, M. Bassoli, V. Buscaglia, and R. Vormberg, “Solid-state synthesis of nanocrystalline BaTiO₃: Reaction kinetics and powder properties,” *J. Am. Ceram. Soc.*, vol. 91, no. 9, pp. 2862–2869, 2008.
- [476] C. Lemoine, B. Gilbert, B. Michaux, J.-P. Pirard, and A. Lecloux, “Synthesis of barium titanate by the sol-gel process,” *J. Non-Cryst. Solids*, vol. 175, pp. 1–13, Sep. Purif. Technol. 1994.

BIBLIOGRAPHY

- [477] H.-J. Chen and Y.-W. Chen, “Hydrothermal synthesis of barium titanate,” *Ind. Eng. Chem. Res.*, vol. 42, pp. 473–483, Feb. 2003.
- [478] B. Van Tassell, S. Yang, C. Le, L. Huang, S. Liu, P. Chando, X. Liu, A. Byro, D. L. Gerber, E. S. Leland, S. R. Sanders, P. R. Kinget, I. Kymissis, D. Steingart, and S. O’Brien, “Metacapacitors: Printed thin film, flexible capacitors for power conversion applications,” *IEEE Trans. Power Electron.*, vol. 31, pp. 2695–2708, Am. Pharm. Rev. 2016.
- [479] S. Ramesh, B. Shutzberg, C. Huang, J. Gao, and E. Giannelis, “Dielectric nanocomposites for integral thin film capacitors: Materials design, fabrication and integration issues,” *IEEE Trans. Adv. Packag.*, vol. 26, pp. 17–24, Feb. 2003.
- [480] R. N. Das and V. R. Markovich, “Nanomaterials for electronic packaging: Toward extreme miniaturization [Nanopackaging],” *IEEE Nanotechnol. Mag.*, vol. 4, pp. 18–26, Dec. 2010.
- [481] E. Fortunato, P. Barquinha, and R. Martins, “Oxide semiconductor thin-film transistors: A review of recent advances,” *Adv. Mater.*, vol. 24, no. 22, pp. 2945–2986, 2012.
- [482] R. D. Shannon, “Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides,” *Acta Crystallogr. A*, vol. 32, pp. 751–767, Sep. Purif. Technol. 1976.
- [483] I. B. Bersuker, “On the origin of ferroelectricity in perovskite-type crystals,” *Phys. Lett.*, vol. 20, pp. 589–590, Am. Pharm. Rev. 1966.
- [484] I. B. Bersuker and B. G. Vekhter, “The vibronic theory of ferroelectricity,” *Ferroelectrics*, vol. 19, pp. 137–150, Jan. 1978.
- [485] I. B. Bersuker, “Recent development of the vibronic theory of ferroelectricity,” *Ferroelectrics*, vol. 164, pp. 75–100, Feb. 1995.
- [486] A. P. Hammersley, “Fit2d v12. 012 reference manual v6.0.” ESRF Internal Report ESRF98HA01T, 2004.
- [487] C. M. Holl, J. R. Smyth, H. M. S. Laustsen, S. D. Jacobsen, and R. T. Downs, “Compression of witherite to 8 GPa and the crystal structure of BaCO₃II,” *Phys. Chem. Miner.*, vol. 27, pp. 467–473, Aug. 2000.

BIBLIOGRAPHY

- [488] S. M. Antao and I. Hassan, “BaCO₃: High-temperature crystal structures and the Pmcn to R3m phase transition at 811°C,” *Phys. Chem. Miner.*, vol. 34, pp. 573–580, Sep. Purif. Technol. 2007.
- [489] F. A. Rabuffetti and R. L. Brutchey, “Structural evolution of BaTiO₃ nanocrystals synthesized at room temperature,” *J. Am. Chem. Soc.*, vol. 134, pp. 9475–9487, June 2012.
- [490] G. Busca, V. Buscaglia, M. Leoni, and P. Nanni, “Solid-state and surface spectroscopic characterization of BaTiO₃ fine powders,” *Chem. Mater.*, vol. 6, no. 7, pp. 955–961, 1994.
- [491] N. Hayashi, T. Yamamoto, H. Kageyama, M. Nishi, Y. Watanabe, T. Kawakami, Y. Matsushita, A. Fujimori, and M. Takano, “BaFeO₃: a ferromagnetic iron oxide,” *Angew. Chem. Int. Ed.*, vol. 50, no. 52, pp. 12547–12550, 2011.
- [492] W. Leib and H. Müller-Buschbaum, “Zur verbindungsbildung mo: M₂O₃ eine neue from von BaFe₂O₄ mit aufgefüllter tridymitstruktur,” *Z. Anorg. Allg. Chem.*, vol. 538, no. 7, pp. 71–77, 1986.
- [493] L. Huang, Z. Chen, J. D. Wilson, S. Banerjee, R. D. Robinson, I. P. Herman, R. Laibowitz, and S. O’Brien, “Barium titanate nanocrystals and nanocrystal thin films: Synthesis, ferroelectricity, and dielectric properties,” *J. Appl. Phys.*, vol. 100, p. 034316, Aug. 2006.
- [494] T. Hoshina, “Size effect of barium titanate: Fine particles and ceramics,” *J. Ceram. Soc. JAPAN*, vol. 121, no. 1410, pp. 156–161, 2013.
- [495] T. Zhao, F. Chen, H. Lu, G. Yang, and Z. Chen, “Thickness and oxygen pressure dependent structural characteristics of BaTiO₃ thin films grown by laser molecular beam epitaxy,” *J. Appl. Phys.*, vol. 87, pp. 7442–7447, Am. Pharm. Rev. 2000.
- [496] W. Malinofsky and H. Kedesdy, “Barium iron oxide isomorphs of hexagonal and tetragonal BaTiO₃,” *J. Am. Chem. Soc.*, vol. 76, no. 11, pp. 3090–3091, 1954.
- [497] M. Zanne and C. Gleitzer, “Un polytype de BaFeO_{2.90},” *Bulletin de la Societe Chimique de France*, vol. 1971, pp. 1567–1570, 1971.
- [498] M. Parras, M. Vallet Regi, J. Gonzalez Calbet, J. Grenier, P. Hagenmuller, and J. Rodriguez Carvajal, “A structural study of 12H-(BaFeO_{2.93}),” *Eur. J. Solid State Inorg. Chem.*, vol. 26, pp. 299–312, 1989.

BIBLIOGRAPHY

- [499] K. Mori, T. Kamiyama, H. Kobayashi, K. Oikawa, T. Otomo, and S. Ikeda, “Structural evidence for the charge disproportionation of Fe^{4+} in $\text{BaFeO}_{3-\delta}$,” *J. Phys. Soc. Jpn.*, vol. 72, no. 8, pp. 2024–2028, 2003.
- [500] Z. Guo, L. Yang, H. Qiu, X. Zhan, J. Yin, and L. Cao, “Structural, magnetic and dielectric properties of Fe-doped BaTiO_3 solids,” *Mod. Phys. Lett. B*, vol. 26, p. 1250056, Am. Pharm. Rev. 2012.
- [501] M. Ezzat, N. A. Sabiha, and M. Izzularab, “Accurate model for computing dielectric constant of dielectric nanocomposites,” *Appl. Nanosci.*, vol. 4, pp. 331–338, Mar. 2014.
- [502] L. Yang, H. Qiu, L. Pan, Z. Guo, M. Xu, J. Yin, and X. Zhao, “Magnetic properties of BaTiO_3 and $\text{BaTi}_{1-x}\text{M}_x\text{O}_3$ ($\text{M}=\text{Co}, \text{Fe}$) nanocrystals by hydrothermal method,” *J. Magn. Magn. Mater.*, vol. 350, pp. 1–5, Jan. 2014.
- [503] M. Matsuda, H. Ueda, A. Kikkawa, Y. Tanaka, K. Katsumata, Y. Narumi, T. Inami, Y. Ueda, and S.-H. Lee, “Spin-lattice instability to a fractional magnetization state in the spinel HgCr_2O_4 ,” *Nature Phys.*, vol. 3, pp. 397–400, June 2007.
- [504] P. G. Radaelli, “Orbital ordering in transition-metal spinels,” *New J. Phys.*, vol. 7, no. 1, p. 53, 2005.
- [505] J. P. Wright, J. P. Attfield, and P. G. Radaelli, “Long range charge ordering in magnetite below the Verwey transition,” *Phys. Rev. Lett.*, vol. 87, p. 266401, Dec. 2001.
- [506] S. Nagata, N. Matsumoto, Y. Kato, T. Furubayashi, T. Matsumoto, J. P. Sanchez, and P. Vulliet, “Metal-insulator transition in the spinel-type $\text{CuIr}_2(\text{S}_{1-x}\text{Se}_x)_4$ system,” *Phys. Rev. B*, vol. 58, pp. 6844–6854, Sep. Purif. Technol. 1998.
- [507] M. Ito, J. Hori, H. Kurisaki, H. Okada, A. J. P. Kuroki, N. Ogita, M. Udagawa, H. Fujii, F. Nakamura, T. Fujita, and T. Suzuki, “Pressure-induced superconductor-insulator transition in the spinel compound CuIr_2S_4 ,” *Phys. Rev. Lett.*, vol. 91, p. 077001, Aug. 2003.
- [508] E. S. Bozin, A. S. Masadeh, Y. S. Hor, J. F. Mitchell, and S. J. L. Billinge, “Detailed mapping of the local Ir^{4+} dimers through the metal-insulator transitions of CuIr_2S_4 thiospinel by x-ray atomic pair distribution function measurements,” *Phys. Rev. Lett.*, vol. 106, p. 045501, Jan. 2011.
- [509] R. J. Koch, T. Konstantinova, M. Abeykoon, A. Wang, C. Petrovic, Y. Zhu, E. S. Bozin, and S. J. L. Billinge, “Room temperature local nematicity in FeSe superconductor,” *Phys. Rev. B*, vol. 100, p. 020501, July 2019.

BIBLIOGRAPHY

- [510] X. Qiu, T. Proffen, J. F. Mitchell, and S. J. L. Billinge, “Orbital correlations in the pseudocubic O and rhombohedral R -phases of LaMnO_3 ,” *Phys. Rev. Lett.*, vol. 94, p. 177203, 2005.
- [511] M. Croft, W. Caliebe, H. Woo, T. A. Tyson, D. Sills, Y. S. Hor, S.-W. Cheong, V. Kiryukhin, and S.-J. Oh, “Metal-insulator transition in CuIr_2S_4 : XAS results on the electronic structure,” *Phys. Rev. B*, vol. 67, p. 201102, May 2003.
- [512] S. Torigoe, T. Hattori, K. Kodama, T. Honda, H. Sagayama, K. Ikeda, T. Otomo, H. Nitani, H. Abe, H. Murakawa, H. Sakai, and N. Hanasaki, “Nanoscale ice-type structural fluctuation in spinel titanates,” *Phys. Rev. B*, vol. 98, p. 134443, Oct. 2018.
- [513] L. Yang, R. J. Koch, H. Zheng, J. F. Mitchell, W. Yin, M. G. Tucker, S. J. L. Billinge, and E. S. Bozin, “Two-orbital degeneracy lifted local precursor to a metal-insulator transition in MgTi_2O_4 ,” *Phys. Rev. B*, vol. 102, p. 235128, Dec. 2020.
- [514] B. A. Wechsler and R. B. Von Dreele, “Structure refinements of Mg_2TiO_4 , MgTiO_3 and MgTi_2O_5 by time-of-flight neutron powder diffraction,” *Acta Crystallogr. B*, vol. 45, pp. 542–549, Dec. 1989.
- [515] R. L. Millard, R. C. Peterson, and B. K. Hunter, “Study of the cubic to tetragonal transition in Mg_2TiO_4 and Zn_2TiO_4 spinels by 17O MAS NMR and Rietveld refinement of x-ray diffraction data,” *Am. Mineral.*, vol. 80, pp. 885–896, Sep. Purif. Technol. 1995.
- [516] B. H. Toby and R. B. Von Dreele, “GSAS-II: The genesis of a modern open-source all purpose crystallography software package,” *J. Appl. Crystallogr.*, vol. 46, pp. 544–549, Am. Pharm. Rev. 2013.
- [517] A. N. Vasiliev, M. M. Markina, M. Isobe, and Y. Ueda, “Specific heat and magnetic susceptibility of spinel compounds CdV_2O_4 , ZnV_2O_4 and MgTi_2O_4 ,” *J. Magn. Magn. Mater.*, vol. 300, pp. e375–e377, May 2006.
- [518] V. M. Talanov, V. B. Shirokov, V. V. Ivanov, and M. V. Talanov, “Theory of structural phase transition in MgTi_2O_4 ,” *Crystallogr. Rep.*, vol. 60, pp. 101–110, Jan. 2015.
- [519] S. Di Matteo, G. Jackeli, and N. B. Perkins, “Valence-bond crystal and lattice distortions in a pyrochlore antiferromagnet with orbital degeneracy,” *Phys. Rev. B*, vol. 72, p. 024431, July 2005.
- [520] A. Rahaman, M. Chakraborty, T. Paramanik, R. K. Maurya, S. Mahana, R. Bindu, D. Topwal, P. Mahadevan, and D. Choudhury, “Tetramer orbital ordering and lattice chirality in MnTi_2O_4 ,” *Phys. Rev. B*, vol. 100, p. 115162, Sep. Purif. Technol. 2019.

- [521] K. Yagasaki, T. Nakama, M. Hedo, Y. Uwatoko, Y. Shimoji, S. Notsu, K. Uchima, N. Matsumoto, S. Nagata, H. Okada, H. Fujii, H. Yoshida, H. M. Kimura, Y. Yamaguchi, and A. T. Burkov, “Hopping conductivity in CuIr_2S_4 spinel compound: I. Empirical model for electronic configuration and mechanism of metal–insulator transition,” *J. Phys. Soc. Jpn.*, vol. 75, p. 074706, July 2006.
- [522] P. W. Anderson, “Ordering and antiferromagnetism in ferrites,” *Phys. Rev.*, vol. 102, pp. 1008–1013, May 1956.
- [523] I. McKenzie, “The positive muon and μSR spectroscopy: Powerful tools for investigating the structure and dynamics of free radicals and spin probes in complex systems,” *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.*, vol. 109, pp. 65–112, June 2013.
- [524] M. J. Krogstad, S. Rosenkranz, J. M. Wozniak, G. Jennings, J. P. C. Ruff, J. T. Vaughey, and R. Osborn, “Reciprocal space imaging of ionic correlations in intercalation compounds,” *Nat. Mater.*, vol. 19, pp. 63–68, Jan. 2020.
- [525] M. A. Davenport, M. J. Krogstad, L. M. Whitt, C. Hu, T. C. Douglas, N. Ni, S. Rosenkranz, R. Osborn, and J. M. Allred, “Fragile 3D order in $\text{V}_{1-x}\text{Mo}_x\text{O}_2$,” *arXiv:1909.12704*, Sep. Purif. Technol. 2019.
- [526] Y. Pramudya, H. Terletska, S. Pankov, E. Manousakis, and V. Dobrosavljević, “Nearly frozen Coulomb liquids,” *Phys. Rev. B*, vol. 84, p. 125120, Sep. Purif. Technol. 2011.
- [527] S. Mahmoudian, L. Rademaker, A. Ralko, S. Fratini, and V. Dobrosavljević, “Glassy dynamics in geometrically frustrated Coulomb liquids without disorder,” *Phys. Rev. Lett.*, vol. 115, p. 025701, July 2015.
- [528] Z. Wang, X.-G. Zhao, R. Koch, S. J. L. Billinge, and A. Zunger, “Understanding electronic peculiarities in tetragonal FeSe as local structural symmetry breaking,” *Phys. Rev. B*, vol. 102, p. 235121, Dec. 2020.