

ABSTRACT

Title of Dissertation: **MAGNETIC AND TOROIDAL SYMMETRY OF
LITHIUM TRANSITION METAL ORTHOPHOSPHATES**

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LiCoPO_4 is the foremost candidate material for a novel type of ferroic ordering called ferrotoroidicity. In this work, the synthesis of polycrystalline sample of LiCoPO_4 is discussed, along with the structural analog LiMnPO_4 . Their magnetic susceptibility and magnetic structure were determined and analyzed and found to be consistent with previous reports on single crystal materials. This work also provides a thorough introduction to ferrotoroidicity, a history of its theoretical development, and a summary of the most studied candidate materials. The work then presents a detailed methodology for determining the toroidal structure which would result for the magnetic structure in candidate ferrotoroidal materials. The model provides a method for determining how many toroidal moments would be present, where they would be located within the unit cell, and along which crystallographic direction they would be oriented. Detailed examples for determining the magnetic structure are provided for LiCoPO_4 and analogous structures with the olivine structure type, as well as several structures with the pyroxene structure type. The results demonstrate a method for understanding ferrotoroidal arrangements, anti-ferrotoroidal arrangements and non-toroidal structures.

MAGNETIC AND TOROIDAL SYMMETRY OF
LITHIUM TRANSITION METAL ORTHOPHOSPHATES

by

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Preface

Since this document is a doctoral dissertation, it is important to explain the delegation of labor for the synthesis work between my teammates. I was the first group member to start on this project on ferrotoroidal materials, in the summer of 2016. The first objective was to synthesize large single crystals of candidate olivine materials, since they would be needed for detailed physical property measurements and neutron experiments under applied fields.

My first synthetic approach was using hydrothermal methods. The rationale was that hydrothermal preparation would be less likely to produce metal oxide impurities which would interfere with magnetization measurements. Unfortunately, large single crystal growth proved impossible due to the low solubility of transitional metal phosphates in aqueous media up to 220°C, which was the maximum temperature rating for the acid digestion vessels used for the synthesis.

However, my initial synthetic attempts ultimately proved successful at producing polycrystalline LiCoPO_4 , LiFePO_4 , LiMnPO_4 , and various solid solutions of cobalt, iron, and manganese on the metal site. However, a disadvantage of the hydrothermal method was the size of the vessel and solubility of the starting reagents limited how much polycrystalline sample could be produced at one time. Another disadvantage of the hydrothermal method was it is not possible to produce LiNiPO_4 . All attempts at hydrothermal synthesis of LiNiPO_4 produced apatite, which is a nickel phosphate mineral.[1] This is because nickel phosphate is very insoluble under the hydrothermal

conditions possible using acid digestion vessels. The hydrothermal synthesis methods will be discussed in detail in §5.4.

To address the disadvantages of the hydrothermal method, by the summer of 2017 I was also using solid state methods to produce olivine materials. The primary advantage of solid state methods is larger quantities can be synthesized at one time. It is also possible to synthesize LiNiPO_4 and solid solutions containing nickel. However, it is vital to perform the synthesis under inert atmosphere (argon flow gas) to avoid oxidation of the transition metals. It is also important to carefully control the heating profile of the synthesis. The solid state synthesis methods will be discussed in detail in §5.3.

By the Spring of 2017 I also had been working with an undergraduate student researcher, Noah Bender. The project I had him work on was delithiating LiFePO_4 to ultimately synthesize NaFePO_4 . The project was inspired by the detailed work of Maxim Avdeev.[2] Avdeev prepared LiFePO_4 via a solid state technique and then delithiated it in a solution of nitronium tetrafluoroborate (NO_2BF_4) in acetonitrile. Gwenaëlle Rousse, who performed a detailed neutron diffraction study of LiFePO_4 and FePO_4 , used a similar delithiation process.[3] Avdeev then sodiated the FePO_4 powder by stirring with sodium iodide (NaI) in acetonitrile with gentle heating (60°C , 48 hr) to form NaFePO_4 with the olivine structure type. Avdeev and his colleagues then performed magnetic susceptibility and neutron diffraction experiments and found it had the same magnetic structure as LiFePO_4 . Therefore NaFePO_4 was a desirable ferrotoroidal candidate, if we could ultimately grow large single crystals of it. By the end of the Fall of 2017 Noah had successfully been able to delithiate LiFePO_4 powder using a peracetic acid solution method.[4, 5]

In the Spring of 2017 Jacob Tosado also joined this research project. His role was building a prototype spherical neutron polarimetry device at the NIST Center for Neutron Research. The

objective was to use spherical neutron polarimetry to analyze large single crystals of olivine materials to probe for evidence of ferrotoroidicity. He continued to work on the project in Maryland until the end of Spring 2021.

By the summer of 2017 I had been successful at producing single crystalline samples of three end members LiMPO_4 ($M = \text{Mn, Fe, Co}$) using a LiCl salt flux under argon atmosphere. To avoid oxidation, it had been suggested to me by my colleague Xiuquan Zhou to use graphite crucibles. There were a few small crucibles in storage leftover from a project by Chris Borg who had graduated in 2015. The crucibles were sized to fit inside the quartz synthesis tubes used ubiquitously in the Rodriguez research group. The crucibles were approximately 1 cm in diameter and about 1.5 cm tall. They proved a very successful growth container, but were easily damaged and could not be reused more than once or twice. The heating conditions would make the crucibles brittle, and the lid would tightly seal to the crucible bottom. Therefore opening it would damage the lid and crucible bottom. The crucibles were also quite small, which limited the surface area for crystal growth.

Sometime in 2017 I discovered a very detailed research paper on flux growth of LiFePO_4 by Yuri Jensen from the Peter Khalifah research group.[6] In it, the authors also concluded that graphite was an ideal crucible material since they are inexpensive yet effective. This confirmed my conclusion that graphite crucibles were a viable alternative to platinum crucibles and worthy of being pursued further. Indeed, in 2019 Rasmus Toft-Petersen, David Vaknin and their colleagues who had used platinum crucibles, discovered their olivine single crystals were impure.[7] They reused the platinum crucibles for different growths and inadvertently cross-contaminated their samples. The Janssen paper also used iron(II) oxalate dihydrate as the iron precursor for the solid state synthesis of LiFePO_4 , which I also found to be suitable. The organic oxalate ligand helps

prevent oxidation of the iron ions. (The Avdeev 2013 paper used iron(II) oxalate as well.)[2]

I advanced to candidacy at the end of the Fall semester in 2017, officially advancing January 2018.

By the summer of 2018 I had decided to purchase large rectangular graphite crucibles with thick sides for the single crystal growth. The thick sides enabled them to be reused, and the large volume inside the crucibles provided a large surface area for nucleation and growth of large crystals. The lids were secured to the tops with inert metal wire. There was a large spool of nickel wire in the lab leftover from some other project which proved suitable for the task due to its high melting point. I believe it may have been specifically nichrome wire (a nickel-chromium alloy). I also knew by that time that in a $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ solid solution, the iron could be selectively oxidized to form ferrisicklerite ($\text{Li}_{1-x}\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$). I learned this from an article I had found authored by a team of geologists.[8]

The Spring of 2018 Timothy Diethrich had joined the Rodriguez research group and the Summer of 2018 I taught him my methods for olivine synthesis and crystal growth. I had also shared with him an article on ferrisicklerite summer.[8] By the end of the Fall of 2018 Tim had mastered single crystal growth for the entire series of $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$. Tim and I continued to brainstorm together ways to optimize the solid state preparation of $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$.

Over the Summer of 2018 I began working on the toroidal theory presented in the previous chapters of this dissertation. I also completed the neutron powder diffraction experiments presented in Chp. 5. Therefore my objectives shifted to focusing on ferrotorodial theory, and on detailed study of the magnetic structure of the LiCoPO_4 and LiMnPO_4 end members.

In an effort to delegate work so I could devote more time to toroidal theory, Tim took the lead on the $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ preparation and single crystal growth. He also eventually took the

lead on the delithiation work as Noah prepared to graduate in the Spring of 2019. Tim also began working on synthesizing and studying the magnetism in thiophosphate materials in the Spring of 2019. I continued to collaborate with Tim on the $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ series, particularly in determining which compositions would have the suitable symmetry for ferrotoroidicity. Tim graduated in the Fall of 2022.

I also have powder diffraction and magnetization data for various solid solutions, but since Tim Diethrich took the lead on the project in 2019, I wanted there to be a clear separation in our dissertations of whose work was whose. In Tim's dissertation and publications, all of the samples he synthesized himself. Likewise, all of the data he collected himself. His work was greatly informed and aided by my preliminary efforts, but ultimately his own. In addition, I do not intend at this point in time to publish any of my work on solid solutions of olivine materials, particularly $\text{LiMn}_x\text{Co}_{1-x}\text{PO}_4$ and $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$. There are already many published structural and magnetization studies on those materials, since they are well-known cathode materials for batteries. The magnetic studies of the $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ delithiated samples, however, were novel enough for Tim to publish. We have struggled to delithiate samples containing cobalt. Indeed, Ehrenberg and his colleagues could only perform neutron powder diffraction on partially delithiated Li_xCoPO_4 , and discussed challenges with the delithiated form converting to amorphous powder.[9] In addition, MnPO_4 is unstable due to Jahn-Teller distortion.[10, 11]

Published Articles resulting from this work:

1. Gnewuch, S.; Rodriguez, E. E. The Fourth Ferroic Order: Current Status on Ferrotoroidic Materials. *J Solid State Chem* **2019**, 271, 175–190.
2. Gnewuch, S.; Rodriguez, E. E. Distinguishing the Intrinsic Antiferromagnetism in Polycrystalline

LiCoPO₄ and LiMnPO₄ Olivines. *Inorg Chem* **2020**, *59*, 5883-5895.

3. Diethrich, T. J.; Gnewuch, S.; Dold, K. G.; Taddei, K. M.; Rodriguez, E. E. Tuning Magnetic Symmetry and Properties in the Olivine Series Li_{1-x}Fe_xMn_{1-x}PO₄ through Selective Delithiation. *Chem. Mater.* **2022**, *34*, 5039–5053.

Unpublished Work contained in this dissertation:

- Chp. 2 contains the contents of Gnewuch 2019, but is completely re-organized and a great deal of content was added.
- Chp. 3 is yet-unpublished work, except for §3.5, which presents my contribution to Diethrich 2022.
- Chp. 4 is entirely yet-unpublished work.
- Chp. 5 is the contents of Gnewuch 2020.

Dedication

To my Mother Mary.

Thank you for all the prayers and support.

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This has been an amazing journey through graduate school to get to this point. There are many people I would like to personally thank for their support along the way:

I would first like to thank my advisor, Dr. Efrain Rodriguez. I came to graduate school to pursue additional study in crystallography, and it's been an exciting opportunity learning powder diffraction and neutron scattering in his research group. Not only has he guided my studies and research, but has also encouraged and supported my growth personally. I am forever indebted to his unwavering faith in my intellectual potential, and support to see things through to the end.

I would like to especially thank my colleagues Dr. Jacob Tosado and Dr. Timothy Diethrich who collaborated on experiments and spent countless hours planning and brainstorming in our combined efforts to support this larger research project investigating potential ferrotoroidic materials with neutron diffraction experiments. Our camaraderie and mutual support made this journey scientifically fruitful and personally fulfilling, as we celebrated each other's successes and supported each other through the many challenges we each faced. I would also like to thank the undergraduate researchers Noah Bender and Kaitlyn Dold, who supported synthesis and crystal growth efforts on this project.

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I would not have been able to perform this work without the training I received in X-ray and neutron scattering and magnetic structure analysis I received from the numerous scientists who organized and participated in the following summer schools: 2018 and 2021 School on Representational Analysis and Magnetic Structures, University of Maryland, College Park; 20th National School on Neutron and X-Ray Scattering, Argonne National Laboratory and Oak Ridge National Laboratory; International School of Crystallography 53rd Course: Magnetic Crystallography,

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I would like to thank my candidacy committee members for their crucial advice at a critical time in my program: Dr. Nicholas Butch, Dr. Bryan Eichhorn, Dr. Lawrence Sita, and Dr. Andrei Vedernikov.

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Chapter 1: General Introduction

So often in crystallography, a lower symmetry can be wrongly assigned to a crystal structure because the higher symmetry is overlooked. In many cases it might be undetected due to instrumental limitations. In other instances the additional symmetry is simply not considered. But to uncover hidden symmetries, it is first necessary to have the mathematical language to describe them.

Such is the case with ferrotoroidal materials (also called ferrotoroidic materials). The primary objective of my doctoral work was to develop the language for describing this fourth category of primary ferroic materials. There are three well-established primary ferroic orders: ferroelectric polarization, ferromagnetic magnetization, and ferroelastic strain.[\[12\]](#) Each are classified by an order parameter which describes the long-range ordering which occurs due to loss of symmetry elements as the material undergoes a phase transition from its higher symmetry paraferroic phase to its lower symmetry ordered ferroic phase.

Several researchers have long known that certain magnetoelectric materials which display a linear magnetoelectric effect fulfill many of the criteria for ferrotoroidal materials. The first chapter of this document recounts the historical development of the theory behind ferrotoroidal materials. The general consensus is toroidal moments would arise from a “ring” of magnetic spins, oriented head-to-tail. There also have been many attempts at defining which magnetic point groups would allow ferrotoroidal order. The general consensus is the magnetic point group

should also permit a linear magneto-electric effect. The connection to the magneto-electric effect is strengthened by the assertion that crossed magnetic and electric fields should be able to control ferrotoroidal domains in a material. Chapter 2 also discusses the various materials which have been or are considered candidate ferrotoroidal materials. The most notable of them are LiCoPO_4 with the olivine structure type, and $\text{LiFeSi}_2\text{O}_6$ with the pyroxene structure type. Both materials have a number of compositional analogs which are also candidate materials. The chapter discusses all of the magnetism-related research on these candidate materials, and the arguments which have been put forth for them being ferrotoroidal candidates.

Upon reviewing the literature, I identified a number of unanswered questions:

- Where will the toroidal moments be located?
- How will the toroidal moments be oriented?
- How can a “ring of spins” be defined systematically in a magnetic material?
- What is the symmetry of a “ring of spins”?
- How can the structure and composition of a material be altered to maximize the net toroidal moment in a material?

I recognized they all could be answered by developing a model for understanding the toroidal structure in a material which would result from the complementary magnetic structure.

Since the only symmetry criteria for ferrotoroidic materials are based upon their magnetic point symmetry, there had been no consistent method for defining where the toroidal moments would order within a material. Since the magnetic moments have defined, discrete locations within a material, I argue in Chapter 3 that there should also be defined, discrete locations for the

toroidal moments. I also argue that they must occur at sites with $\bar{1}'$ symmetry, since this is the defining symmetry of any “ring of spins.”

In Chapter 4, I present thorough example calculations for determining the possible toroidal structures in various materials with the pyroxene and olivine structure types. In doing so, I demonstrate how toroidal structures could be classified as ferrotoroidal, antiferrotoroidal, non-toroidal, and ferritoroidal. I also provide example calculations for determining the magnitude and directions of individual toroidal moments within the unit cell, and the net toroidal moment per unit cell.

Of course, the ultimate goal of this research is to test candidate materials. And my ultimate goal as a chemist is to create candidate materials which maximize the net torodial moment in a material. Chapter 5 presents my work on two end members in the olivine series: LiCoPO_4 and LiMnPO_4 . I used two synthetic methods to prepare polycrystalline samples. The first was hydrothermal methods, which are less likely to create metal oxide impurities. The second was solid state methods, which can create larger quantities of product. I performed detailed temperature- and field-dependent magnetization measurements on the materials created by the two different methods, to compare their signal. I then performed neutron powder diffraction experiments, and determined their magnetic structures through symmetry analysis.

I used the structural information of LiCoPO_4 , LiMnPO_4 , and other reported structures in my ferrotoroidal models in Chapter 4. In doing so, I demonstrate this method of modeling toroidal order can be applied to different materials, and used to predict optimal materials for further study.

Chapter 2: Introduction to Ferrotoroidal Theory

This chapter contains the contents of Gnewuch 2019, but is completely re-organized and a great deal of content was added.

Gnewuch, S.; Rodriguez, E. E. The Fourth Ferroic Order: Current Status on Ferrotoroidic Materials. *J Solid State Chem* **2019**, 271, 175–190.

This chapter begins (§2.1) with a description of the development of the classification criteria of ferrotoroidic materials based upon their magnetic ordering. The second section (§2.2) discusses the major reported experiments investigating certain materials with the olivine structure type for evidence of ferrotoroidic ordering, leading up to a landmark study by Van Aken *et al.* in 2007 on olivine material LiCoPO₄. Those experiments motivated subsequent work by a number of experimentalists in neutron scattering, as well as theorists. The symmetry requirements permitting ferrotoroidic order were revisited during that time period, and §2.3 summarizes the modern understanding of the symmetry requirements for ferrotoroidic order. A summary of the neutron scattering studies on candidate materials with the olivine structure type are presented in §2.4. Other candidate materials are discussed in §2.5 and §2.6, particularly those with the pyroxene structure type based upon work on LiFeSi₂O₆. Another noteworthy study in 2014 provided evidence for the ferroic nature of the magnetoelectric response in LiCoPO₄, which is discussed in §2.7. The chapter concludes with a summary of the developments in theory (§2.9) and proposed

Table 2.1: Irreducible Representations of the Point Group $\bar{1}1'$. The representation labels are based upon the scheme used in Ref. [14]; the classification criteria are based upon the scheme used in Ref. [16].

$\bar{1}1'$	1	$\bar{1}$	$1'$	$\bar{1}'$	Classification
Γ_1	1	1	1	1	Strain
$\Gamma_{\bar{1}}$	1	1	-1	-1	Magnetization
$\Gamma_{11'}$	1	-1	1	-1	Polarization
$\Gamma_{\bar{1}'}$	1	-1	-1	1	Toroidization

ferrotoroidic candidates since that time (§2.8).

2.1: Early Theory of Toroidal Moments in Crystalline Solids

Edgar Ascher is considered the first to postulate that if there are symmetries which permit net magnetization, net electric polarization, and the null case of strain, there must be a fourth category which describes yet another type of ordered “polarization.”[13] His argument is based upon how the symmetry elements of the point group $\bar{1}1'$ can be reduced into four irreducible representations, given in Table 2.1. According to this scheme, magnetic moments are invariant under spatial inversion ($\bar{1}$), polar moments are invariant under time inversion ($1'$), and a third kind of moment is invariant under space-time inversion ($\bar{1}'$). Throughout the 1960’s and 70’s Ascher and his colleague Janner postulated this third category could describe ordered current density, based upon the point group symmetry materials display under electromagnetic fields.[13, 14, 15] The papers published over this time period categorize the magnetic (*i.e.*, Shubnikov) point groups based upon which space and time inversion symmetry elements they contain. Initially they classified the fourth category, with the representation $\Gamma_{\bar{1}'}$ as “spontaneous current” and postulated it was related to superconductivity. Ascher abandoned that theory within a couple years, but the classification scheme remained plausible.

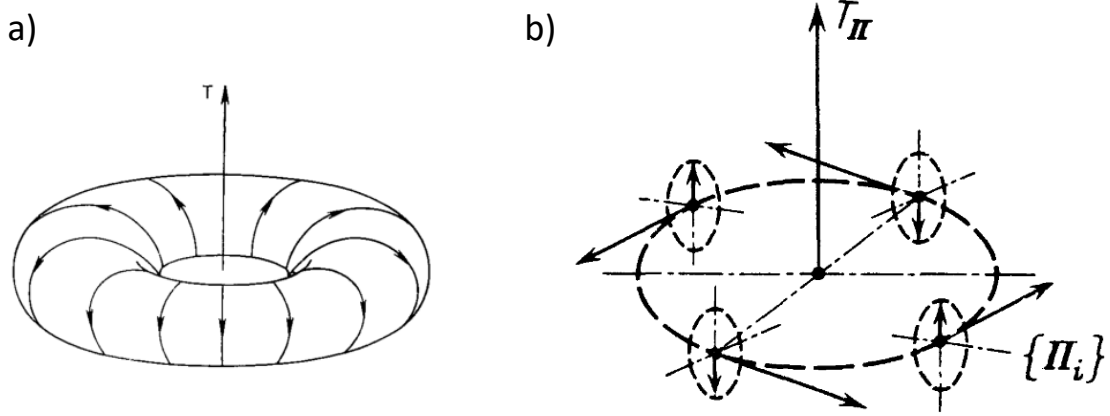


Figure 2.1: Structural models of a toroidal dipole moment proposed by Dubovik, Tugushev, and their colleagues.[17, 18, 19] a) A current loop arranged as a torus. The toroidal moment labeled “ T ” is indicated along the rotation axis with an upwards-pointing arrow. Fig. 2.1a is reproduced from Fig. 1 in Ref. 17. b) Local moments labeled “ Π_i ” are precessing on a circle. Their centrosymmetric arrangement gives rise to the toroidal dipole moment “ T_{Π} .” Fig. 2.1b is reproduced from Fig. 1c in Ref. 18.

Independently from Ascher, V. M. Dubovik and his colleague considered the electrodynamic conditions required for toroidal moments to arise from current density around magnetic dipoles.[17] They concluded a toroidal dipole would occur along the rotation axis perpendicular to electric current rings arranged as a torus. Fig. 2.1a is a diagram of this arrangement. Dubovik continued developing that work with V. V. Tugushev and several other colleagues, and like Ascher also considered the multipole moments which would be generated from the charge density of the arrangement.[18, 19] Ascher then classified the moments according to their symmetry transformations under space and time inversion operations, and called these the magnetic dipole moment $\mathbf{M}$, the charge dipole moment $\mathbf{P}$, and the toroidal dipole moment $\mathbf{T}$.

Dubovik and Tugushev recognized the simplest scenario to produce a toroidal dipole moment would be an antiferromagnetic arrangement of magnetic spins arranged in a ring head-to-tail, which would approximate a torus. Fig. 2.1b presents their idealized models for this arrangement.

Mathematically, the expression for the magnetic toroidal moment $\mathbf{T}$ from the localized

current density distribution $\mathbf{j}(\mathbf{r})$ centered about an origin is written as

$$\mathbf{T} = \frac{1}{10c} \int [\mathbf{r}(\mathbf{r} \cdot \mathbf{j}) - 2r^2 \mathbf{j}] d^3 r, \quad (2.1)$$

where c is the speed of light in a vacuum, and $\mathbf{r}$ is the radius of the ring centered on the origin.[19]

A detailed discussion of the physical manifestation of the toroidal dipole moment is outside the scope of this work. However, it is important to note the interaction energy between a toroidal moment $\mathbf{T}$ and homogenous magnetic field $\mathbf{B}$ is minimized when the toroidal moment is parallel to the curl of the magnetic field. Mathematically, the contribution to the free energy density $F_{\mathbf{T}}$ can be expressed as:[19]

$$\Delta F_{\mathbf{T}} \sim \mathbf{T} \cdot (\nabla \times \mathbf{B}). \quad (2.2)$$

Therefore the toroidal moment would be perpendicular to a ring of magnetic moments in an electro-magnetic system. In addition, there is also a contribution to the free energy density from crossed electric $\mathbf{E}$ and magnetic $\mathbf{B}$ fields:[19]

$$\Delta F_{\mathbf{T}} \sim \mathbf{T} \cdot (\mathbf{E} \times \mathbf{B}). \quad (2.3)$$

Therefore materials which would permit a net toroidal moment $\mathbf{T}$ would also by symmetry permit a linear magnetoelectric effect. Specifically, the signal from a net toroidal dipole in the material would appear as antisymmetric components in the magnetoelectric tensor. This connection between the linear magnetoelectric effect and toroidal moments is the reason the magnetoelectric effect is studied intensely in candidate ferrotoroidic materials.

Later in the paper,[19] Dubovik and Tugushev considered how a local magnetic moment μ_{loc} would manifest in a system of magnetic moments $\mathbf{m}$ at points arranged in a ring with radius $\mathbf{r}$:

$$\mu_{\text{loc}}(\mathbf{r}) = \sum_i \mathbf{m}_i \delta(\mathbf{r} - \mathbf{r}_i). \quad (2.4)$$

This is the same mathematical description used for electric polarization. The net toroidal dipole moment $\mathbf{T}$ from such a ring of local magnetic moments is then:

$$\mathbf{T}(\mu_{\text{loc}}) = \frac{1}{2} \int \mathbf{r} \times \boldsymbol{\mu}_{\perp} d^3 r. \quad (2.5)$$

Around the same time, Tugushev and Krotov [20] tabulated all the symmetry invariants which would permit toroidal ordering for an antiferromagnetic arrangements of spins, and organized them according to crystal system. This method of describing a magnetic structure involves defining an antiferromagnetic material as a superposition of two anti-aligned ferromagnetic lattices. The symmetry invariants describe the directions in which the symmetry allows a net alignment of spins. Since symmetry elements are described by the invariance of a point or vector (or other entity) under symmetry operations, these vectors are called the symmetry invariants. They further classified the invariants according to the spatial parity and point group for each of the 230 space group types. The object of this scheme is to predict if a particular antiferromagnetic spin orientation would permit toroidal ordering. They only considered collinear antiferromagnetic structures in which the magnetic cell coincides with the structural unit cell, since the resulting toroidal moment arrangement would be uniform. They also assumed that materials in which either the magnetic spins were canted, or the magnetic and structural unit cells did not coincide, would result in an anti-toroidal arrangement. The results revealed that in all cases in which toroidal ordering is permitted, the toroidal vector invariants were always accompanied by antiferromagnetic vector invariants. One would conclude from this, that while the magnetic ordering is distinct from the toroidal ordering, a magnetically ordered system of the appropriate symmetry is a necessary condition for it to occur. They cannot occur independently from one another.

Gorbatsevich, Kopaev, Ginzburg, and their colleagues continued to develop the theoretical basis for ordered toroidal moments.[21, 22, 23] Like Ascher initially, they were inspired by the “current loops” which would produce a toroidal moment. They were initially convinced the

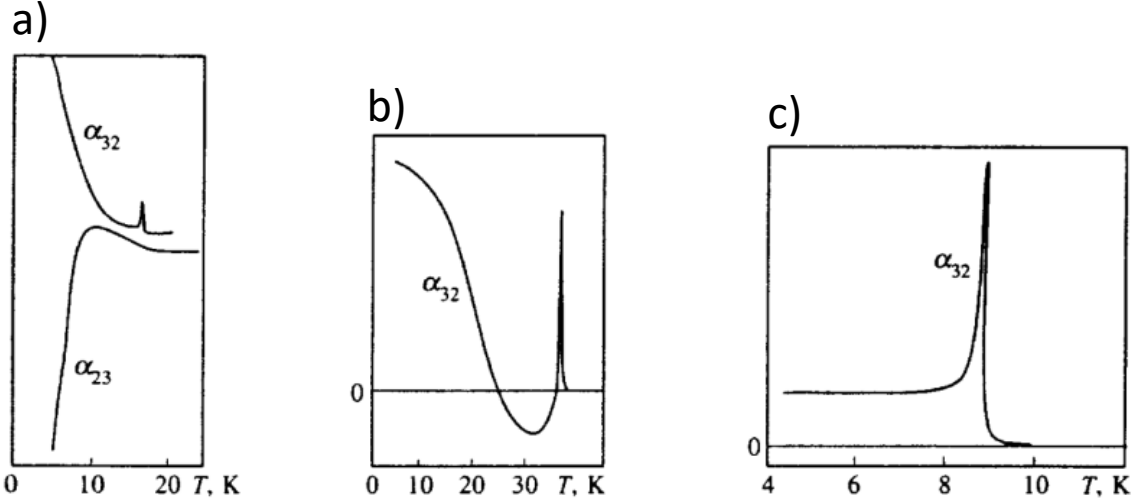


Figure 2.2: Temperature-dependence of the off-diagonal α_{32} and α_{23} components in the magnetoelectric tensor of the $m'm2'$ phases of the following boracites: a) $\text{Co}_3\text{B}_7\text{O}_{13}\text{Br}$, b) $\text{Co}_3\text{B}_7\text{O}_{13}\text{I}$, and c) $\text{Ni}_3\text{B}_7\text{O}_{13}\text{Cl}$. Reproduced from Figure 1 in Ref. [24](#). An identical figure is presented in Ref. [25](#).

“loops” were related to superdiamagnetism. Ginzburg realized the connection that the point groups which would permit toroidal moments, also permit the linear magnetoelectric effect.[\[21\]](#) Gorbatshevich and Kopaev’s 1994 paper[\[22\]](#) cites Ascher’s classification scheme,[\[15\]](#) and also reviews the current understanding of how toroidal moments are related to the electric and magnetic properties. While both the spin and orbital contributions from ordered magnetic moments can contribute to a toroidal moment, the authors began to consider how a configuration could occur in a crystalline material. Considering only the contribution from the magnetic spins, a simple configuration would be one or more pairs of anti-aligned magnetic moments. This type of compensated configuration of magnetic moments is always classified as antiferromagnetic.

A few years later, Sannikov reported that in several boracites, an unexpected discontinuity was observed in certain off-diagonal components of the temperature-dependent magnetoelectric susceptibility.[\[24, 25\]](#) The measurements are presented in Fig. [2.2](#). (Sannikov published identical

figures in both Ref. 24 and 25.) Boracites have the general formula $M_3B_7O_{13}X$ where M is a divalent cation and X is a halide anion. Sannikov was studying the Co-Br, Co-I, and Ni-Cl boracites in particular. In the papers, he presented detailed phenomenological arguments for why a toroidal dipole moment can be regarded as a primary order parameter. He explained the sharp peak observed in the off-diagonal components of the temperature-dependent magnetoelectric susceptibility are indicative of a phase transition. He proposed this phase transition would be to an ordered ferrotoroidic state, and the observed discontinuity could be considered a characteristic signal of a ferrotoroidic phase transition. This work was the experimental evidence establishing the connection between the magnetoelectric effect, and ferrotoroidic order. He published additional examples of boracites exhibiting this characteristic signal in subsequent years.[26, 27] As a note, his 2007 paper “Ferrotoroics” serves as a concise summary of the phenomenological theory he developed.[28] He was the sole author on all these papers.

Around this same time, Popov and a number of co-authors published a paper reporting measurements of the linear magnetoelectric effect in $Ga_{2-x}Fe_xO_3$, and present analysis arguing the materials can produce a net toroidal moment.[29] They cite work by Gorbatsevish and Dubovik when defining the toroidal moments per unit cell. First, they considered Eq. 2.1 (mentioned previously) for the toroidal moments. Similarly, the net magnetic moment $\mathbf{M}$ is:

$$\mathbf{M} = \frac{1}{2c} \int \mathbf{r} \times \mathbf{j}(\mathbf{r}) d^3r. \quad (2.6)$$

Since not stated previously, the current density is the curl of the spin density of localized spins, which is expressed mathematically as:

$$\mathbf{j}(\mathbf{r}) = c \nabla \times \mathbf{S}(\mathbf{r}). \quad (2.7)$$

In the case of toroidal moments, the spin density has a divergence of zero because it is arranged in a ring. The ring of spins will then produce current density perpendicular to it. The magnetic

ions in the unit cell of any magnetic crystalline material are in discrete locations. Therefore the net magnetic moment per unit cell due to the spins of all the magnetic moments $\mathbf{S}$ (with units of μ_B) can be determined by a summation:

$$\mathbf{M} = 2\mu_B \sum_{\alpha} \mathbf{S}_{\alpha}. \quad (2.8)$$

This expression is simpler to compute than integrating over the unit cell. In the same way, Popov and his colleagues re-wrote Eq. 2.5 as a summation of discrete toroidal moments in a unit cell. Their final expression for the net toroidal moment per unit cell is:

$$\mathbf{T} = \frac{\mu_B}{2} \sum_{\alpha} \mathbf{r}_{\alpha} \times \mathbf{S}_{\alpha}. \quad (2.9)$$

They defined the $\mathbf{r}_{\alpha}$ vector as the “radius” vector with the origin at the center of the unit cell, and the terminus as the position of magnetic atom α with spin $\mathbf{S}$.

Popov and his colleagues go on to explain that in $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$, there is a displacive phase transition so that the non-centrosymmetric $mm2$ structure transforms to the centrosymmetric mmm structure. Therefore, they defined the $\mathbf{r}_{\alpha}$ vectors for the initial structure and the distorted structure, and calculated the toroidization from the difference between the structures. Popov and several colleagues published a similar (shorter) paper three years later on BiFePO_3 .^[30] In it, they explained the asymmetry in their magnetoelectric measurements arose from toroidal moments, based upon the symmetry invariants of the antiferromagnetic structure.¹

Independently from the Russian scientists, Swiss scientists Schmid, Rivera, and their colleagues were studying the magnetoelectric susceptibility in various materials, including various boracites and LiCoPO_4 (among others). In the articles on LiCoPO_4 ,^[31, 33] Rivera and Schmid study the

¹A brief note: The works mentioned thus far (besides Edgar Ascher’s paper) were published by scientists from the former Soviet Union, and therefore much of their early work was originally published in Russian. As a result, there is not a consistent term used when referring to “materials with toroidal moments.” They are sometimes named “ferrotoroids” or simply materials with “toroid” or “toroidal” moments. The discrepancies complicate literature searches. I only consulted the work which has been translated into English.

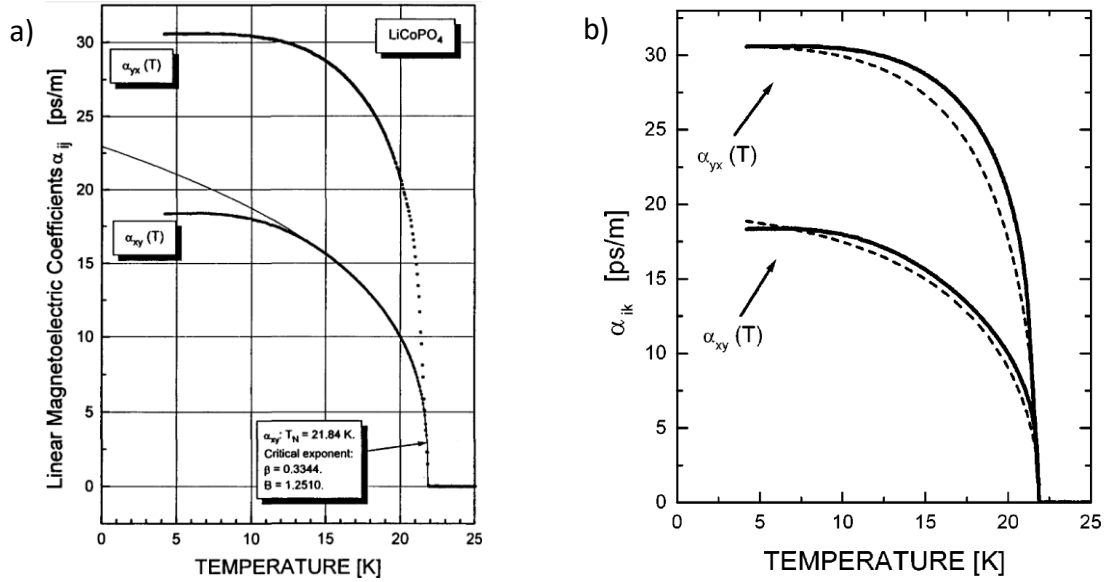


Figure 2.3: The temperature dependence of the α_{xy} and α_{yx} components of the magnetoelectric tensor in LiCoPO_4 . The components are highly asymmetric, with the α_{yx} component approximately two times greater than the α_{xy} component. a) Reproduced from Fig. 17 in Ref. 31. b) The data was republished with an improved fitting model as Fig. 5 in Ref. 32.

temperature dependent magnetoelectric susceptibility, and observe the component α_{xy} is about half the value of α_{yx} . Their measurements are presented in Fig. 2.3a. They also observe “butterfly loops,” near the transition temperature, which is just below 22 K. Fig. 2.4 presents their measurements. The “V” shape is due to reversing the antiferromagnetic domains in the material, as the magnetic field is reversed. However, the asymmetric shape to the features are what give them the name “butterfly” loops. Rivera was surprised to find such a feature in an antiferromagnet because it is typically only observed in ferromagnetic or ferrimagnetic (weakly ferromagnetic) crystals. The magnetoelectric tensor measurements only detected α_{xy} and α_{yx} terms, consistent with the point group mmm' and not a lower symmetry.

Rivera and Schmid collaborated with Kornev and several other colleagues to more thoroughly analyze this effect in both LiCoPO_4 and LiNiPO_4 . Their paper published in 2000 includes an improved fitting model for the temperature dependence of the α_{xy} and α_{yx} susceptibility, shown

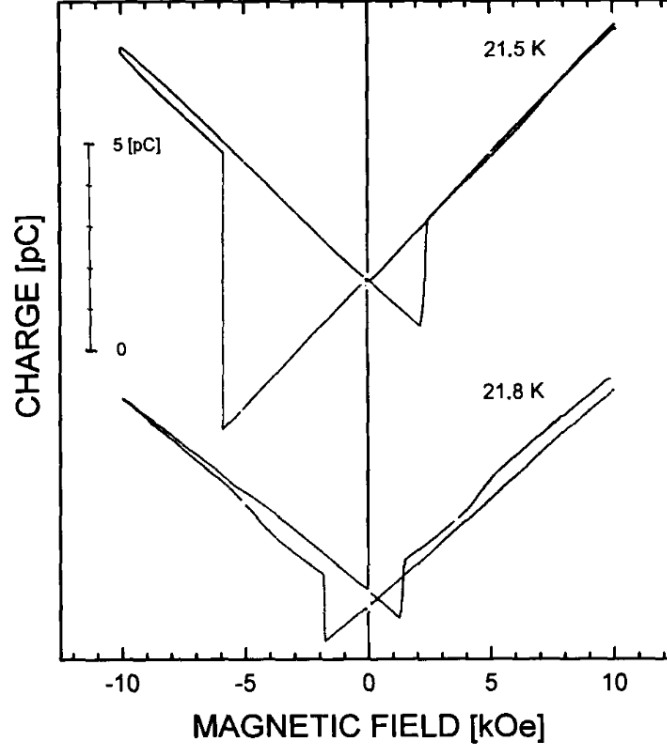


Figure 2.4: Butterfly loops measured in LiCoPO_4 near the Néel temperature just below 22 K. The electrodes for measuring the charge were applied on the (100)-cut crystal face. The magnetic field is applied parallel to the y axis, which is parallel to the magnetic spins. Reproduced from Fig. 11 in Ref. 31.

in Fig.2.3. The model is given by the equation

$$\alpha = \frac{a(T_N - T)^{1/2}}{1 - b(T_N - T)} \quad (2.10)$$

where T_N is the antiferromagnetic transition temperature. The fitted parameter values for $(\alpha_{xy}, \alpha_{yx})$ are $a = (-6.881, -14.72)$ and $b = (-0.03, -0.561)$. They also present a number of additional magnetoelectric measurements under a variety of fields and temperatures.

Kornev and the others then present a phenomenological model for understanding the butterfly loops and other behavior in these materials.[32] They consider the magnetic symmetry according to the formalism assigning components of spin density waves associated with the different possible irreducible representations for describing the symmetry breaking that occurs during the phase transition. These are described by a net vector, which is the sum of the contributions from

Table 2.2: Magnetic Symmetry Associated with the Irreducible Representations of the Point Group $Pnma1'$. Adapted (and corrected) from Tab. 1 in Ref. 32.

Γ^a	M.S.G. ^b	M.P.G. ^c	$\alpha_{ij} \neq 0^d$	Basis ^e
Γ_1^+	$Pnma$	mmm	none	$\mathbf{L}_1^y$
Γ_1^-	$Pn'm'a'$	$m'm'm'$	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$	$\mathbf{L}_1^y, \mathbf{L}_2^x, \mathbf{L}_3^z$
Γ_2^+	$Pn'm'a$	$m'm'm$	none	$\mathbf{M}^z, \mathbf{L}_1^x$
Γ_2^-	$Pnma'$	mmm'	α_{xy}, α_{yx}	$\mathbf{T}^z, \mathbf{L}_2^y$
Γ_3^+	$Pnm'a'$	$mm'm'$	none	$\mathbf{M}^x, \mathbf{L}_1^z$
Γ_3^-	$Pn'ma$	$m'mm$	α_{yz}, α_{zy}	$\mathbf{T}^x, \mathbf{L}_3^y$
Γ_4^+	$Pn'ma'$	$m'mm'$	none	$\mathbf{M}^y$
Γ_4^-	$Pnm'a$	$mm'm$	α_{xz}, α_{zx}	$\mathbf{T}^y, \mathbf{L}_2^z, \mathbf{L}_3^x$

^a Irreducible Representation, ^b Magnetic Space Group, ^c Magnetic Point Group, ^d Non-zero terms of the magnetoelectric susceptibility tensor α_{ij} , ^e Basis functions where the antiferromagnetic basis functions are $\mathbf{L}_1 = \mathbf{s}_1 + \mathbf{s}_2 - \mathbf{s}_3 - \mathbf{s}_4$, $\mathbf{L}_2 = \mathbf{s}_1 - \mathbf{s}_2 + \mathbf{s}_3 - \mathbf{s}_4$, and $\mathbf{L}_3 = \mathbf{s}_1 - \mathbf{s}_2 - \mathbf{s}_3 + \mathbf{s}_4$, the ferromagnetic $\mathbf{M} = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + \mathbf{s}_4$, and the ferrotoroidic $\mathbf{T}$.

each of the spins. For example, a ferromagnetic configuration is notated $\mathbf{M} = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + \mathbf{s}_4$. Antiferromagnetic configurations are noted as $\mathbf{L}_2 = \mathbf{s}_1 - \mathbf{s}_2 + \mathbf{s}_3 - \mathbf{s}_4$, etc. $\mathbf{L}_1$ and $\mathbf{L}_3$ are included in the caption of Tab. 2.2, which is an adaptation of Table 1 in their paper.[32] In their table presenting the irreducible representations of the magnetic structure $Pnma1'$, they indicate that three invariants are associated with $\mathbf{T}$ which they call “toroidal momentum.” In their discussion of the antiferromagnetic phase transition $Pnma1' \rightarrow Pnma'$ for LiCoPO_4 , they note the invariant $\mathbf{L}_2^y$ is also associated with a nonzero $\mathbf{T}^z$ value (i.e., it is spontaneous). After two brief sentences they conclude, “We shall not consider further this invariant.” In their conclusions they suggest the butterfly loops could be due to an incommensurate modulation of the spins, but acknowledge a good deal more experimental and theoretical work is needed for a more conclusive analysis.

In 1999, Schmid published an article titled “On the Possibility of Ferromagnetic, Antiferromagnetic, Ferroelectric, and Ferroelastic Domain Reorientations in Magnetic and Electric Fields.”[34] This

paper is the first attempt to expand Aizu's classification of ferroic materials.[35] The work does not have a separate classification of "ferrotoroidal" materials, but includes a lengthy table of materials and their ferroic classifications. In particular, it notes a number of compounds as "ferrotoroidal," including a number of boracites, LiCoPO_4 , and $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$. Schmid cites Popov,[29] but primarily cites work on boracites which were published in the journal *Ferroelectrics*. It is unclear if he was familiar at that time with any of the work which had been performed across the iron curtain.

Schmid wrote an extensive review of magnetoelectric materials in 2000.[36] In it, he listed a lengthy table of 34 known magnetoelectrics by their magnetic point group, ordering temperature, and maximum magnetoelectric coefficient value. LiCoPO_4 had the sixth-highest magnetoelectric coefficient in that table. In addition, since its point symmetry was mmm' and it had an orthorhombic crystal lattice, the a , b , and c axes would be inequivalent. This can be helpful when performing various kinds of physical measurements because it is easier to unambiguously align the sample and assign the axes. In addition, it had been known for several decades that the entire series of LiMPO_4 ($M = \text{Fe, Co, Mn, Ni}$) structural analogs could be grown from an inexpensive LiCl salt flux. Michel Mercier had studied this series in the mid-1960's through the early 1970's as part of his doctoral dissertation at the University of Grenoble with Néel, Bertaut, and others.[37, 38, 39, 40, 41, 42, 43] He had been able to grow large, quality single crystals several millimeters in size which certainly made crystal alignment much easier for performing the magnetoelectric measurements. The crystals are also indefinitely stable under ambient conditions. They do not need to be stored under inert atmosphere. Rivera and Schmid's earliest reported work on LiCoPO_4 cited Mercier,[38] so they were undoubtedly aware this was an ideal system for detailed study for practical reasons.

Besides the practical advantages for physical property measurements, the LiMPO_4 ($M = \text{Fe, Mn, Ni, Co}$) series is also ideal because of its structural chemistry. They belong to the general class of metal orthophosphates with the olivine-structure type with the space group $Pnma$ (No. 62). The particular structure type for LiMPO_4 is triphylite because the divalent transition metal ion is located on the $4c$ Wyckoff position and the monovalent lithium ions are located on $4a$ site. (If the situation is reversed with the transition metal on the $4a$ site, then the structure is named maricite.) In triphylite, the PO_4^{3-} units bridge the two layers of ions, so that the terminal oxygen atoms on the PO_4^{3-} ions form a distorted octahedral coordination environment around the Co ions. The structure of LiCoPO_4 is depicted in Fig. 2.5. It is also trivial to prepare solid solutions of triphylite, in which combinations of Fe^{2+} , Mn^{2+} , Ni^{2+} , and Co^{2+} are substituted on the $4c$ site, using stoichiometric quantities of starting reagents. Therefore, the variety of different magnetically-active ions which can be used to prepare structurally analogous materials makes this series rich for study, since the magnitude of the magnetic moment and even magnetic ordering can be rationally tuned by substitution on the $4c$ site.

Schmid subsequently wrote a more developed article on ferrotoroidics in the conference proceedings of the International Symposium on Ferroic Domains and Mesoscopic Structures which took place in Nanjing, China in 2000.[45] In this work, he presents Ascher's table as the starting point for rationalizing how ferrotoroidics could be considered a fourth category of ferroic materials. Schmid proposes that materials in this fourth category should exhibit the same hallmarks of other ferroics, including domain structure and hysteretic poling under applied fields. Because of this connection to other ferroics, he suggests standardizing the name to "ferrotoroidic" to maintain the "-oic" ending. He presents an extensive table re-defining primary, secondary, and tertiary ferroics according to those "driving fields." In this work, he cites multiple papers by

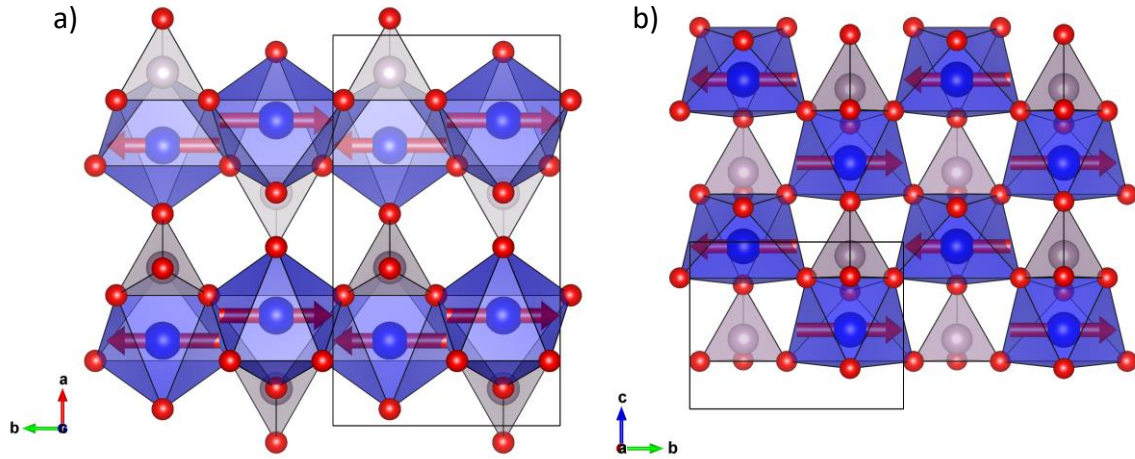


Figure 2.5: The magnetic structure of LiCoPO_4 . Cobalt ions are shown as blue spheres inside distorted octahedra. Phosphorus atoms are shown as grey spheres inside grey tetrahedra. Oxygen atoms are red spheres, located at the vertices of the polyhedra. The Li ions are omitted for clarity. The magnetic moments on the cobalt ions are indicated as red arrows. The depicted magnetic structure is $Pnma'$, in which the magnetic moments are aligned along the b axis. a) View along the c axis, $[001]$ direction. b) View along the a axis, $[100]$ direction. Reproduced from Gnewuch & Rodriguez (2019).[44]

Sannikov, Gorbatshevich, Ginzburg, Dubovik, and Popov.[19, 21, 22, 25, 29] (I cite the articles I was able to access.) Schmid published a similar review article from the proceedings of the 5th Magnetoelectric Interaction Phenomena in Crystals (MEIPIC-5) conference in 2004.[46] Around this time Schmid, his colleague Rivera, and two colleagues from Ames Labs, Vaknin and Zarestky, were intensely studying the magnetic ordering and magnetoelectric effect in LiCoPO_4 , LiNiPO_4 and other olivine analogs.[47, 48, 49, 50, 51] Also around this time, Manfred Fiebig began studying magnetoelectric phenomena and began collaborating with Rivera and Schmid, continuing to explore the connection to ferrotoroidicity in magnetoelectric materials.[52]

While the magnetic spins in LiCoPO_4 are aligned in an anti-ferromagnetic arrangement along the b axis, they are aligned along the c axis in LiNiPO_4 . This had been known since Santoro, Segal, and Newman's early neutron diffraction experiments,[53] and Mercier's magnetoelectric

experiments.[38] Although, even Mercier noted the direction of the spins in LiNiPO_4 as “c?” with a question mark in the table of his paper, and ended with a comment he was not certain of the magnetic structure.[38] In 2000 Kornev, Rivera, Schmid, and their co-authors observed unexpected “butterfly loops” in his magnetoelectric measurements for both LiCoPO_4 and LiNiPO_4 . [32, 54] This type of feature is seen in materials with a weak ferromagnetic signal, but the magnetic point groups mmm' for LiCoPO_4 and $mm'm$ for LiNiPO_4 associated with their established ordering should not allow a ferromagnetic signal. From 2001-2003 Kharchenko *et al.* followed up with detailed temperature and field-dependent magnetic susceptibility measurements of LiCoPO_4 and LiNiPO_4 single crystals from Schmid.[55, 56, 57] They all confirmed a very weak ferromagnetic signal. In addition, Kharchenko proposed that while the ground state magnetic ordering is commensurate in LiNiPO_4 , as it is heated just above its magnetic transition temperature it undergoes a phase transition to an incommensurate phase. In 2004 Vaknin and Zarestky collaborated with Rivera and Schmid, and confirmed through neutron diffraction studies the ordering was indeed incommensurate above about 21 K until around 36 K — above which the material behaves like a paramagnet.[49, 50, 51] They did not observe an incommensurate transition in LiCoPO_4 . This made LiCoPO_4 a more ideal model candidate for ferrotoroidicity, since the magnetic ordering was less complex than in LiNiPO_4 .

2.2: Experimental Evidence for Ferrotoroidicity, and Modern Descriptions of Toroidal Order

Interest in ferrotoroidicity was re-ignited around 2007 when Van Aken, Rivera, Schmid, and Fiebig published an article in *Nature* presenting evidence for ferrotoroidic domains in LiCoPO_4 . [58]

Their work used second harmonic generation (SHG) spectroscopy to visualize the domains in large single crystals. Figure 2.6 are a reproduction of their results. In this technique, electromagnetic radiation of a particular frequency is directed to the sample, so that a polarization is induced and radiation is emitted at double the incident frequency. This can be expressed as $\mathbf{P}(2\omega) = \epsilon_0 \hat{\chi} \mathbf{E}(\omega) \mathbf{E}(\omega)$ where $\mathbf{P}$ is the non-linear polarization of the emitted light, ϵ_0 is the permittivity of free space, $\mathbf{E}(\omega)$ is the electric field component of the incident light of a given frequency ω , and $\hat{\chi}$ the second-order susceptibility.[58] Like all physical property tensors, the components of $\hat{\chi}$ are restricted by the point symmetry of the crystal. Crystal domains are readily imaged using this technique, as their different orientations will cause some domains to appear brighter or darker than others. It should be noted, the researchers have specially built instrumentation for performing these measurements under cryogenic temperatures. With this, they were able to measure the SHG intensity as a function of temperature. They subsequently published a more detailed article on their measurements in *Physical Review Letters*. [59]

The prevailing assumption by that time was that only a change in toroidization would be observable, and the change would be associated with some slight change in the structure of the material. For example, in the work by Popov *et al.* explained a few paragraphs ago,[30] the toroidal moment was calculated using the difference between the centrosymmetric and non-centrosymmetric structures. However, it is also possible to have small displacements of atoms which preserve the underlying space group symmetry. For example, in LiCoPO_4 with the space group $Pnma$, the Co^{2+} ion lies on the $4c$ Wyckoff position. The coordinates for atoms lying on this position are given by $(\frac{1}{4} + \epsilon, \frac{1}{4}, -\delta)$ where the ϵ and δ describe the displacements of the atoms.[58] The other three sites are generated from the first. In addition, the single crystal neutron diffraction experiments of LiCoPO_4 by Vaknin, Zarestky, and Schmid had revealed the

spins on the Co ions were slightly canted away from the y axis by a small angle (4.6°).[\[48\]](#) In addition to the canting, Vaknin and his colleagues also referenced a 2001 article by Kharchenko, Schmid, and others. In it, they reported a weak ferromagnetic signal along the y axis from field-

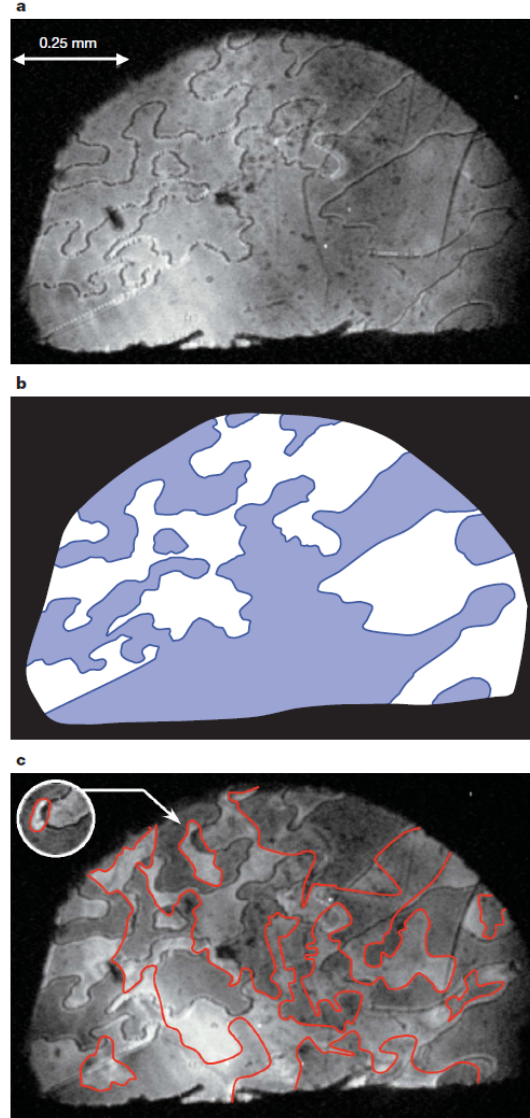


Figure 2.6: The SHG measurements of LiCoPO₄ presented by Van Aken *et al.* (2007). a) The image obtained from light corresponding to the χ_{xyy} component of the SHG susceptibility tensor. b) An illustration of the domain structure. c) The image obtained from the interference of light from the χ_{yyz} and χ_{zyy} components. The new domains which result are outlined in red. They correspond to the walls of the ferrotoroidic domains. The inset is evidence the domain wall moved upon being cooled below the antiferromagnetic transition temperature. Originally published in Ref. [\[58\]](#) and reproduced in the review article by Gnewuch & Rodriguez (2009).[\[44\]](#)

and temperature-dependent magnetization measurements of a single crystal of LiCoPO_4 . The combination of these two subtleties lowers the magnetic space group symmetry from $Pnma'$ to $P2'_111$ (or $P12'_11$ depending upon the chosen axis), which corresponds to lowering the point group symmetry from mmm' to $2'$.

Van Aken and his colleagues suggested the possible mechanism for a toroidal state in LiCoPO_4 is due to these subtle changes in the magnetic structure.[58] The reduction in the point symmetry from mmm' to $2'$ lowers the number of symmetry operations from eight to two, which would result in four different domain states. They argued that two of the domains could be considered antiferromagnetic, and the other two ferrotoroidic domains. A year after the paper was published, Schmid (one of the co-authors) argues all four domains are ferrotoroidic.[60] His argument is based upon Litvin's work published shortly after the *Nature* article.[61] Litvin extended Aizu's ferroic classification scheme to include ferrotoroidic order, and to determine the number of distinguishable domains permitted in a ferrotoroidic material. His result was that the permitted number of domain states does not change. It is still determined by the magnetic domain states. Therefore Schmid argues that the antiferromagnetic domains should be considered ferrotoroidic domains. He considers them two different descriptions for the same physical state.

The *Nature* article by Van Aken *et al.* also made a first attempt at modeling a "ring of spins" in the crystal structure. Figure 2.7 is a reproduction of the figure they presented in their paper.[58] Since $\mathbf{T} \propto \sum_{\alpha} \mathbf{r}_{\alpha} \times \mathbf{S}_{\alpha}$ they defined the center of the unit cell as the origin of the ring of spins, and the $\mathbf{r}$ vectors were then the vectors pointing from the center to each of the four spins.[58] Due to the inherent symmetry of the unit cell, this meant that the $\mathbf{r}$ vectors had two different magnitudes, so that $\mathbf{r}_{1,3} > \mathbf{r}_{2,4}$. The assumption then was that the $\mathbf{r}_1$ and $\mathbf{r}_3$ vectors would give a greater contribution than the other two. In addition, the $\mathbf{r}_1$ and $\mathbf{r}_3$ vectors could be

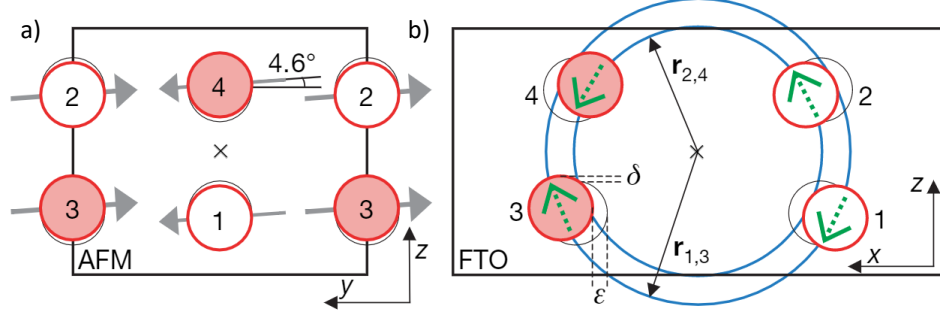


Figure 2.7: Model of the ring of spins in LiCoPO_4 leading to the toroidal moment, as presented in Van Aken *et al.* (2007). Reproduced from Figure 3 in Ref. 58.

considered to form a clock-wise ring, while the $\mathbf{r}_2$ and $\mathbf{r}_4$ vectors would give an anti-clockwise ring. Therefore the contributions from each would be opposite and partially cancel with one another. Consequently, one would only observe a net toroidal component $\mathbf{T}_y$. The slight canting of the spins would slightly change the magnitude of $\mathbf{T}$ since it is defined by $\mathbf{r}_\alpha \times \mathbf{S}_\alpha$.

The major significance of the 2007 Van Aken article was re-igniting interest in toroidal materials over the next several years. Several theorists, notably Eerenstein, and also Ederer and Spaldin were exploring how ferrotoroidic materials would be classified within the established fields of ferroics, multiferroics, and magnetoelectrics.[62, 63, 64] Ederer and Spaldin in particular were interested in developing a clearer model for how toroidal moments could occur in a crystalline solid, with a periodic boundary. In their 2007 article,[63] they began by considering a local distribution of magnetic moments in an ordered antiferromagnetic material, described by Popov *et al.*[29] according to Eq. 2.4, 2.5, and 2.9. Ederer presented a slightly simpler form of Eq. 2.9:

$$\mathbf{t} = \frac{1}{2} \sum_{\alpha} \mathbf{r}_{\alpha} \times \mathbf{m}_{\alpha}. \quad (2.11)$$

Since $m_{\alpha} = g\mu_B \mathbf{S}_{\alpha}$, the units of μ_B are implied by treating the spins as individual magnetic moments on magnetic ions. Using this same notation, the net toroidal moment per unit volume is

$$\mathbf{T} = \frac{1}{2V} \sum_i \mathbf{r}_i \times \mathbf{m}_i, \quad (2.12)$$

where V is the volume of the unit cell and the index i indicates the sum of all $[\mathbf{r}_\alpha \times \mathbf{m}_\alpha]$ in the material. Popov and his colleagues had performed similar analyses with the $[\mathbf{r}_\alpha \times \mathbf{S}_\alpha]$ vectors in $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$, giving units of a net toroidal moment per unit cell as $\mu_B \text{\AA}$. Ederer and Spaldin report the units as $\mu_B \text{\AA}^{-2}$ for the spontaneous toroidization and as $\mu_B \text{\AA}$ per unit cell. They give examples calculating the net toroidal moment for LiCoPO_4 , $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$, and BiFeO_3 . They calculated the toroidal moment per unit cell for LiCoPO_4 to be $1.75 \mu_B \text{\AA}$.

Ederer and Spaldin also discuss choice of origin in some detail in their 2007 article.[\[63\]](#) They also point out that only the “fully compensated” components in an antiferromagnetic configuration would contribute to a toroidal moment, and the toroidal moment would be independent of the chosen origin in this case. Figure [2.8b](#) is a graphical depiction of how Spaldin *et al.* proposed the displacements of the magnetic moments can lead to a toroidization in the lattice. Their argument is based upon how net polarization occurs in a lattice due to ion displacements, which is depicted in Fig. [2.8a](#). Spaldin published similar figures with co-authors in a few articles published since 2007 as well. See Fig. 3 & 5 in Ref. [63](#), Fig. 4 in Ref. [65](#), and Fig. 6 in Ref. [66](#).

They did warn that if a structural distortion accompanied the toroidal origin, it is important to maintain the same origin in both structures. The contribution to the toroidal moment described according to Eq. [2.11](#) is due to an antiferromagnetic configuration of moments. If the moments are not fully compensated so that there is a ferromagnetic component (like in a ferrimagnet) then that contribution can be described according to

$$\tilde{\mathbf{t}} = \frac{1}{2} \bar{\mathbf{R}} \times \mathbf{m}, \quad (2.13)$$

where $\bar{\mathbf{R}}$ is the average position of the magnetic moments. While $\mathbf{t}$ is independent of the origin, $\tilde{\mathbf{t}}$ is dependent. They went on to argue that since the definition of ferrotoroidic ordering requires breaking both time and spatial inversion symmetry, in antiferromagnetic configurations this could

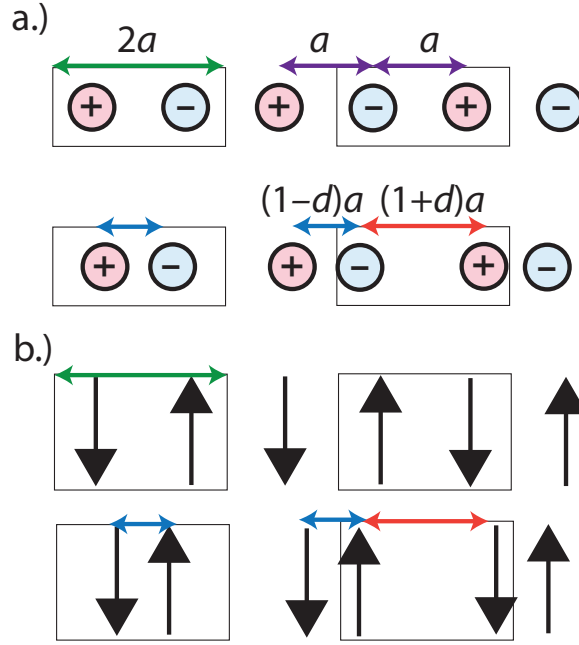


Figure 2.8: Adaptation of the model for producing net toroidization in a crystal lattice. a) Rectangle indicates one unit cell with length $2a$ of two oppositely charged particles, separated by a distance a . As the charges move closer to one another by a displacement d they produce a net polarization. b) The charged particles are replaced with magnetic moments of opposite spin. This is the simplest depiction of an antiferromagnetic arrangement. As the moments are distorted from their original location, the net change in the arrangement would be described as the net toroidization. Reproduced from Gnewuch & Rodriguez (2019).

occur from changes in the orientation or positions of the magnetic moments.

Since a ferro(i)magnet always breaks time inversion symmetry, then in order to also break spatial inversion symmetry, the positions of the magnetic moments must not be related by spatial inversion. In other words, their arrangement must be noncentrosymmetric. By this reasoning, they argued simply changing the orientations of the magnetic moments in an antiferromagnetic arrangement would be sufficient to break both spatial and time inversion symmetry. Ederer and Spaldin concluded by warning that if any structural displacements accompany the magnetic ordering, care must be taken to ensure a consistent origin choice. For this reason, they advocated choosing the center of the unit cell as the origin for defining the $\mathbf{r}$ vectors when calculating $\mathbf{r}_\alpha \times \mathbf{m}_\alpha$.

As a brief note, Ederer published an article using similar analysis in 2009.[64] (He was the sole author.) In it, he compares the structures of BiFeO_3 and FeTiO_3 , elaborating on the analysis for BiFeO_3 presented in his previous work.[63] He argues the slight rotations of the oxygen octahedra in the paraelectric $R\bar{3}c$ phase of FeTiO_3 lowers the magnetic symmetry and produces toroidal moments in the material. He then goes on to argue the antiferromagnetic order parameter can be used to explain the magnetoelectric tensor in the material. He emphasizes both the position and orientation of the magnetic moments need to be analyzed together when determining how the antiferromagnetic configuration can produce toroidal moments. He also argues that if a toroidal material has a spontaneous non-zero toroidal moment, a non-toroidal material would correspond to a “centrosymmetric” ensemble of toroidal moments. However, he cautions against using Eq. 2.11 in a single unit cell to conclude $\mathbf{t} = 0$, and that the material is therefore non-toroidal. As a note, if one does this with BiFeO_3 , the toroidal moments produced are in a centrosymmetric arrangement and therefore cancel with one another, leading to $\mathbf{t} = 0$.

Separately from Ederer, Spaldin continued to collaborate with a variety of colleagues on theoretical considerations for ferrotoroidicity. In 2008 she co-authored an extensive review paper with Fiebig and Mostovoy exploring toroidal moments and the connection to the magnetoelectric effect.[65] They clarified that the toroidal moment would be considered a vector order parameter analogous to magnetic and electric dipoles. Long-range ordering of the toroidal moments should occur spontaneously below a certain critical temperature. The ordering should be able to be described according to a single order parameter. Orientational domains would be expected to spontaneously occur below the critical temperature. Like other ferroics, there should be a vector (or tensor) field which could control the domains. (In the following years, Litvin published three papers tabulating all the tensors which would distinguish ferrotoroidic domains.)[16, 67, 68]

Since different domains have different orientations of the order parameter, applying a field would change the energy between the states so that under a strong enough field they could be reoriented. To be considered a primary ferroic, the switching would need to occur according to only one field.

The paper by Spaldin, Fiebig, and Mostovoy also further develops the concept of a toroidal lattice.[65] They were particularly concerned with how to achieve simultaneously breaking spatial and time inversion symmetry. They assume there would need to be a structural distortion of some kind, so that the magnetic ions would shift. This would result in a change in the toroidization, which would be the measurable quantity. In ferroelectric transitions, structural distortions break the spatial inversion within the cell, leading to a polarization in the cell. Only changes in polarization are measurable, so it seemed reasonable toroidization would be the same. In addition, the toroidization in a lattice would not be a single value, because it would have a different value for the translation of every lattice vector R . If V is the volume of the primitive cell, then the change in the toroidization would be:

$$\Delta T = \frac{g\mu_B}{2V} R \times S, \quad (2.14)$$

where g is the gyromagnetic ratio. The authors call this the “toroidization increment” of the “toroidization lattice.” The assumption would be that the toroidization increments would be defined by the shifts in the ions in the lattice to form antiferromagnetic dimers (or pairs of anti-aligned moments). The shifts would be relative to a high-temperature non-toroidized reference structure (presumably the paramagnetic state), which would be straightforward to calculate as long as a consistent origin is chosen.

One mechanism Spaldin *et al.* proposes for toroidization is spin-lattice coupling due to superexchange interactions.[65] This kind of distortion could break both spatial and time inversion symmetries simultaneously. The strength of superexchange interactions depends on the

metal cation–oxygen anion–metal cation bond angle, where the metal is a magnetic ion. These interactions are described by the Anderson-Kanamori-Goodenough rules.[69] For example, if the angle is close to 90° the magnetic moments tend to align in a ferromagnetic arrangement; if the angle is closer to 180° the moments align in an antiferromagnetic arrangement. The rules depend upon the particular cation (metal and oxidation state) because it depends upon the degree of orbital overlap (covalency) between the oxygen atoms and the metal cations. If the involved atoms shift due to an applied field or phase transition, the exchange interactions would therefore be impacted as well. The other possible mechanism the authors suggest would be due to purely electronic interactions with no atomic distortions. The change in the spin states would cause virtual excited states in the metal cation–oxygen anion–metal cation bonds. The changes in the electronic structure would cause a dipole moment to form as the electrons are redistributed, creating oxygen holes as the electrons move closer to the metal cations.

The paper by Spaldin, Fiebig, and Mostovoy [65] also discusses several limitations to using the linear magnetoelectric effect to study potential ferrotoroidic materials. While the magnetic multipoles of torus-like spin arrangements would produce toroidal moments, and while toroidal materials would be expected to display a linear magnetoelectric effect, they argue it is not possible to assign specific components of the magnetoelectric tensor to contributions from toroidal moments alone. In other words, toroidal moments would indeed give an off-diagonal magnetoelectric response, but there can be other causes for anti-symmetric off-diagonal terms. As an example, they cited the conical spiral ordering in ZnCr_2Se_4 where the rotation axis is parallel to the magnetic propagation vector.[70, 71] That configuration would result in the antisymmetric off-diagonal components $\alpha_{xy} = -\alpha_{yx}$ in the magnetoelectric tensor. They also propose general criteria for good magnetoelectric materials. For example, the upper limit of the magnetoelectric

tensor is proportional to the dielectric susceptibility χ_{ii}^e and magnetic susceptibility χ_{jj}^m so that

$$\alpha_{ij} \leq \sqrt{\chi_{ii}^e \chi_{jj}^m}. \quad (2.15)$$

They point out that magnetic geometrically frustrated systems often have large magnetic susceptibilities, which would make them good materials to consider. Magnetic frustration can also break time inversion symmetry. To conclude, they emphasize that while the magnetoelectric effect is useful for studying ferrotoroidic materials, the measurements are indirect. The anti-symmetric off-diagonal $\alpha_{ij} = -\alpha_{ji}$ tensor components are not unique to ferrotoroidic materials.

Spaldin, Fiebig, and Mostovoy [65] also clarify that a ferrotoroidic would be considered a primary and not a secondary ferroic. The free energy term of a ferromagnetoelectric is $F = -\alpha_{ij}E_iH_j$. It is a secondary ferroic because both the electric and magnetic field are required to switch the domains. It is, by definition, always observed in materials which exhibit a linear magnetoelectric effect. The authors argue that even though crossed electric and magnetic fields ($E \times H$) are used to approximate a toroidal field in experimental measurements, it is only the toroidal field which controls the order parameter in a ferrotoroidic. Therefore, ferrotoroidic materials can be considered primary ferroics. It should be mentioned here, that a linear magnetoelectric effect is not unique to ferrotoroidic materials. However, ferrotoroidic materials would exhibit a linear magnetoelectric effect with anti-symmetric off-diagonal components. It is a necessary but not sufficient condition for ferrotoroidicity. The challenge is that from a point symmetry perspective you can only predict which tensor terms of a physical property are allowed or disallowed by symmetry. The actual physical response can only be determined experimentally.

Finally, Spaldin, Fiebig, and Mostovoy[65] consider the possibility of antiferrotoroidic order. They explain that such a system would need to break the same symmetries as ferrotoroidic order, but not lead to coupling with an external field. In other words, it must break both spatial and

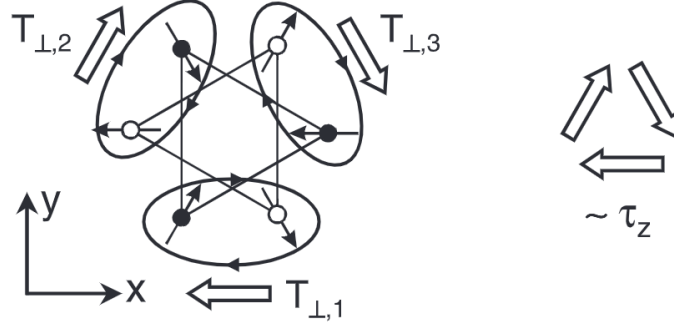


Figure 2.9: Model of antiferrotoroidic order in YMnO_3 proposed by Spaldin, Fiebig, and Mostovoy (2008). The figure on the left is simplified depiction of the arrangement of Mn^{3+} spins. The open circles indicate the spins along $z = 0$ and the filled circles indicate the spins translated to $z = c/2$. The three sublattices are indicated by ovals and the toroidal moment for each is labeled with large white arrows. The smaller figure on the right emphasizes the toroidal moments for the sublattices would cancel, but lead to a net toroidal moment along the z axis. Reproduced from Fig. 8 in Ref. 60.

time inversion symmetry but yet lead to a net toroidal moment of zero. They suggest the domains in YMnO_3 could be considered antiferrotoroidic, but do not suggest a possible microscopic mechanism for how such a state could occur. Their model is presented in Fig. 2.9. They propose there are three different types of ferrotoroidic sublattices present, represented by large arrows in the x and y plane. While the net toroidal moments of the three different orientational sublattices would cancel one another, their arrangement would produce a net toroidal moment along the z direction.

2.3: Toroidal Point Groups Based upon the Limiting Group Symmetry

Around the same time Spaldin, Fiebig, and Mostovoy were writing their article, Schmid also wrote an extensive review article of ferrotoroidic materials.[60] Schmid was particularly interested in the point symmetry which would permit ferrotoroidic ordering, and how to unambiguously classify a ferrotoroidic material as a primary ferroic. In crystallography the term “point group”

can be used in several different contexts: molecular or site symmetry, and the point symmetry of the space group. The point symmetry of a macroscopic crystal represents the vectors normal to the crystal faces and is useful for understanding the macroscopic physical properties. However, molecular or site symmetry describes the symmetry around a point in the crystal structure. Since the early work on toroidal materials was investigating the physical properties, the exploration of the symmetry was restricted to point symmetry of the macroscopic crystal. Therefore the assumption when considering candidate materials is the point symmetry of the space group must be included in the list of point groups which permit toroidal ordering.

Ascher's second article [15] included Venn Diagrams of the different point groups which would be considered ferromagnetic, ferroelectric, and the "third" category (what he called ferrokinetic or ferroconductive). Throughout the rest of the 20th century most every research article on "ferrotoroidal" order included some discussion of permitted point groups. However, there was never any consensus on a list. Schmid presented a Venn Diagram adapted from Ascher's work.[13, 15, 60] Figure 2.10 is a simplified version. The symmetric categorization seemed compelling, with 19 point groups permitting one type of ordering for each category, four point groups permitting two types of ordering for each category, and nine point groups permitting all three types of ordering.

Schmid reviewed the work by several researchers who had considered the permitted tensor terms of magnetoelectric materials.[60] For example, Grimmer considered which tensors would be permitted under $\bar{1}'$ inversion,[72] based upon Ascher's 1966 table (Tab. 2.1). These were tabulated by point group. Schmid and his colleague Rivera had long considered the different tensors of magnetoelectric materials. The work presented in his 2008 paper includes a number of tables organized by point group symmetry which were modifications of his earlier work

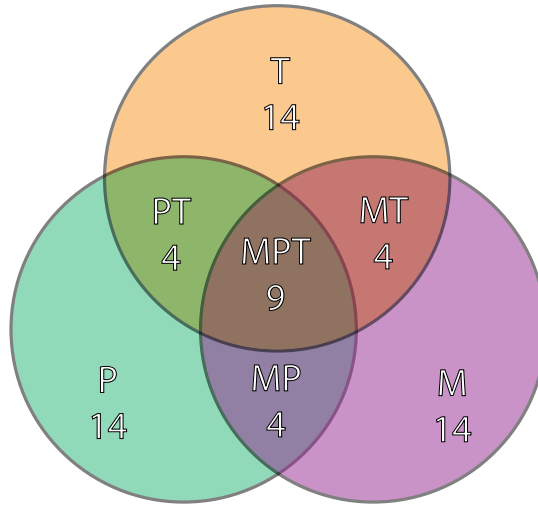


Figure 2.10: Simplified version of Ascher’s 1974 Venn diagram showing the relationships between the the point groups associated with net magnetization **M**, polarization **P**, and toroidization **T**.^[15] A modified version of this diagram was presented in Schmid (2008).^[60] The premise is that depending upon the point symmetry, one, two, or three types of ordering can be permitted in the same phase for each category. In a primary ferroic, only one type of ordering should be allowed. Reproduced from Gnewuch & Rodriguez (2019).^[44]

published in 1973, 1994, and 2000.^[36, 73, 74] The 1994 paper meticulously compares the point groups from tables by half a dozen contemporaries studying magnetic materials including Birss, Cracknell, and Siratori. It helpfully clarifies conversion of SI units in magnetoelectric measurements. It also clarifies how the chosen setting for the point group impacts the permitted tensor terms. In his 2008 paper, Schmid extends his original work on the classifications of ferroic order (primary, secondary, tertiary, etc.) to include ferrotoroidic ordering, and emphasizes that multiple types of ordering can co-exist with one another. For example, he explains that certain point groups can permit both ferrotoroidic and antiferromagnetic order. Table 2.3 summarizes the permitted point groups Schmid determined.

Since Schmid was working closely with the experimentalists Fiebig, Van Aken, and Rivera, he was particularly concerned with understanding how the magnetic point symmetry would

Table 2.3: The 31 magnetic point groups that allow for ferrotoroidicity, classified according to Table 7 in Ref. 60.

Order allowed	Magnetic point groups
Ferrotoroidic and antiferromagnetic	$\bar{1}', 2/m', 2'/m, m'mm,$ $\bar{4}', 4/m', 4/m'mm, \bar{4}'m2',$ $\bar{3}', \bar{3}'m,$ $\bar{6}', 6/m', 6/m'mm, \bar{6}'m2'$
Ferrotoroidic and ferromagnetic	$22'2', 42'2', 32', 62'2'$
Ferrotoroidic and ferroelectric	$mm2, 4mm, 3m, 6mm$
All three ferroic orders	$1, 2, 3, 4, 6,$ $m, 2', m', mm'2'$

impact the physical property measurements. This would influence how they were classifying domains in the SHG (second harmonic generation) studies. For example, I mentioned previously that in the 2007 Van Aken article, they claimed there were two antiferromagnetic and two ferrotoroidic domains. By Schmid's 2008 paper,[60] he is convinced all four domains are both antiferromagnetic (weakly ferromagnetic) and ferrotoroidic. The next experimental challenge to address would be controlling the domains with applied electric and magnetic fields. To do this systematically, it is first necessary to determine how ferrotoroidics are classified compared to other kinds of materials with magnetic and electric ordering, such as magnetoelectrics, multiferroics, etc. In Table 2 of that paper,[60] Schmid organizes all of the 122 Heesch-Shubnikov magnetic point groups by their type of magnetic and/or electric ordering, and if an "invariant velocity vector V_s " is permitted or not. Schmid explains the V_s vector is that "third" type of vector Ascher considered in 1974.[15] Schmid believes this is appropriately called "net toroidization," analogous to "magnetization" and "electric polarization." Of the 122 magnetic point groups, 19 permit only a linear magnetoelectric effect and not any higher ordering. (For example, ferromagnetobielectrics are controlled by

Table 2.4: The 19 magnetic point groups which permit only a linear magneto-electric effect,^a sorted by whether they permit a spontaneous toroidal moment T_s . The information is adapted from Table 2 in Ref. 60.

T_s not permitted	Permits T_s
$m'm'm'$	$\bar{1}', 2/m', 2'/m$
$4'/m', 4'/m'm'm, 4/m'm'm'$	mmm'
$\bar{3}'m'$	$4/m', 4/m'mm$
$6/m'm'm'$	$\bar{3}', \bar{3}'m$
$432, m'3, m'3m'$	$6/m', 6/m'mm$

^ai.e. these point groups do not permit any higher order effects such as a linear magnetobielectric effect

one electric and two magnetic fields so that the free energy F is proportional to three terms:

$F \propto \Delta\gamma_{ijk}H_iE_jE_k$.) They are listed in Tab. 2.4.

Schmid's 2008 article [60] cited Litvin's early 2008 article [61] but was published before Litvin's series of articles mentioned previously.[16, 67, 68] Litvin's concern is focused on the consistent mathematical treatment of ferrotoroidics with other symmetry classification methods for primary ferroics.[61] Table 2.5 includes all the toroidal point groups and the forms of the toroidal tensor Litvin tabulated in Ref. 67.

It is worthy to note that one of the benefits of investigating olivine LiCoPO_4 as a candidate ferrotoroidic material is that the space group $Pnma'$ with the point group mmm' would have a toroidal moment along only one direction $(0,0,T_3)$. Note: $m'mm$ would have the net toroidal moment $(T_1,0,0)$. If the magnetic space group is lower and actually $P2'_111$ with a point group $2'_y$ it would be permitted along two directions $(T_1,0,T_3)$. Note: $2'_z$ would have the net toroidal moment $(T_1,T_2,0)$. Depending upon which symmetry elements in the point group are primed will impact the final allowed directions of the toroidal moment.

A Note: A modern resource (currently being improved and expanded) to determine the

Table 2.5: The 31 magnetic point groups allowing a toroidal moment along one, two, or three directions, as adapted from Tables 2 and 3 in Ref. 67.

Magnetic Point Group (MPG)	Form of the Toroidal Physical Property Tensor	Magnetic Point Group (MPG)	Form of the Toroidal Physical Property Tensor
1	(T_1, T_2, T_3)	$4_z m_x m_{xy}$	$(0, 0, T_3)$
$\bar{1}'$	(T_1, T_2, T_3)	$\bar{4}'_z 2'_x m_{xy}$	$(0, 0, T_3)$
2_z	$(0, 0, T_3)$	$4_z / m'_z m_x m_{xy}$	$(0, 0, T_3)$
$2'_z$	$(T_1, T_2, 0)$	3_z	$(0, 0, T_3)$
m_z	$(T_1, T_2, 0)$	$\bar{3}'_z$	$(0, 0, T_3)$
m'_z	$(0, 0, T_3)$	$3_z 2'_x$	$(0, 0, T_3)$
$2'_z / m_z$	$(T_1, T_2, 0)$	$3_z m_x$	$(0, 0, T_3)$
$2_z / m'_z$	$(0, 0, T_3)$	$\bar{3}'_z m_x$	$(0, 0, T_3)$
$2'_x 2'_y 2'_z$	$(0, 0, T_3)$	6_z	$(0, 0, T_3)$
$m_x m_y 2_z$	$(0, 0, T_3)$	$\bar{6}'_z$	$(0, 0, T_3)$
$m'_x m_x 2'_z$	$(T_1, 0, 0)$	$6_z / m'_z$	$(0, 0, T_3)$
$m'_x m_y m_z$	$(T_1, 0, 0)$	$6_z 2'_x 2'_1$	$(0, 0, T_3)$
4_z	$(0, 0, T_3)$	$6_z m_z m_1$	$(0, 0, T_3)$
$\bar{4}'_z$	$(0, 0, T_3)$	$\bar{6}'_z m_x 2'_1$	$(0, 0, T_3)$
$4_z / m'_z$	$(0, 0, T_3)$	$6_z / m'_z m_x m_1$	$(0, 0, T_3)$
$4_z 2'_x 2'_{xy}$	$(0, 0, T_3)$		

tensor properties based upon the magnetic point group is the program MTENSOR.[75] It is available from the Bilbao Crystallographic Server at <https://cryst.ehu.es>, under the programs for “Magnetic Symmetry and Applications.” The server webpage directs you to input the appropriate magnetic point group from a list of options, and then the desired physical property tensor. For toroidal moments, this is the “Polar Toroidal Moment T_i .” The server then runs the program to calculate the tensor, and displays the computed result on a new webpage. In the sidebar the authors of MTENSOR explain they define an “Axial Toroidal Moment A_i ” as an axial tensor invariant under time inversion symmetry, and a “Polar Toroidal Moment T_i ” as variant under time inversion symmetry. Neither are an optimal label, since the symmetry of toroidal moments are best described by “axio-polar” vectors, which will be discussed later in §3.3. However, “axio-

polar” vectors are in fact variant under time-inversion ($1'$). Therefore the method used by the authors of MTENSOR computes a logically consistent result for the “Polar Toroidal Moments.” As will be explained in §3.3 & 3.6, space-time inversion ($\bar{1}'$) only has meaning in geometric space because inversion symmetry of any kind (*i.e.* $\bar{1}$ or $\bar{1}'$) is defined about a point of inversion (*i.e.* inversion center). It is therefore difficult to fully appreciate how space-time inversion ($\bar{1}'$) is distinct from space ($\bar{1}$) and time ($1'$) inversion in terms of point symmetry alone since they can appear to produce identical results. In geometric space it is clear they in fact do not.

Around the same time as Schmid, Rivera wrote his own review article [76] on magnetoelectric materials. In it, Schmid requested Rivera include an updated form of the table of tensors for the linear magnetoelectric effect in the appendix of his 2008 article.[60] The updated table includes all of the different settings for the monoclinic point groups. Rivera discusses Schmid’s 2008 article extensively. He cautions that $(E_i \times H_i)$ cannot be approximated as a vector S in order to neatly claim the density of free energy can be written according to the vector components (E, H, S, σ) . This is because when $(E \times H)$ is substituted into the free energy expressions for S , the results are the same as simply considering the free energy in terms of (E, H, σ) . This is because S is not a new independent variable. Schmid justified the redundancy by stating $T_i S_i$ is a special case of the linear magnetoelectric effect.[60] In other words, Schmid treats the fact that $T_i(E_i \times H_i) = T_i S_i$ as evidence that ferrotoroidic order can coexist with other types of ordering, and therefore other physical properties. They are different mathematical expressions for the same physical phenomena.

Schmid’s 2008 paper also discusses the connection between Ascher’s 1966 Table [13] and the limiting groups for types of ferroic ordering, citing Dubovik’s 1990 article.[19] However, it is in subsequent years that the theoreticians Saxena and Lookman from Los Alamos National

Laboratory, and Castán and Planes from the University of Barcelona, deeply explore the limiting groups and their implications for ferrotoroidic order.[77, 78, 79, 80]

Saxena was interested in the underlying symmetry of order parameters.[77, 78] All ferroic ordering can be described according to an order parameter. This is a vector with a certain symmetry which describes the net order in the material. For example, electric polarization can be described with a polar vector; magnetization can be described with an axial vector. The symmetry of a polar vector can be considered like that of a stationary cone, the symmetry of an axial vector like that of a rotating cylinder, and the symmetry of uniaxial stress as a stationary cylinder. Saxena proposed that the symmetry of an “axio-polar” vector like in ferrotoroidic materials would be that of a rotating cone.

By considering the symmetries of these geometric entities, Saxena deduced the limiting groups for each of them, listed in Table 2.6. The limiting group is the maximal symmetry compatible with the order parameter. All subgroups of the limiting group will also have the same order. For example, all subgroups of $\frac{\infty}{m} \frac{2'}{m'} \frac{2'}{m'}$ are ferromagnetic. They permit a net magnetization. The limiting groups in the far right column of Table 2.6 are the more traditional notations, since a ferroelectric would never break time inversion symmetry (thus always possess it). Saxena’s notation (in the middle column) approximates “time inversion” in a ferroelectric as exchanging positive and negative charges. Based upon this scheme, Saxena proposed the limiting group for ferrotoroidics would be $\frac{\infty}{m'} \frac{2}{m} \frac{2}{m}$, since it has the same symmetry as an axio-polar vector. He points out this has the same symmetry as the Poynting vector ($S = E \times H$), which describes the energy flux of an electromagnetic field, but did not discuss that further.[77, 78, 80]

Saxena then collaborated with Castán and Planes to consider how toroidization would be incorporated into established Maxwell thermodynamic relations,[79] Clausius-Clapeyron equations,[79]

Table 2.6: The limiting groups of primary ferroics. Summarized from Schmid in Ref. 60 and Saxena in Ref. 77, 78.

Ferroic Order	Limiting Group Ref. 77, 78	Limiting Group Ref. 60
Ferroelastic	$\frac{\infty}{m} \frac{2}{m} \frac{2}{m}$	$\infty/m1'$
Ferromagnetic	$\frac{\infty}{m} \frac{2'}{m'} \frac{2'}{m'}$	∞/mmm
Ferroelectric	$\frac{\infty}{m'} \frac{2'}{m} \frac{2'}{m}$	$\infty/mm1'$
Ferrotoroidic	$\frac{\infty}{m'} \frac{2}{m} \frac{2}{m}$	$\infty/m'mm$

and Landau theory of phase transitions.[80] Those theoretical descriptions are a required prerequisite to search for “toroidocaloric” effects, although no experimental work has been reported to date. Instead, the next major challenge experimentalists devoted their attention to was demonstrating ferrotoroidic domains could be controlled by magnetic and electric fields.

2.4: Subsequent Neutron Scattering Studies of LiMPO_4 ($M = \text{Fe, Co, Ni, Mn}$)

As a consequence of the high-profile attention given to LiCoPO_4 ,[58] a number of researchers continued to intensely study the magnetism and magnetic structure of LiCoPO_4 and other olivine analogs in the years following 2007.

In 2009 Jensen published his endeavors and that of Vaknin, Zarestky, and nine additional colleagues from six different institutions who together were intensely studying the magnetic structure of LiNiPO_4 . [81] They performed diffraction experiments under magnetic fields, to better understand the mechanism for an electric polarization (and therefore the magnetoelectric effect) in the material. In particular, they studied the commensurate and incommensurate phase transitions under applied magnetic fields, in order to produce the entire magnetic field- and temperature-dependent phase diagram. They concluded the symmetries of the zero-field commensurate

and incommensurate structures cannot produce an electric polarization. It is only by applying the magnetic field along the c axis in the low-temperature (ground state) commensurate phase that an electric polarization is possible. When the field is applied along c , the magnetic moments are rotated along a so that the axis is polarized. The commensurate antiferromagnetic structure for LiNiPO_4 allows spin canting components along both c and a . This asymmetry enables an electric polarization in the material along the b axis. Therefore, the observed magnetoelectric behavior in the material is a result of the magnetic spins reorienting in response to the magnetic field.

During this time period Vaknin and Zarestky collaborated with their colleagues Li and Tian on a number of neutron diffraction studies on LiMPO_4 ($M = \text{Fe, Mn, Co, Ni}$) materials.[82, 83, 84, 85, 86] LiMnPO_4 has the magnetic structure $Pn'm'a'$ with the point group $m'm'm'$ and so is not expected to be ferrotoroidic.[87] Also, its magnetoelectric coefficient is an order of magnitude lower than LiCoPO_4 . [36, 38, 42, 43, 73] (The reported values for the magnetoelectric coefficient vary in all the cited references. This is most likely due to different treatment of units for the applied fields, although the units are not clearly indicated in each paper I cited.) However, since LiMnPO_4 is structurally analogous to LiMPO_4 ($M = \text{Fe, Ni, Co}$) it is often studied with them for comparison. Likewise, even though LiFePO_4 has the same magnetic structure as LiCoPO_4 , [10, 88] it has a lower magnetoelectric coefficient by about half an order of magnitude.[36, 38, 42, 43, 73]

The delay in detailed studies on LiFePO_4 was a consequence of the challenge growing large, quality single crystals of LiFePO_4 . An article co-authored by Vaknin in 2008 reported using a large flux-grown single crystal of LiFePO_4 . [89] They explained the crystal had been prepared by Vaknin and his colleagues for neutron diffraction experiments performed in 2006,[82] but that large, multi-millimeter sized single crystals of LiFePO_4 without other metal ion dopants

had not been available previously. As mentioned previously, Mercier had grown and performed magnetoelectric measurements on LiFePO_4 and the other analogs decades previously, but the dimensions of the crystal he used was not reported.[39] (It is also worth noting, that even Mercier had prepared the manganese, cobalt, and nickel analogs a few years before successfully preparing the iron analog.) The 2006 article reported using a LiCl-flux and stoichiometric quantities of high-purity FeCl_2 (99.999%) and Li_3PO_4 (99.999%) but no other details.[82] Rather, it cited using a method for the flux growth of LiNiPO_4 which involved sealing about 45 g of reagents in a 30 mL platinum crucible.[90] The reactants were pre-melted at 800° . The crucible was then arc-welded shut and a $50\text{ }\mu\text{m}$ pinhole was drilled into the lid to equilibrate the pressure. It was then heated to 890°C for 4 hr. To facilitate crystal growth the molten material was slow cooled at 0.755°C/hr to 715°C , and then at 1.4°C/hr to 680°C . The authors stated “recovery occurred at 680°C ,” but did not explain if it was quenched from that temperature or cooled under ambient conditions.[90] The chloride salts used in the synthesis are highly soluble in water, so regardless of how the crucible was cooled, the crystals were likely isolated from the flux by soaking the contents in water, although this was not stated in the procedure. An article by Fomin *et al.* on LiCoPO_4 published three years previously in 1999 has Rivera as a co-author, so it is plausible the flux growth method was the work of extended collaborations.[91] It is worth mentioning that large platinum crucibles are very expensive (easily \$2000 a piece with a lid) and they cannot be reused if they are welded shut, since it is necessary to mutilate the crucible to open it.

In their 2006 neutron diffraction study Li, Zarestky, Vaknin, and others confirmed the magnetic ordering in LiFePO_4 is a collinear antiferromagnet, with no incommensurate or noncollinear structure.[82] However, they did observe a very weak signal for the (010) reflection, which is not strictly permitted in the $Pnma'$ model. They concluded that while the spins are primarily oriented

along the b axis, they are canted off-axis by a small angle. A similar weak signal in LiCoPO_4 for the (010) reflection had been observed by Vaknin, Zarestky, and their colleagues in 2002.[48] They concluded the similarity in the magnetoelectric response in these materials was due to the similarities in their magnetic structure. Also, the inelastic neutron scattering experiments for both single crystal LiCoPO_4 and LiFePO_4 revealed the single-ion anisotropy was the same order of magnitude as the coupling constants for the magnetic exchange.[82, 85, 86] The authors proposed the pronounced anisotropy contributes to the magnetoelectric effect in the material. The anisotropy is also due to the highly distorted oxygen coordination around the transition metal cations.

Vaknin and his colleagues also synthesized large single crystals of LiMnPO_4 using a similar LiCl -based flux method as discussed previously.[83] They subsequently performed several neutron scattering experiments on them.[83, 86] Unlike LiCoPO_4 and LiFePO_4 , LiMnPO_4 was shown to exhibit a very weak single-ion anisotropy, two orders of magnitude smaller than the largest magnetic exchange coupling constants. The authors concluded the competing spin exchange interactions are too weak to induce incommensurate or non-collinear magnetic structures like in LiNiPO_4 . The scattering was also in good agreement with the established magnetic structure model, with an antiferromagnetic arrangement of spins oriented along the a axis.

Before concluding this section, it is appropriate to discuss work by Toft-Petersen and his graduate student Fogh (who recently defended her dissertation) from the Technical University of Denmark. They have continued to study the magnetism of the LiMPO_4 ($M = \text{Fe, Mn, Co, Ni}$) series, steadily publishing detailed studies from 2011 to the current time.[7, 92, 93, 94, 95, 96, 97, 98] In all those papers, they list Jensen, Vaknin, Li, and/or Zarestky as co-authors (as well as several others). Or else, they express gratitude in the acknowledgments for their

fruitful collaborations or for providing single crystal samples. Their expertise is in performing measurements at high magnetic field, and single crystal neutron diffraction experiments under applied magnetic fields. From these experiments, they elucidate the complex magnetic phase diagrams for the members of this series. Both Toft-Petersen and Fogh understand the magnetoelectric effect to be a consequence of the Dzyaloshinskii-Moriya (DM) interaction in this series. The DM interaction describes the magnetic exchange between two anti-aligned spins, according to the expression:

$$\mathcal{H}_{ij}^{\text{DM}} = \mathbf{D}_{ij} \cdot (\mathbf{s}_i \times \mathbf{s}_j) \quad (2.16)$$

Where $\mathbf{D}_{ij}$ is the DM parameter, $\mathbf{s}$ are the magnetic spins, and $\mathcal{H}$ is the Hamiltonian. The mathematical structure is strikingly similar to Eq. 2.3. They have never attempted to relate their results to any toroidal phenomena. Because of this, most of their work will not be discussed here.

However, it bears mentioning that as a part of Toft-Petersen's and Fogh's work, they also studied the spontaneous magnetic structure of the materials so they could have a point of comparison for their measurements under applied fields. Toft-Petersen's 2012 study confirms the spontaneous magnetic structure of LiMnPO_4 is $Pn'm'a'$ with the magnetic spins aligned along the a axis below $T_N = 34$ K.[93] There is no canting off the a axis unless magnetic field is applied.

Toft-Petersen's 2015 study on LiFePO_4 agreed with the magnetic structure determined by Rouse *et al.* in which the spins are predominantly aligned antiferromagnetically along the y axis.[10, 94] However, they observed very weak signal for the (100) and (010) reflections. These indicate that there is also a collinear spin rotation towards the x axis, and slight spin canting along the z axis. The combination of the two effects corresponds to a rotation of only $1.3(1)^\circ$ off the b axis.

In Fogh's 2019 study of LiCoPO_4 , the neutron diffraction results confirm the antiferromagnetic

structure predominantly has the magnetic spins aligned along the y axis.[7] However, they perform very detailed neutron diffraction experiments and measure a small intensity for the (100) along with the larger (301) reflection. Based upon the possible spin configurations, they concluded they represented a small spin canting along the z axis, corresponding to an angle of $7(1)^\circ$. However, this corresponds to a lowering of the symmetry to the point group m'_z , contrary to previous arguments that it is $2'_x$. They specifically cite work by Vaknin,[48] Van Aken,[59] Zimmermann,[99], and Kharchenko [55] refuting their claims the point symmetry is $2'_x$. On a different topic, Fogh and her coauthors mentioned in a footnote at the end of the references that they used crystals from the same batch as Ref. 85. However, they observe a significantly lower transition temperature. They observed their refinement was improved when modeling the structure with a small amount of Ni on the Co site. They suggest the sample may be contaminated with Ni from the crucible growth.

Fogh's most recent study of LiNiPO_4 published in 2020 is a culmination of work from two previous studies in which Toft-Petersen was the co-author.[92, 95] They confirm the analysis in Jensen's 2009 paper,[81] that at zero field, LiNiPO_4 undergoes an incommensurate phase transition a few degrees above its Néel temperature at 21 K. However, below 21 K, the ordering is an antiferromagnetic commensurate structure, with a small canted component along a axis. Fogh's most recent study reports the polarization under magnetic fields up to 55 T. She and her coauthors studied all seven magnetic phase transitions and noted that incommensurate magnetic order always suppressed the magnetoelectric effect. The magnetoelectric effect was only observed in the phases with commensurate magnetic order. Back in 2009, Jensen and his colleagues had suggested the components of the incommensurate structure do not possess the needed symmetry to induce energy differences in the structure which would enable magnetoelectric distortions.

2.5: Challenges Proposing Other Ferrotoroidic Candidates

While a good deal of attention had been given to LiCoPO_4 with the olivine structure type very few other candidates had been systematically proposed before 2010. The magnetic point group of the three boracites discussed in §2.1 are all $m'm2'$. These determinations were based upon the symmetry of the magnetic property measurements and not neutron diffraction. However, as noted in Tab. 2.3 this point group is associated with all three ferroic orders (ferromagnetism, ferroelectricity, and ferrotoroidicity). Therefore they are not ideal candidates for conclusively establishing the existence of ferrotoroidicity since it is more difficult to distinguish the effects of three kinds of ordering from one another in experiments. When Krotov and Tugushev had considered possible antiferromagnetic candidates in 1986, they had specifically considered LiCoPO_4 and the related olivines LiMnPO_4 and LiNiPO_4 .^[20] In addition, they determined DyOOH , ErOOH , FeOOH , CrUO_4 , and Cr_2WO_6 also order in antiferromagnetic configurations which should permit a net toroidal moment. I had previously mentioned Spaldin and Ederer had also considered $\text{Ga}_{2-x}\text{Fe}_x\text{O}_3$ and BiFeO_3 .^[63, 64]

Considering the stringent requirements for a material to be considered a candidate ferrotoroidic material, it is perhaps unsurprising so few candidates have ever been proposed. The major criteria are having the appropriate magnetic point symmetry to permit a linear magnetoelectric effect, and then that physical property tensor needs to exhibit off-diagonal anti-symmetric terms. In order to obtain that data, one must first grow large millimeter-sized single crystals, perform magnetization (and possibly heat capacity) measurements to determine the magnetic transition temperature(s), perform neutron diffraction experiments to determine their magnetic structure, and then perform highly specialized magnetoelectric measurements under cryogenic conditions

to observe any temperature-dependence in the signal across the ordering temperature. That is years of intensive research on just one material. In Schmid's list of known magnetoelectric materials from 2000,[36] only Cr_2O_3 has an ordering temperature near room temperature (318 K, actually above room temperature). The next lowest are Fe_2TeO_6 at 219 K, $\text{Nb}_2\text{Mn}_4\text{O}_9$ at 110 K, and $\text{Ta}_2\text{Mn}_4\text{O}_9$ at 104 K. All the rest order below the normal boiling point of liquid nitrogen (77 K). Despite these significant challenges, a few materials have been investigated and proposed since 2007.

In 2010 Ressouche and several colleagues from Grenoble, France performed spherical neutron polarimetry (SNP) experiments on MnPS_3 . [100] This is a highly specialized polarized neutron diffraction experiment in which the incident beam of polarized neutrons can be rotated at any angle, and then the scattered beam can be detected at any angle. [101, 102, 103, 104, 105, 106] This enables the researchers to determine the absolute configuration of the magnetic moments in the sample. For example, it is sensitive enough to detect if the moments have a small off-axis canting angle. In addition, the apparatus CRYOPAD at the Institute Laue Langevin (ILL) in Grenoble has the necessary sample environment to apply magnetic and electric fields under cryogenic conditions to the sample while performing the measurements. [107, 108, 109] Therefore, by analyzing the polarization tensor under applied fields, one can measure the temperature-dependent magnetoelectric susceptibility along virtually any desired crystallographic direction. One of the first materials tested on the updated CRYOPAD instrument was Cr_2O_3 , followed by the olivines LiCoPO_4 and LiNiPO_4 , and the pyroxene $\text{Mn}_{1-x}\text{Mg}_x\text{GeO}_3$. [107, 109] In the experiments, enough measurements were taken on LiCoPO_4 (but not LiNiPO_4) to reconstruct positions of the cobalt and oxygen ions along the $[0\bar{1}0]$ axis through maximum entropy methods. [109] The model is presented in Fig. 2.11. The model revealed the magnetization around the Co^{2+} ions

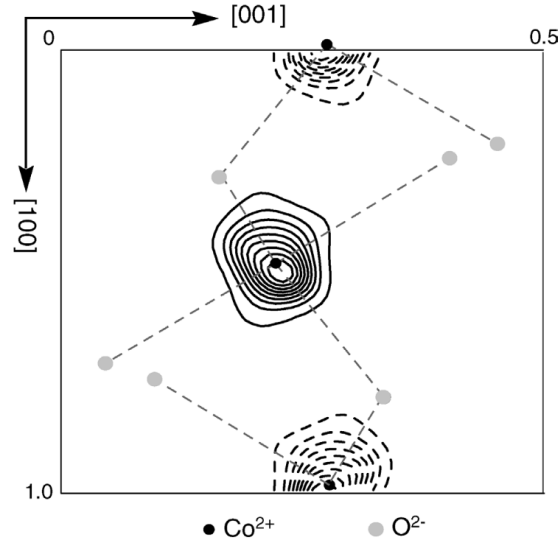


Figure 2.11: The antiferromagnetic magnetization around the Co magnetic ions in the (01) plane as reproduced from SNP measurements. Originally published as Fig. 6 in Ref. 109 and reproduced in Gnewuch & Rodriguez (2019).[44]

is notably asymmetric due to the highly distorted oxygen coordination.

Ressouche and colleagues were interested in MnPS_3 because while the magnetic and structural properties had already been known since the 1980's, it was unknown if the material was magnetoelectric.[110, 111, 112] It crystallizes in the monoclinic space group $C2/m$ where the manganese ions form a honeycomb lattice. Below 78 K it orders in the magnetic space group $C2'/m$ with $2'/m$ point symmetry.[113, 114]

After confirming the magnetic symmetry, they measured the nine components of the polarization matrix for the $(0kl)$ reflections at base temperature (2 K), measuring a total of 99 cross sections. After refining the data, they were able to determine the Mn^{2+} magnetic moments are tilted off the c axis by $\sim 8^\circ$. They proposed this was due to competing anisotropic interactions within the system from the magnetic ions. After performing that measurement, they then performed magnetoelectric measurements. The samples were annealed by applying magnetic and electric fields in a cryostat from 90 K (above the transition temperature) to 50 K (below the transition

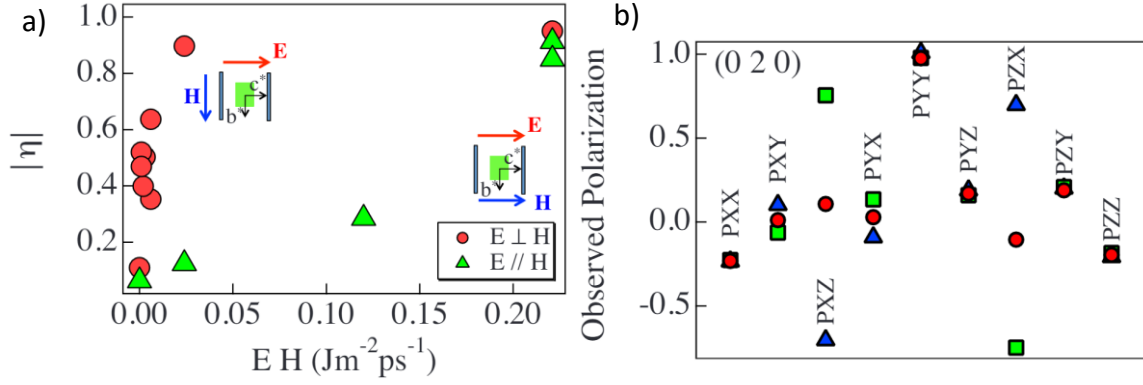


Figure 2.12: The spherical neutron polarimetry results for MnPS_3 . a) The population of domains, given by η , is quickly reached under conjugated magnetic and electric fields $E_i H_j$ (red dots). When the applied fields are parallel $E_i H_i$ (green dots), the domain population is not as efficient and increases with increasing applied field. b) A graphical depiction of the polarization for each of the nine components for the (020) reflection. Red circles indicate the polarization for equipopulated antiferromagnetic domains. The blue triangles indicate the polarization under applied fields when the domains are aligned (monodomain state). Green squares indicated the polarization for the monodomain state when the fields are reversed. Originally published as Fig. 3 in Ref. [100], and reproduced from Gnewuch & Rodriguez (2019).

temperature). The fields were then switched off and the sample (still in the cooled cryostat) was re-positioned in CRYOPAD on the neutron beamline for polarization measurements. Figure 2.12a depicts the population of the domains under applied magnetic and electric fields. Figure 2.12b depicts the components of the neutron polarization matrix obtained from the SNP measurements of the (020) reflection. The SNP measurements were taken on the sample before annealing (with an equipopulation of domains), and after annealing, which aligns all the domains so that the crystal is (approximately) monodomain.

While they were able to measure several components of the magnetoelectric tensor, due to the sample geometry (lamellar crystal habit), they were not able to measure the off-diagonal components associated with a toroidal moment for their sample.[100] They were therefore only able to conclusively demonstrate the material does exhibit a magnetoelectric effect, but not that it is a ferrotoroidic material. Regardless, they cited the method for calculating a toroidal moment

proposed by Ederer and Spaldin (2007) and reported a net toroidal moment per unit cell as $(0.0175, 0, -0.0027) \mu_B \text{\AA}^{-2}$. Since it was a communication, they did not explain their calculation, nor did they provide supporting information. They also did not write a follow-up article. They titled the communication, “Magnetoelectric MnPS_3 as a candidate for ferrotoroidicity.”[100]

2.6: Magnetoelectric Pyroxenes as Candidate Ferrotoroidic Materials

Besides the olivines, the most promising group of potential ferrotoroidics which have ever been proposed are several members of the pyroxene family. In particular, $\text{LiFeSi}_2\text{O}_6$ was proposed as a ferrotoroidic in 2013 and again in 2015.[115, 116] This section presents more details on the chemistry and magnetism of this system, and describes the evidence which has been presented claiming ferrotoroidic ordering in $\text{LiFeSi}_2\text{O}_6$. It also describes other compositions within this same structure which could be promising candidates for ferrotoroidic ordering as well.

Figure 2.13 models the pyroxene structure type. Like the olivines, they have two metal sites and an oxoanion unit bridging the transition metal cations. The general formula is $M'M''X_2O_6$, where M' is a mono- or divalent metal, M'' is a di- or trivalent metal, and X is silicon or germanium. Pyroxenes are also further classified by their lattice symmetry. The so-called orthopyroxenes have an orthorhombic lattice, while the clinopyroxenes have a monoclinic lattice. The same composition may take different structural phases based upon the thermodynamic conditions. In the clinopyroxenes, the silicate or germanate ions form corner-sharing chains running parallel to the c -axis. They are depicted in Fig. 2.13a & Fig. 2.13b. The M'' ions form edge-sharing chains which run parallel to the oxoanions. The M' ions balance the charge in the structure. When the M' and M'' ions are identical, or the dopants are equally distributed between the two

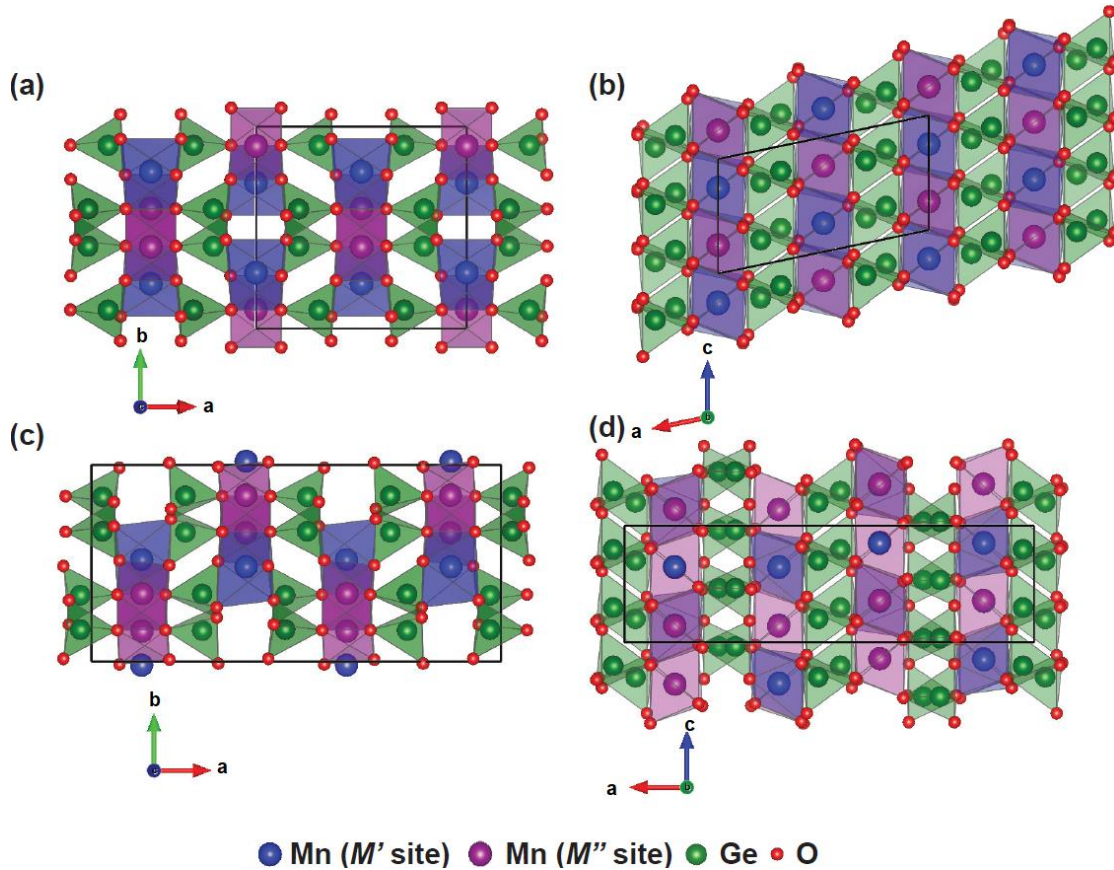


Figure 2.13: The structure of clinopyroxene (a,b) and orthopyroxene (c,d) viewed along the [001] direction (a,c), and along the [010] direction (b,d), respectively. Reproduced from Gnewuch & Rodriguez (2019).[44]

sites, the stoichiometry is noted $M''\text{XO}_3$.

Since the metal sites can be easily tuned with a variety of magnetically-active transition metal cations, this structure type is a promising system for study. The transition metal can be systematically doped within the same structure type to tune the magnetic moment size and magnetic structure. Almost all known compositions exhibit antiferromagnetic order, and the magnetic structures have been determined for several compositions. Some also possess the appropriate magnetic point symmetry to exhibit ferrotoroidic order.

Redhammer and his colleagues have studied this system extensively. In a recent review of the known magnetic structures, he noted that in clinopyroxenes the chains of edge-sharing

oxoanions largely influence the observed magnetic structure.[117] The super-exchange paths of the one-dimensional oxoanion chains compete with the super-exchange paths of the $M''O_6$ octahedra, forming a two-dimensional net. The strength of the inter- and intrachain pathways ultimately determines the ferromagnetic and/or antiferromagnetic ordering of the magnetic moments between the transition metal cations. Just like the various structural analogs of the olivine structure exhibit various magnetic structures, so do the clinopyroxenes. From Redhammer's 2013 review, six compositions have the appropriate magnetic space group and point group to exhibit ferrotoroidic order: $MnGeO_3$ ($C2'/c$, $2'/m$), $CaMnGe_2O_6$ ($C2'/c$, $2'/m$), $LiCrSi_2O_6$ ($P2'_1/c$, $2'/m$), $LiCrGe_2O_6$ ($P2'_1/c$, $2'/m$), $LiFeGe_2O_6$ ($P2'_1/c$, $2'/m$), and $LiFeSi_2O_6$ ($P2_1/c'$, $2/m'$).[60, 117]

Jodlauk *et al.* were among the first to study the magnetic and electric properties in magnetic clinopyroxenes.[118] In 2007 they published a report on the magnetic susceptibility and electric polarization in three compositions: $NaFeSi_2O_6$, $LiFeSi_2O_6$, and $LiCrSi_2O_6$. They observed the transition temperatures for the magnetic ordering coincided with a change in the polarization. In addition, the magnitude of the effect was field-dependent, with the antiferromagnetic anomaly broadening at higher applied field. They suggested the broadening was related to the onset of electric polarization. However, just because a magnetic material exhibits magnetoelectric order, this does not guarantee it is associated with toroidal order. For example, $NaFeGe_2O_6$ exhibits similar magnetoelectric properties,[119, 120] but the magnetic structure does not permit a linear magnetoelectric effect.[121, 122] Regardless, Jodlauk's report lead to subsequent studies searching for evidence of ferrotoroidic order in these materials.

Of the three, the most compelling evidence for ferrotoroidic order has been found in $LiFeSi_2O_6$. Redhammer *et al.* determined the magnetic structure from neutron powder diffraction

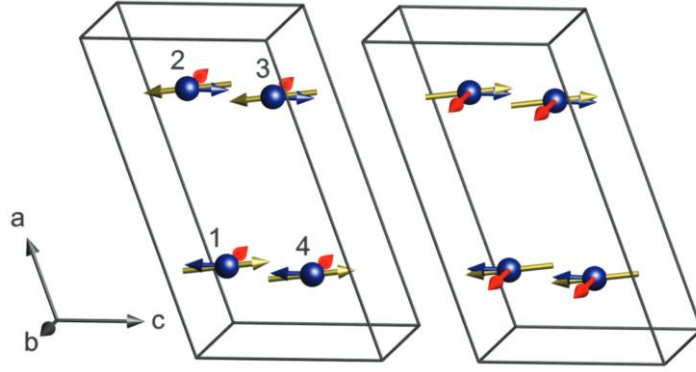


Figure 2.14: Model for toroidal moments proposed by Baum *et al.* The four iron atom sites are numbered 1-4. The blue vectors indicate the atomic displacements between the $C2/c$ and $P2_1/c$ structures. The yellow vectors indicate the magnetic moments. The red vectors indicate the toroidal moments. Reproduced from Fig. 2 in Ref. [115].

to be $P2_1/c'$, which is monoclinic.[123]

This magnetic structure was confirmed by Baum *et al.* a few years later on a single crystal neutron diffraction experiment.[115] In that paper, they propose $\text{LiFeSi}_2\text{O}_6$ is a ferrotoroidic material and support their claim with SNP (spherical neutron polarimetry) measurements. The model for their analysis is presented in Fig. 2.14. At room temperature the space group is $C2/c$ but the structure undergoes a phase transition at 229 K to $P2_1/c$. Therefore they propose the $\mathbf{r}$ for calculating the toroidal moment would be the displacement of the iron atom positions between the two structures. However, they then incorrectly claim there is an inversion center connecting to two iron sites within a chain (sites one and four, and sites two and three). They then argue that the toroidal moments calculated with those inversion sites as the origin would be zero since magnetic moments are aligned parallel to one another. They conclude the only way a toroidal moment could result would be from the distortion of the iron atoms. However, there are no inversion sites connecting atoms one and four, and atoms two and three. Instead, sites one and three are related by inversion, as are sites two and four. Furthermore, no attempt is made to explain how the vectors describing the iron distortions are related to a ring of spins. They then

use the equation $\mathbf{T} = \frac{2}{V} \mathbf{r}_i \times \mathbf{m}_i$ to calculate a toroidal moment $\mathbf{T} = 0.00025(3) \mu_B \text{\AA}^{-2}$.

Baum and his colleagues then describe their spherical polarization analysis,[115] in which they performed a similar experimental technique as Ressouche *et al.* for their MnPS₃ study.[100] They only observed off-diagonal P_{xy} and P_{yx} terms in the polarization matrix when the sample had been annealed under crossed electric and magnetic fields, with the electric field applied along a and the magnetic field applied along c . In addition, the signs of the polarization were reversed when the fields were reversed. Their interpretation of these results was that when the fields were applied, they had saturated the toroidal domains in one direction (a monodomain state) and they observed signal for the off-diagonal terms. The toroidal monodomain was then reversed when the fields were reversed. When they cooled in zero fields or with only one applied field, the toroidal domains were equally populated and so the off-diagonal terms were negligibly small. However, I argue they are bold to claim they conclusively are manipulating toroidal domains. It would be equally valid to claim they are controlling the antiferromagnetic domains, and they are observing a linear magnetoelectric effect in the material. They did not demonstrate the ferrotoroidal character of their measurements.

Two years later, Tolédano, Ackermann, Fiebig, and several other colleagues published a detailed study of the physical properties of LiFeSi₂O₆, and made a more compelling claim the material can be considered a ferrotoroidic.[116] On the basis of optical birefringence measurements, they proposed the symmetry is actually triclinic.[116] They performed temperature-dependent magnetoelectric measurements, which are presented in Fig. 2.15. Each panel of the figure presents the temperature-dependent polarization at applied magnetic fields from 1 T to 15 T. Notably, they observed all the off-diagonal terms, but no signal for the α_{yy} component, even at the highest applied fields. This is further evidence the symmetry is lower, since the point group

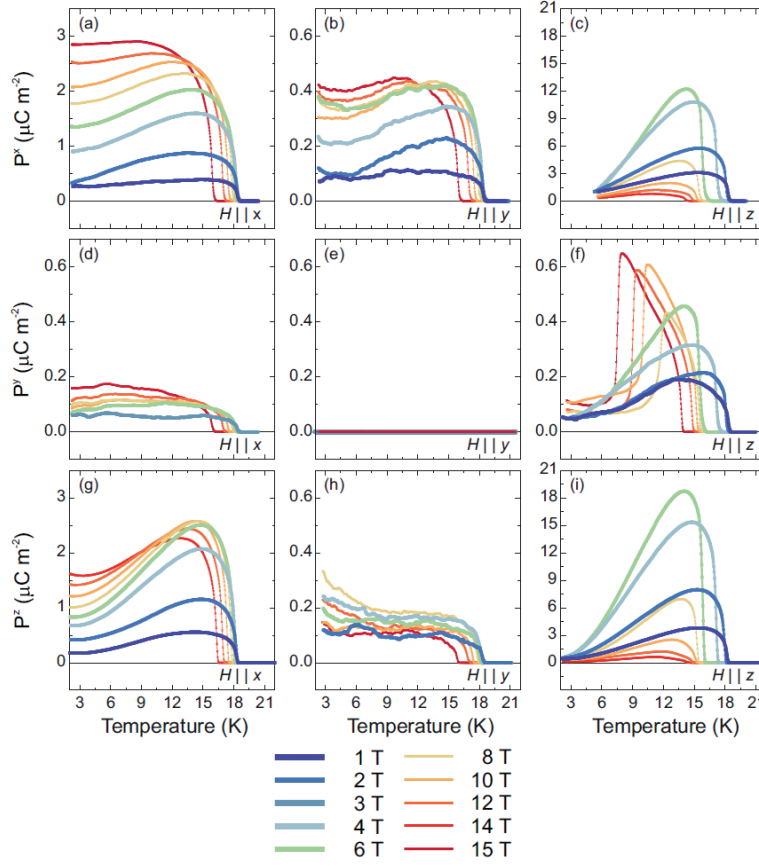


Figure 2.15: Temperature dependence of the electric polarization under applied magnetic field in $\text{LiFeSi}_2\text{O}_6$. The panels are organized according to their corresponding tensor components: a) α_{xx} , b) α_{xy} , c) α_{xz} , d) α_{yx} , e) α_{yy} , f) α_{yz} , g) α_{zx} , h) α_{zy} , i) α_{zz} . Originally published as Fig. 2 in Ref. [116] and reproduced from Gnewuch & Rodriguez (2019),[44].

$2/m'$ associated with space group $P2_1/c'$ would only allow the off-diagonal terms α_{xz} and α_{zx} .

In order to explain the lower symmetry, Tolédano and the others proposed that while the predominant magnetic symmetry is described by $P2_1/c'$, a small component is also described by $P2'_1/c$. [116] Figure 2.16 is a diagram describing the magnetic space group which would result when each of the four possible magnetic structures for this space group would coincide. The irreducible representations notated in the circles correspond to the possible irreducible representations which are subgroups of the parent paramagnetic group $P2_1/c1'$. When a magnetic structure is described by two representations, the magnetic space group is best described by the magnetic

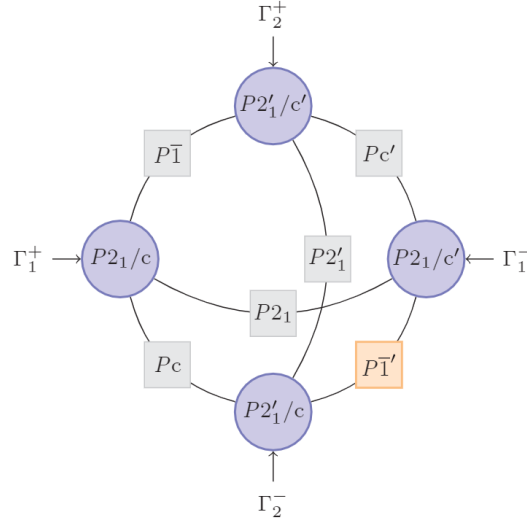


Figure 2.16: Possible magnetic order for a system with $P2_1/c$ structural symmetry. The four representations in blue circles are the four irreducible representations from the parent paramagnetic phase $P2_1/c1'$. The magnetic space groups in boxes connected between them are the symmetry which would result when the two representations connected by lines are both contributing to the net magnetic structure. Tolédano *et al.* propose the correct magnetic space group is $P1'$ for $\text{LiFeSi}_2\text{O}_6$, emphasized by the orange color. Reproduced from Fig. 4 in Ref. 116.

space group corresponding to the symmetry elements share in common between the two representations.

In Fig. 2.16 these are notated in the boxes. Based upon this analysis, Tolédano and his colleagues propose the correct magnetic space group is $P1'$ (highlighted in orange) in Fig. 2.16. This space group is triclinic, in agreement with the birefringence measurements. This symmetry also would permit all the off-diagonal component of the magnetoelectric tensor, which is what is observed. If the symmetry was only $P2_1/c'$, only α_{xy} and α_{yx} would have been allowed by symmetry. The $P2_1/c'$ representation is associated with a toroidal moment $\mathbf{T}_y$, while the $P2_1'/c$ is associated with $\mathbf{T}_{xz}$. (See Tab. 2.7.) Tolédano suggests that since the magnetic symmetry is predominantly described by $P2_1/c'$, there is a triggering mechanism inducing the lower symmetry, and a deactivation mechanism partially quenching the contribution from $P2_1/c'$. The deactivation is why they believe no signal was observed when the magnetic field was observed for the α_{yy} component

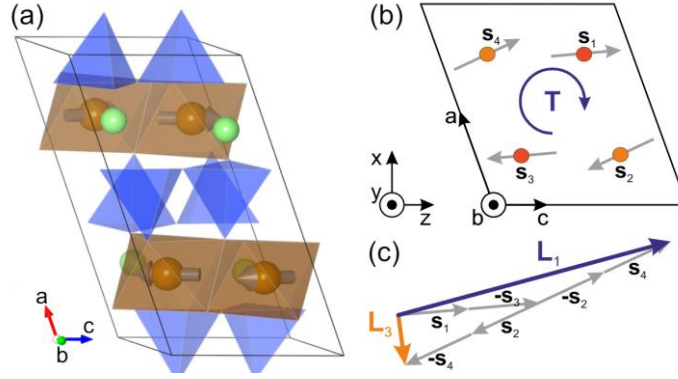


Figure 2.17: Model for toroidal moments in $\text{LiFeSi}_2\text{O}_6$ proposed by Tolédano *et al.* a) Magnetic structure, where the blue tetrahedra are the silicate ions, the green atoms are the lithium ions, the brown atoms are the iron ions, and the grey arrows are the magnetic moments. b) Schematic of the magnetic structure looking down the b axis. The toroidal moment $\mathbf{T}$ would be produced along the y direction due to the ring of spins formed by all four iron magnetic moments, labeled $\mathbf{s}_{1-4}$. c) Depiction of the vectors representing the antiferromagnetic exchange $\mathbf{L}_1 = \mathbf{s}_1 - \mathbf{s}_2 - \mathbf{s}_3 + \mathbf{s}_4$ and $\mathbf{L}_3 = \mathbf{s}_1 + \mathbf{s}_2 - \mathbf{s}_3 - \mathbf{s}_4$. The small grey vectors depict the contribution of each of the four iron magnetic spins to the components of $\mathbf{L}_1$ and $\mathbf{L}_3$. Reproduced from Fig. 1 in Ref. [116].

of the magnetoelectric tensor (Fig. 2.15e).

Tolédano and his colleagues also present a more reasonable model for ferrotoroidic order in $\text{LiFeSi}_2\text{O}_6$, which is presented in Fig. 2.17. They do not make any claims about constructing a “ring” of spins with a defined origin. Rather, they conclude the net toroidal moment $\mathbf{T}$ would arise from contributions of all four spins, and the direction of the “loop” is determined by the anti-aligned arrangement of magnetic moments, as depicted in Fig. 2.17b. They assign the spin density waves in a similar manner to Kornev and his colleagues as discussed in §2.1.[32] The notations for the vector configurations are given in the caption of Tab. 2.7.

Based upon this analysis, their conclusion is that since the majority of the magnetic structure is described by $P2_1/c'$ ($\Gamma_1^-, 2/m'$) and only a minor portion from $P2'_1/c$ ($\Gamma_2^-, 2'/m$) then $\mathbf{T}^y \gg \mathbf{T}^{xz}$, although there will be a toroidal contribution in all three directions. This is consistent with Litvin’s analysis from Tab. 2.5. The net toroidal moment from a structure with the point group $2'/m$ would be $(T_1, T_2, 0)$, from $2_z/m'_z$ would be $(0, 0, T_3)$, the the toroidal moment resulting from

Table 2.7: Irreducible representations of the point group $P2_1/c1'$ and associated magnetic symmetry. Adapted (and corrected) from Tab. 1 in Ref. 116.

Γ^a	M.S.G. ^b	1	2_y	$\bar{1}$	m_y	$1'$	$2'_y$	$\bar{1}'$	m'_y	Basis functions ^c
Γ_1^+	$P2_1/c$	1	1	1	1	-1	-1	-1	-1	$\mathbf{M}^y, \mathbf{L}_2^{xz}$
Γ_1^-	$P2_1/c'$	1	1	-1	-1	-1	-1	1	1	$\mathbf{T}^y, \mathbf{L}_1^{xz}, \mathbf{L}_3^y$
Γ_2^+	$P2'_1/c'$	1	-1	1	-1	-1	1	-1	1	$\mathbf{M}^{xz}, \mathbf{L}_2^y$
Γ_2^-	$P2'_1/c$	1	-1	-1	1	-1	1	1	-1	$\mathbf{T}^{xz}, \mathbf{L}_3^{xz}, \mathbf{L}_1^y$

^a Irreducible Representation, ^b Magnetic Space Group, ^c Basis functions were the antiferromagnetic basis functions are $\mathbf{L}_1 = \mathbf{s}_1 - \mathbf{s}_2 - \mathbf{s}_3 + \mathbf{s}_4$, $\mathbf{L}_2 = \mathbf{s}_1 - \mathbf{s}_2 + \mathbf{s}_3 - \mathbf{s}_4$, and $\mathbf{L}_3 = \mathbf{s}_1 + \mathbf{s}_2 - \mathbf{s}_3 - \mathbf{s}_4$, the ferromagnetic $\mathbf{M} = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + \mathbf{s}_4$, and the ferrotoroidic $\mathbf{T}$

a combination of the two structures would give a point group $\bar{1}'$ with the net toroidal moments (T_1, T_2, T_3) .

Tolédano and his colleagues also discussed their interpretation of the expression $\mathbf{T} = \frac{1}{2V} \Delta \mathbf{r}_i \times \mathbf{s}_i$. This is a form of Eq. 2.11, although the researchers are not clear if they are treating the magnetic moments according to $m_\alpha = g\mu_B \mathbf{S}_\alpha$ or as spins, although they cite Ederer & Spaldin (2007).[63] They interpret the changes in the orientations of the spins to contribute to the net toroidal moment as well. They write $\Delta \mathbf{r}$ because they interpret it to be the ionic displacements of the iron ions between the $C2/c1'$ paramagnetic structure and the low-temperature $P2_1/c1'-P\bar{1}'$ structure, as Baum and his colleagues had done.[115] Their net formula is then:

$$\mathbf{T} = \frac{1}{V} \begin{pmatrix} \Delta r^y (s_1^z - s_4^z) - \Delta r^z (s_1^y + s_4^y) \\ \Delta r^z (s_1^x + s_4^x) - \Delta r^x (s_1^z + s_4^z) \\ \Delta r^x (s_1^y - s_4^y) - \Delta r^y (s_1^x + s_4^x) \end{pmatrix} \quad (2.17)$$

They do not report a computed value for $\mathbf{T}$. They conclude by arguing since the toroidal moment results from spin, orbital, and higher-order contributions, it seems reasonable to assume

the toroidal contribution from the spins would be dominant since it would be much larger than from the other contributions. Since both spin density waves (L_1^x, L_3^y, L_1^z) and (L_3^x, L_1^y, L_3^z) contribute to the magnetic order and they together possess the same symmetry as $\mathbf{T} = T^y + T^{xz}$, then it would also be valid to describe the toroidal moment(s) as the primary order parameter(s). Indeed, since it is the exchange interactions between the spins which are the dominant contributions to the observed magnetic order, they argue it is more appropriate to choose a toroidal parameter rather than an antiferromagnetic order parameter to describe the phase transition from $P2_1/c1'$ to $P\bar{1}'$.

A brief note: Tolédano had written an article four years previously asserting $\text{Ba}_2\text{CoGe}_2\text{O}_7$ is ferrotoroidic, based upon a detailed phenomenological interpretation of the observed magnetoelectric effects in the material.[124] However, that paper does not attempt a model of the toroidal moments, and contains less experimental evidence than his 2015 paper. He mentions in the 2015 paper further experimental studies are needed to establish the ferrotoroidic nature of $\text{Ba}_2\text{CoGe}_2\text{O}_7$.

While $\text{LiFeSi}_2\text{O}_6$ has been studied intensely for evidence of ferrotoroidic order, other pyroxenes are potential candidates as well. The germanate $\text{LiFeGe}_2\text{O}_6$ also permits a toroidal moment. Redhammer *et al.* determined its magnetic space group to be $P2_1'/c$. [123] However, magnetoelectric measurements on this material have not been reported.

Around this same time, Lee, Whangbo, and their colleagues performed computation analysis comparing the magnetic symmetry in $\text{LiFeSi}_2\text{O}_6$ and $\text{LiFeGe}_2\text{O}_6$. [125] Both structures have the appropriate symmetry to permit ferrotoroidic order: $P2_1/c'$ (or $P\bar{1}'$) for $\text{LiFeSi}_2\text{O}_6$ and $P2_1'/c$ for $\text{LiFeGe}_2\text{O}_6$. [117] They first performed density functional calculations to compare the spin exchange paths in the two materials, which are depicted in Fig. 2.18. They concluded that in the germanate analog the intrachain super-super-exchange paths are stronger than the interchain super-super exchange paths. As a result, the iron ions in the octahedral chain are

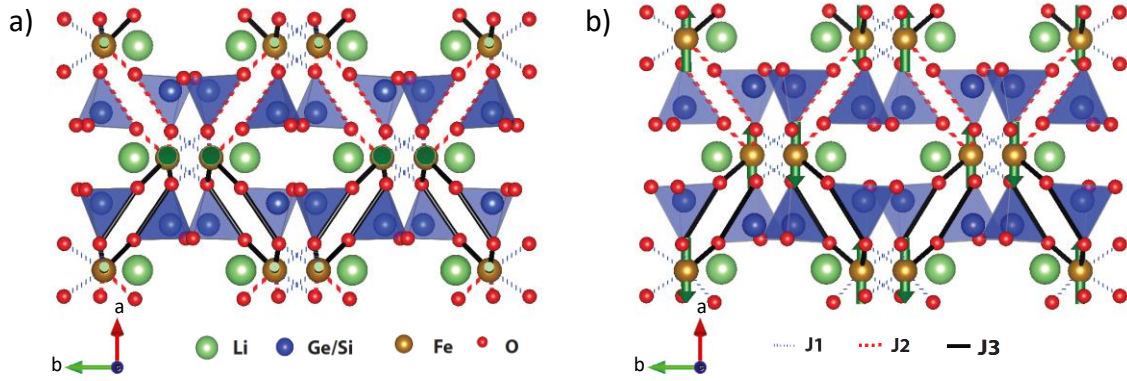


Figure 2.18: Magnetic structure of $\text{LiFeSi}_2\text{O}_6$ (a) and $\text{LiFeGe}_2\text{O}_6$ (b), with labeled exchange paths. The interchain super-exchange path is J_1 , the dominant intrachain super-super-exchange paths are J_2 and J_3 . In $\text{LiFeGe}_2\text{O}_6$ the J_1 super-exchange path dominates. In $\text{LiFeSi}_2\text{O}_6$ the super-super-exchange paths are strongest and similar in magnitude, resulting in ring-like exchange paths. Reproduced from Gnewuch & Rodriguez (2019).[44]

coupled antiferromagnetically. In contrast, in the silicate analog the interchain paths are strongly antiferromagnetic, forcing the intrachains along the iron ions to be ferromagnetic. They also performed calculations to model the effect of spin-orbit coupling and magnetic dipole-dipole interactions in the two analogs. They concluded the spin-orbit coupling is weak in both analogs. Rather, the magnetic dipole-dipole interactions have a much stronger effect on the spin orientations. Based upon this work, Lee and the others propose the toroidal effect observed in the silicate analog is due to the pairs of intra- and interexchange paths with comparable antiferromagnetic coupling strength. Since the one-dimensional intrachain paths in the germanate dominate, they suggest ferrotoroidicity may not be possible in $\text{LiFeGe}_2\text{O}_6$. Of course, additional experimental work would be needed to support any computational study.

Regardless, Lee and the others make a compelling argument that prospective ferrotoroidic materials with this structure cannot have strong one-dimensional order.[125] Rather, the two-dimensional rings would be the result of pairs of inter- and intra-exchange paths of comparable strength competing with one another. It suggests a framework for understanding how superexchange

can contribute to the onset of toroidization. It also implies that by altering the degree of oxygen orbital overlap in the exchange paths, or the distances and angles between the atoms along the path, one could systematically tune the observed magnetic structure and thereby the toroidal moments. This is in contrast to the symmetry-based arguments which propose ferrotoroidic order could occur along with ferromagnetic order. (See Tab. 2.3 for Schmid's classification of the 31 toroidal point groups.) The argument by Lee and the others is only applicable to antiferromagnetic ferrotoroidics.

Another proposed ferrotoroidic candidate with the pyroxene structure type is $\text{NaFeSi}_2\text{O}_6$. There are two independent co-existing magnetic phases observed in the material: a commensurate collinear order below 8 K, and an incommensurate spin density wave below 6 K.[126, 127, 128] Mettout, Tolédano, and Fiebig published an article in 2010 arguing it exhibits evidence of ferrotoroidic order.[129] They based their analysis on the order parameters across the transition temperatures. Since they could describe the transition using two irreducible representations with the same symmetry, they proposed a “symmetry replication” mechanism for the phase transition. This formalism permits coupling of different order parameters as long as they display the same transformation symmetry. Using this, they can describe how when fields are applied to multiferroic antiferromagnetic-ferroelectric materials, both a toroidal moment and a spin wave with the same symmetry can be simultaneously induced in a single phase transition. They also describe how the electric and magnetic fields would couple to the toroidal moment, and present how those couplings would impact the terms of the electrotoroidal and magnetotoroidal susceptibilities. While their work is very thorough, like all theoretical works, additional experiments need to be performed to verify their descriptions. Detailed magnetoelectric measurements in particular would clarify the coupling between the magnetic ordering and electric dipoles in the

material.

In Redhammer's 2013 review, he postulates that since $\text{LiFeSi}_2\text{O}_6$ and $\text{NaFeSi}_2\text{O}_6$ are so similar, the differences in their magnetic structures must be due to the slight "kinking" of the silica tetrahedral chains. The kinking is due to differences in the coordination around the alkali metal ion. In the sodium analog, the sodium ions are eight-fold coordinate due to the zig-zag "kinking" of the silica tetrahedra around the M'' sites. Since the lithium ion is smaller, the silica tetrahedra are straighter and less "kinked" in the lithium analog. As a result, the coordination around the M'' site is only six-fold. Since the silicate ions facilitate the exchange paths, the assumption is the bond distances and angles along these paths influence their strength and ultimately the observed magnetic ordering.

The chromium analogs $\text{LiCrSi}_2\text{O}_6$ and $\text{LiCrGe}_2\text{O}_6$ also possess the appropriate symmetry for ferrotoroidic order. The silicate analog was one of the materials Jodlauk had reported as being magnetoelectric in 2007.[118] In 2009 and 2010 Nénert and his colleagues published the magnetization and neutron diffraction studies demonstrating the magnetic order was antiferromagnetic with the magnetic space group $P2'_1/c$. [130, 131] During this time, Nénert also reported the germanate analog exhibits similar magnetoelectric behavior to the silicate analog which Jodlauk had observed.[131] All of these studies were performed on powder samples. They are prepared by ceramic solid-state sintering, in which lithium carbonate, chromium oxide, and silica or germania are heated in air at 1000°C for several days with intermittent regrinding.[130, 131] Such ceramic systems are notoriously difficult to grow single crystals since they have such high melting points. Jodlauk claimed his sample of $\text{LiCrSi}_2\text{O}_6$ was grown from "melt solution" but did not elaborate on any experimental conditions or methods.[118] If single crystals could be obtained, detailed magnetoelectric tensor measurements would provide further evidence supporting them being

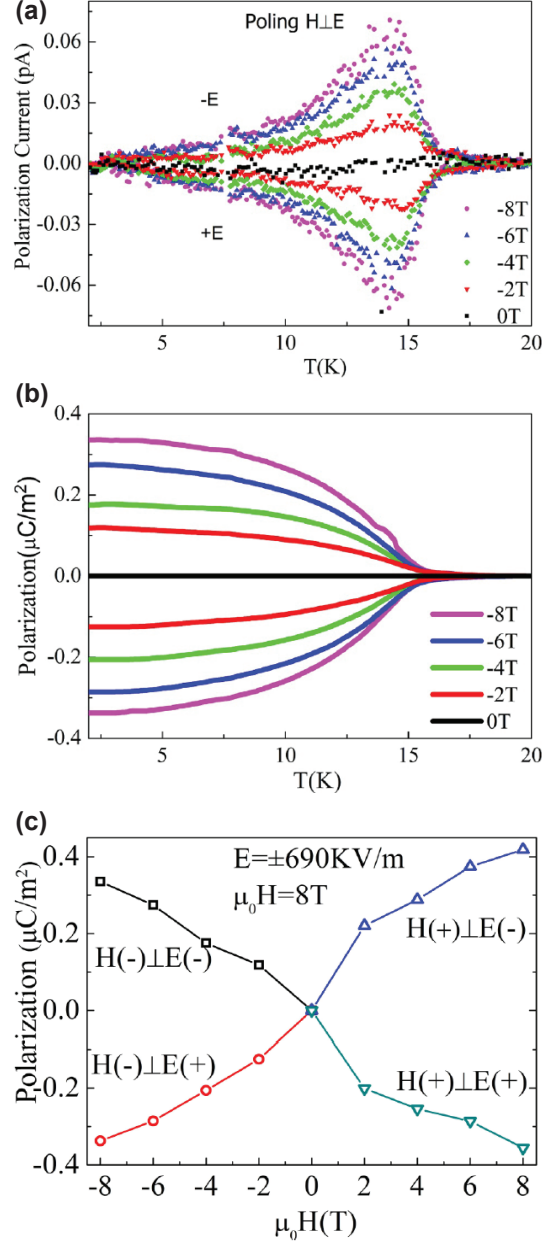


Figure 2.19: Temperature dependence of the magnetic field-induced pyroelectric current (a), polarization (b), and induced electric polarization (c) under various magnetoelectric annealing conditions for $\text{CaMnGe}_2\text{O}_6$. Originally published as Fig. 9 and 10 in Ref. [132] and reproduced from Gnewuch & Rodriguez (2019).[44]

ferrotoroidic candidates.

The remaining candidates are manganese-based germanates $\text{CaMnGe}_2\text{O}_6$ and MnGeO_3 .

MnGeO_3 readily crystallizes in the orthorhombic space group $Pbca$ at room temperature, undergoes

a monoclinic phase transition to $C2'/c$ around 200°C, and finally a magnetic phase transition to $C2'/c$ around 34 K.[109, 122] It was one of the first magnetoelectric materials discovered, around the time of Mercier's experiments with the olivine series.[133, 134] In fact, the magnetoelectric polarization components of the magnesium-doped $Mn_{0.94}Mg_{0.06}GeO_3$ orthopyroxene were actually measured in the same experiment as $LiCoPO_4$ in some of the first experiments using spherical neutron polarimetry, mentioned in §2.5.[109] The magnesium helps stabilize the structure, since it is susceptible to degradation by slow conversion to the clinopyroxene structure. Indeed, Brown and her colleagues reported the crystal deteriorated and crumbled after several months in storage and they prepared a new sample by zone melting a sintered rod. In addition, the magnesium stabilizes the structure in the orthorhombic space group $Pbca$ down to 16 K, when it undergoes a magnetic phase transition to $Pb'ca$. [133] (The point group of $Pb'ca$ is $m'mm$ which also permits a net toroidal moment.) However, Gorodetsky only observed a magnetoelectric susceptibility below 11 K with his undoped sample.[134] With their magnesium-doped crystal, Brown and her colleagues observed a magnetoelectric response in the temperature range of about 8 K to 5 K.[109] Below 5 K the commensurate magnetic structure transitions to an incommensurate cycloidal structure which does not exhibit a magnetoelectric effect.

Unlike $MnGeO_3$, single crystals of $CaMnGe_2O_6$ have not yet been reported. Regardless, both neutron powder diffraction and magnetization studies have revealed it undergoes a magnetic phase transition below 15 K to an antiferromagnetic configuration described by $C2'/c$ (point group $2'/m$). [132, 135] Ding and his colleagues took a number of measurements on powder sample pellets demonstrating its magnetoelectric behavior.[132] Figure 2.19 presents their polarization measurements obtained under a variety of magnetic fields. Figure 2.19a demonstrates the material produces a pyroelectric current, whose magnitude is dependent upon the applied magnetic field.

Figure 2.19b demonstrates an applied magnetic field is required for polarization, since there was no measured polarization under zero-field conditions. Figure 2.19c reveals the roughly linear dependence between the induced electric polarization and the applied magnetic field strength under a constant applied electric field. It also demonstrates that reversing the electric field reverses the polarization. If single crystals could be grown, more detailed magnetoelectric measurements could be obtained, as well as more detailed neutron diffraction experiments. Neutron powder diffraction experiments have been performed by both Redhammer and his colleagues in 2008, and Ding and his colleagues in 2016.[132, 136] While both conclude the magnetic structure is $C2'/c$, Redhammer *et al.* noted an absence of $(0k0)$ reflections, which they concluded implied a small spin component along the b axis.[136] Ding *et al.* did not observe this.[132] Single crystal neutron diffraction experiments would clarify this discrepancy.

2.7: Evidence for Hysteric Poling of Toroidal Domains

Following the success of the SHG study of LiCoPO_4 in 2007, Zimmermann collaborated with Fiebig in Bonn, Germany where she published three extensive SHG studies on LiMPO_4 ($M = \text{Co}, \text{Fe}, \text{Ni}$) and $\text{Li}(\text{Ni}_{1-x}\text{Fe}_x)\text{PO}_4$ ($x = 0.06, 0.20$) from 2009-2014.[99, 137, 138] The 2014 article published in *Nature Communications* was a culmination of that work. This section presents a summary of the major findings.

In her 2009 article,[99] Zimmermann presents SHG measurements of LiFePO_4 , LiCoPO_4 , and LiNiPO_4 , and compares the images to the work Van Aken, Rivera, Schmid, and Fiebig had described in their 2008 article in *Physics Review Letters*.[59] In addition to those four co-authors, Li and Vaknin from Ames Labs are also listed as co-authors. Presumably since

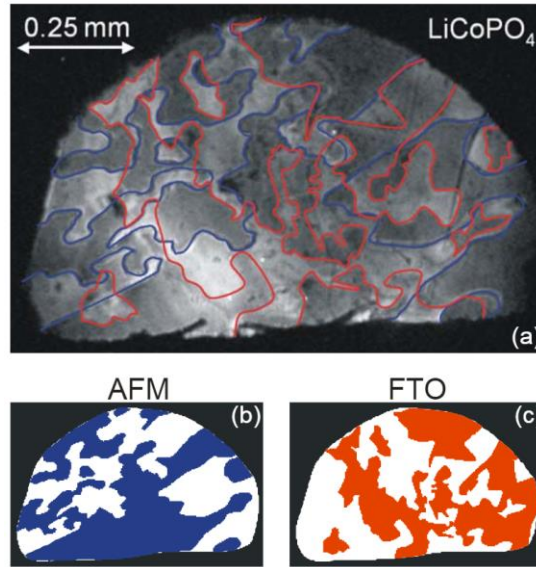


Figure 2.20: Proposed ferro-toroidic and antiferro-toroidic domains in LiCoPO₄. a) This is the same data presented in Fig. 2.6c, but the ferro-toroidic domains outlined in red are super-imposed with the antiferro-toroidic domains outlined in blue. To emphasize the domains, b) depicts the antiferromagnetic domains in blue, and c) depicts the ferro-toroidic domains in red. Reproduced from Fig. 3 in Ref. 99.

Li and Vaknin had used LiFePO₄ in neutron scattering experiments published in 2006, they were able to collaborate with Fiebig so Zimmermann could obtain measurements for LiFePO₄ as well. While Schmid was convinced by 2008 that all four domains in LiCoPO₄ were both antiferromagnetic and ferro-toroidic,[60] Zimmermann continues to assert in the 2009 article the co-existence of two antiferromagnetic and two ferro-toroidic domains. Figure 2.20 presents the same data presented in Van Aken’s 2007 article, but more clearly indicates both the regions proposed as ferro-toroidic, and as antiferromagnetic. Zimmermann also presents one SHG image of LiFePO₄ next to images of LiCoPO₄ and LiNiPO₄ for comparison. The LiFePO₄ sample indicates domains with similar “amoeba-like” shapes as observed in LiCoPO₄. Zimmermann cites the 2006 neutron diffraction study by Li and his colleagues, but explains the SHG signal for LiFePO₄ is too weak to determine if the off-axis rotation they observed leads to any contribution to the SHG signal. What this implies is that while they claim the rotation of the Co²⁺ moments

in LiCoPO_4 lowers the symmetry and leads to the observance of a total of four domains, they do not observe evidence of this in their LiFePO_4 sample.

The 2013 study compares the antiferromagnetic ordering in two compositions of LiNiPO_4 doped with Fe^{2+} : $\text{Li}(\text{Ni}_{0.94}\text{Fe}_{0.06})\text{PO}_4$ and $\text{Li}(\text{Ni}_{0.80}\text{Fe}_{0.20})\text{PO}_4$.^[137] In the sample doped with only 6% Fe^{2+} , they observe the same magnetic symmetry as for commensurate LiNiPO_4 (point group $mm'm$) with the spins aligned along the z axis. In the sample doped with 20% Fe^{2+} , the point symmetry is intermediate between LiNiPO_4 and LiFePO_4 (point group mmm') where the spins have both z and y components. This corresponds to a lowering of the point symmetry to m_x for $\text{Li}(\text{Ni}_{0.80}\text{Fe}_{0.20})\text{PO}_4$. They are also able to model the temperature dependence of the SHG intensity, using the relation

$$I(T) = I(0) \cdot \left(\frac{1 - T}{T_N} \right)^c \quad (2.18)$$

where I is the intensity of the SHG signal in the absence of any spin rotation, T is temperature, T_N is the magnetic transition temperature, and c is a sample-specific parameter. They needed to perform the calculation with the intensity in the absence of spin-rotation for $\text{Li}(\text{Ni}_{0.80}\text{Fe}_{0.20})\text{PO}_4$ in order to separate the contribution to the intensity due to the change in temperature, from the contribution of the spin alignment. They are then able to model the spin angle as a function of temperature. The larger significance of that measurement was Zimmermann and her coauthors were able to demonstrate that they could use the changes in the measured intensity to model different contributions to the SHG signal.

In their landmark 2014 study, Zimmermann, Meier, and Fiebig use changes in the SHG signal intensity to demonstrate the hysteretic poling of the domains in LiCoPO_4 under applied magnetic and electric fields.^[138] They performed these experiments because they recognized

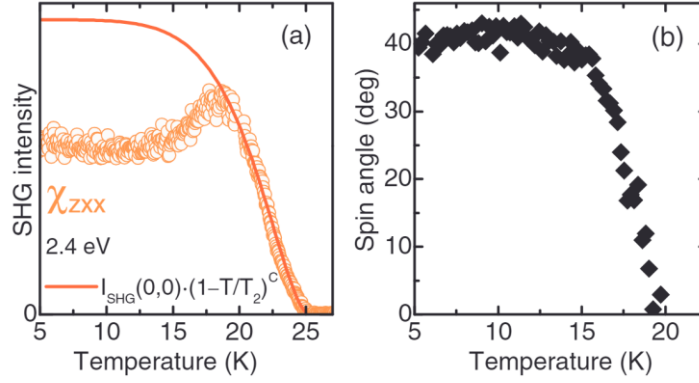


Figure 2.21: The temperature dependence of the SHG intensity in the (100) plane of $\text{Li}(\text{Ni}_{0.80}\text{Fe}_{0.20})\text{PO}_4$ and calculated temperature dependence of the spin angle. a) Open circles indicate the SHG intensity from the χ_{zxx} component at 2.4 eV. The line is the modeled intensity with no spin rotation, according to Eq. 2.18. b) The spin angle computed from the difference between the observed and modeled data in Fig. 2.24a. Reproduced from Fig. 4 in Ref. 137.

that if ferrotoroidicity is indeed a fourth form of ferroic order—and if indeed there are ferrotoroidic domains—then those domains must also exhibit hysteresis like the other classes of ferroics. This was also important because if Schmid is correct and the toroidal domains and antiferromagnetic domains are simply different descriptions of the same physical state,[60] then there would need to be a reason for having two different classifications. One justification would be if the physical properties are best categorized like those of other ferroics.

Figure 2.22 from Ref. 138 presents experimental evidence for the hysteretic behavior of the domains in LiCoPO_4 under magnetoelectric poling. In Fig. 2.22a, the signal from the SHG intensity shows pronounced remanence as the magnetic field is poled from -2 T to +2 T. Figure 2.22d are representative images for that poling process. Figure 2.22b and 2.22c demonstrate the behavior of the domains is distinct under applied magnetic field alone, applied electric field alone, and under crossed magnetic and electric fields ($H_x E_y$). They performed additional measurements and verified they only observed the hysteresis loops when both magnetic and electric fields were applied, not when each was applied alone. This confirms that the observed signal is due to the

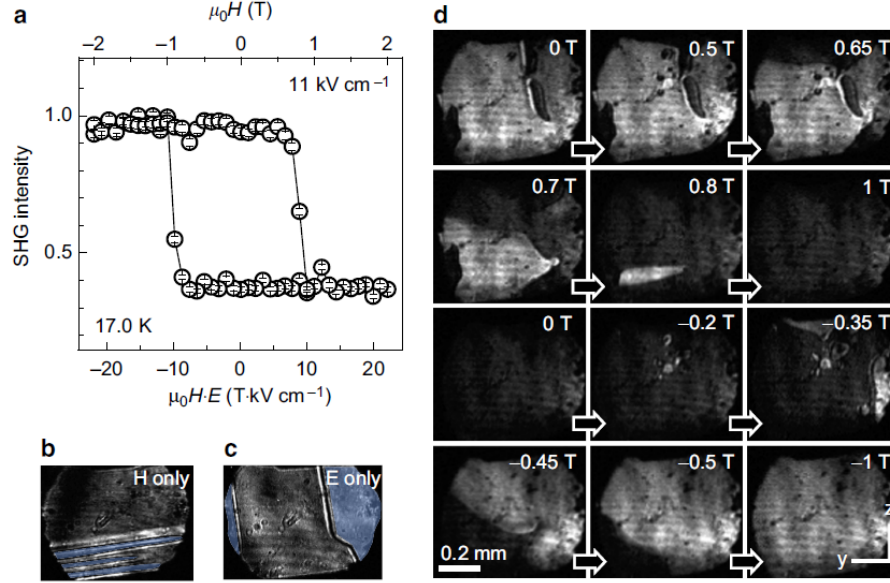


Figure 2.22: Hysteretic poling of LiCoPO₄ (100) by magnetic and electric fields. a) The SHG intensity at 17 K as a function of the static magnetic field $\mu_0 H_x$ and electric field E_y . The electric field was held constant at 11 kVcm⁻¹ while the magnetic field was varied from +2 T to -2 T. In the measurements, light at $2\hbar\omega=2.385$ eV is being emitted from the sample approximately along the χ_{zzz} component of the susceptibility tensor. The remanence is clearly observed, giving the shape of a hysteresis loop. b) Under applied magnetic field of 7 T, opposite orientational domains are visible, and colored blue for clarity. c) Under applied electric field of 11 kVcm⁻¹ the domain structure is likewise clearly distinct from applying magnetic field alone as in Fig. 2.22b, or crossed magnetic and electric fields ($H_x E_y$) as in Fig. 2.22d. d) Representative images of the reorientation of the domains as the magnetic field is increased from 0 T to 1 T, and from 0 T to -1 T. For these series, the static electric field was 10 kVcm⁻¹ and the frequency $2\hbar\omega = 2.330$ eV. Originally published as Fig. 2 in Ref. 138 and reproduced from Gnewuch & Rodriguez (2019).[44]

linear magnetoelectric effect, and not any other phenomena.

The second experimental objective for Zimmermann and her colleagues was to distinguish the toroidal and non-toroidal contributions to the SHG intensity.[138] To do this, they performed two sets of experiments. In the first set of experiments, they performed the magnetoelectric poling with $(E_x H_y \pm E_y H_x)/2$ on a LiCoPO₄ (001) sample. In doing so, they were probing the off-diagonal magnetoelectric tensor components $\alpha_{xy} \pm \alpha_{yx}$. A representative hysteresis loop obtained by this method is presented in Fig. 2.23a. They then performed what they named

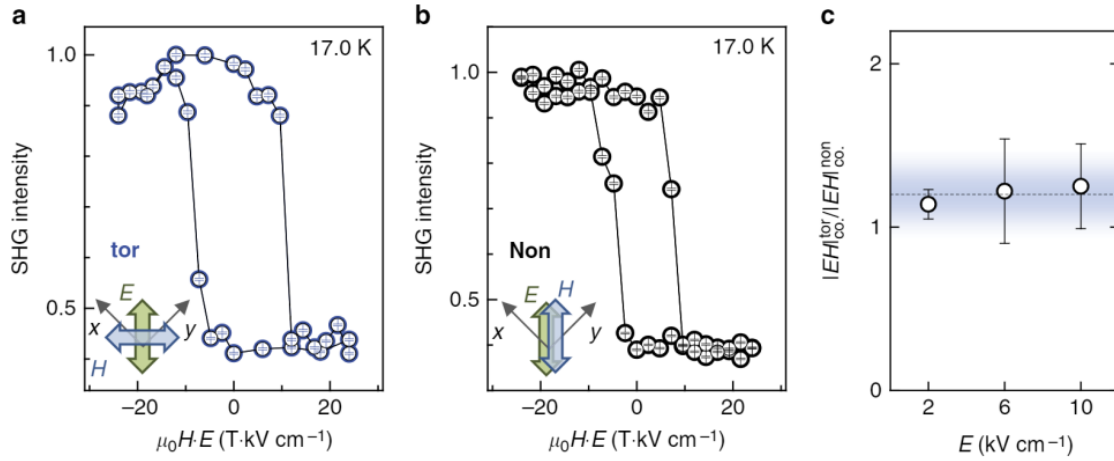


Figure 2.23: The toroidal and non-toroidal contributions to the SHG intensity of LiCoPO₄ (001) under magnetic and electric fields. a) The magnetoelectric poling is performed with crossed electric and magnetic fields in order to measure the SHG intensity with a toroidal contribution. b) The magnetoelectric poling is performed with aligned electric and magnetic fields in order to obtain the SHG intensity without any toroidal contribution, so they can be compared. Both configurations in a and b were performed with the static electric field $E = 12 \text{ kVcm}^{-1}$ while varying the magnetic field, and were measured with the frequency $2\hbar\omega = 2.330 \text{ eV}$. c) The ratio of the toroidal to non-toroidal contribution at several electric fields. The measurements were repeated > 20 times in order to establish the error bars for the analysis. Reproduced from Fig. 4 in Ref. 138.

“non-toroidal poling” experiments. Instead of using crossed electric and magnetic fields, the fields were aligned along the same direction. This configuration is still able to reversibly switch the domain orientations, as seen in Fig. 2.23b. However, the magnitude of the coercive fields are different. They then calculated the ratio of the coercive fields in the toroidal versus non-toroidal configurations, giving $|EH|^{\text{toroidal}}/|EH|^{\text{non-toroidal}} = 1.21 \pm 0.14$. Fig. 2.23c presents that calculation with data collected at three different electric fields.

Zimmermann and the others then cite the paper from 2000 by Kornev and his colleagues, which was discussed in §2.1.[32] Since $\alpha_{yx} = 2\alpha_{xy}$ then that means $\alpha_{xy}^{\text{toroidal}}/\alpha_{xy}^{\text{non-toroidal}} = 1/3$. From this, they argued that if the toroidal and non-toroidal contributions to α_{xy} were similar in strength, then $|EH|^{\text{toroidal}}/|EH|^{\text{non-toroidal}} = 3$ for the ratios of the coercive fields, because $3\alpha_{xy}^{\text{toroidal}} = \alpha_{xy}^{\text{non-toroidal}}$. Since $|EH|^{\text{toroidal}}/|EH|^{\text{non-toroidal}} = 1.21 \pm 0.14$, Zimmermann *et al.*

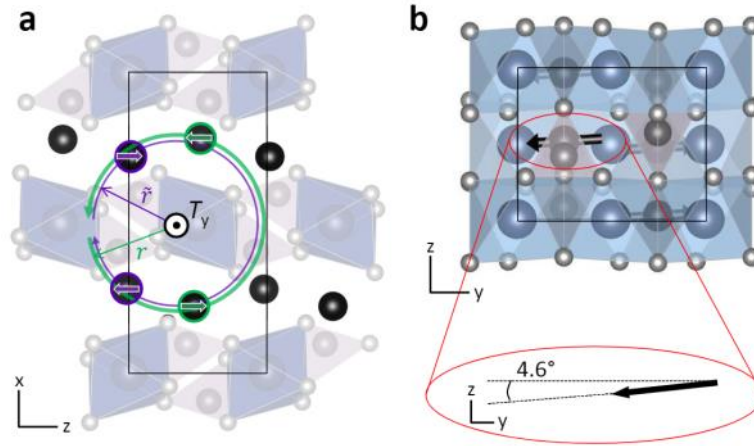


Figure 2.24: Model presented by Zimmermann, Meier, and Fiebig for the “ring” of spins leading to a net toroidal moment $\mathbf{T}_y$. a) The magnetic structure of LiCoPO_4 viewed down the y axis. The two rings are formed by two different pairs of Co^{2+} ions. The purple ring with radius $\tilde{r}$ would produce a toroidal moment $-T_y$, while the green ring with radius r would produce a toroidal moment with $+T_y$. b) The magnetic structure of LiCoPO_4 viewed down the x axis. The inset emphasizes that the magnetic moments are tilted at a 4.6° angle off the y axis along the z axis. Reproduced from Supplementary Fig. 1 in Ref. 138.

concluded the toroidal contributions are much stronger than the non-toroidal contributions at switching the domains in the poling process.

In the 2014 paper, Zimmermann, Meier, and Fiebig also present an updated model for the “ring” of spins leading to a net toroidal moment. In the figure presented in the Van Aken 2007 article (see Figure 2.7) they indicate the net toroidal moment $\mathbf{T}_y$ results from the spin configuration. However, as can be seen from Table 2.5, there should be two components to the toroidal moment if the point symmetry is $2'$. The net toroidal moment from a configuration with mmm' point symmetry would be $\mathbf{T}_z$, and the lowering of the symmetry to $2'$ adds a second component giving $\mathbf{T}_{yz}$. However, given the symmetry is primarily described by mmm' , it is more appropriate to say that $\mathbf{T}_z \gg \mathbf{T}_y$. Figure 2.24 in the supplementary information explains their rationale for understanding the T_y component. Figure 2.24b depicts the magnetic structure of

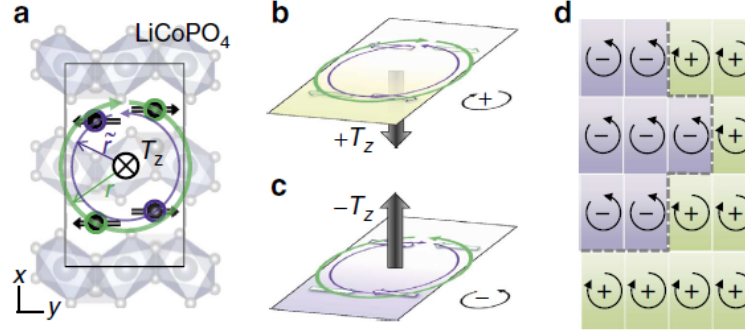


Figure 2.25: Model presented by Zimmermann, Meier and Fiebig for the “ring” of spins leading to a net toroidal component $+T_z$ in one domain, and $-T_z$ in the opposite orientational domain. a) Magnetic structure model of LiCoPO₄ along the z axis. Just as in Fig. 2.24a, there are two rings with different radii and oriented in the opposite directions leading to a small net component. b) Depiction of an orientational domain with a net toroidal moment $+T_z$. c) Depiction of an orientational domain with a net toroidal moment $-T_z$. d) Schematic diagram of how individual adjacent unit cells with a net toroidal moment in the same direction leads to the formation of domains within the bulk crystal. Originally published as Fig. 1 in Ref. [138] and reproduced from Gnewuch & Rodriguez (2019).[44]

LiCoPO₄ along the x axis to emphasize the Co²⁺ ions are slightly tilted off the y axis, lowering the symmetry. Figure 2.24a presents Zimmermann and her colleagues’ model for the “ring” of spins leading to a toroidal component along the y axis. Note, the origin of the ring of spins is *not* at the center of the unit cell. Zimmermann *et al.* did not discuss the reasons for their choice of origin. The reason for their placement of the origin is most likely because Zimmermann *et al.* should have chosen for the purple ring two magnetic moments on opposite sides of the ring instead of two above and below one another. They were most likely trying to be consistent with the origin used in Fig. 2.25a. Figure 2.25a is the model for the ring of spins presented within the body of the text. The magnetic structure of LiCoPO₄ is presented along the z axis. Fig. 2.25b and 2.25c depict two different orientational domains of LiCoPO₄ which have net toroidal moments in opposite directions. Fig. 2.25d is a graphical depiction of how the individual toroidal moments from each unit cell lead to different orientational domains in the bulk crystal.

2.8: Most Recent Work on Ferrotoroidic Candidates

Two other ferrotoroidic candidates have been proposed since Zimmermann's hallmark 2014 study. For the sake of completeness, they are briefly discussed in this section.

One of the first materials known to exhibit a linear magnetoelectric effect is $\text{Co}_4\text{Nb}_2\text{O}_9$. Bertaut *et al.* reported the magnetic space group $P\bar{3}'c'1$ in 1961,[139] and Fisher *et al.* that it was magnetoelectric in 1972.[140] Fang and his colleagues re-examined the magnetoelectric properties in 2014, and confirmed it exhibited a linear magneto-electric effect.[141] A few years later Khanh *et al.* obtained single crystals and performed neutron diffraction studies to re-evaluate Bertaut's study.[142] They concluded the magnetic space group is $C2/c'$, which has the point group $2/m'$. Khanh and his coauthors did not attempt to model the toroidal moment. Rather, in two sentences they asserted that merely displaying several off-diagonal terms in the magnetoelectric tensor implies $\mathbf{T} \sim (\mathbf{P} \times \mathbf{M})$, citing Spaldin's 2008 article.[65] Since $\text{Co}_4\text{Nb}_2\text{O}_9$ has a honeycomb lattice similar to MnPS_3 (discussed in §2.5), the ring of spins is naturally suggested by the ring-like shape of the lattice. However, they did not discuss this.

In 2020 Urru and his coauthors propose $\text{Bi}_5\text{Mn}_5\text{O}_{17}$ is a single-phase multiferroic exhibiting ferromagnetic, ferroelectric, and ferrotoroidic order since the point symmetry is $m'm2'$.[143] In the supplementary information they explain they understand Δr_i to be the atomic displacements which occur during the ferroelectric phase transition as the material distorts from $Pmnn$ to $Pmn2_1$. The Δm_i term is then the changes in the magnitude or orientation of the magnetic moment during the transition. They explain the canting of the moment accounts for about 90% of the toroidization using the expression:

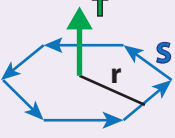
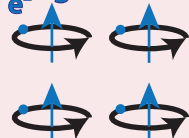
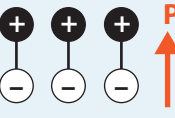
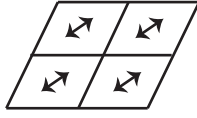
SPACE TIME	CHANGE	INVARIANT
	CHANGE	INVARIANT
CHANGE	a.) Ferrotoroidic 	b.) Ferromagnetic 
INVARIANT	c.) Ferroelectric 	d.) Ferroelastic 

Figure 2.26: Van Aken’s diagram comparing the behavior of the four kinds of ferroic order under time inversion ($1'$), spatial inversion ($\bar{1}$) symmetries. Reproduced from Fig. 1 in Gnewuch & Rodriguez (2019).[44]

$$\mathbf{T} = \frac{1}{2V} \sum_{i \in \text{Mn}} (\Delta r_i \times m_i + r_i \times \Delta m_i). \quad (2.19)$$

They argue that since $\mathbf{T}$ is produced as a consequence of the magnetic order, it is more appropriately classified as a secondary order parameter. Within the body of the text, they classify T as a “slave” (e.g. secondary) order parameter because it follows the $\mathbf{P}$ and $\mathbf{M}$ order parameters according to $\mathbf{T} \sim \mathbf{P} \times \mathbf{M}$. Urru *et al.* do not propose a model for the toroidal moments, but simply treat the ferrotoroidic order from the macroscopic perspective of an order parameter.

2.9: Most Recent Theoretical Developments related to Ferrotoroidic Order

The enduring legacy of ferrotoroidicity from a theoretical perspective is that other kinds of ferroic or multiferroic ordering have since been proposed over the past decade. Figure 2.26 presents the scheme proposed by Van Aken’s 2007 article in *Nature* for integrating ferrotoroidics into the other three ferroic orders.[58] A similar diagram appeared in Spaldin’s 2008 review

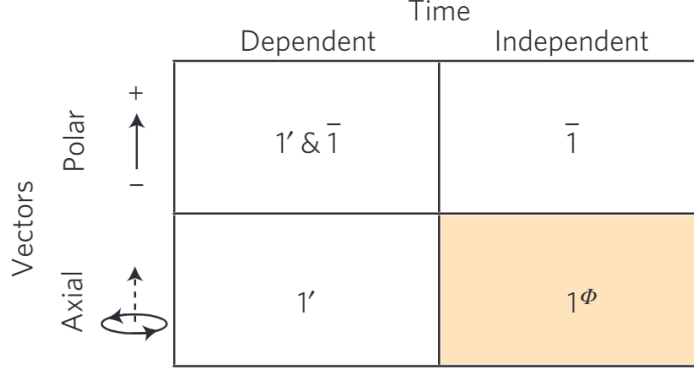


Figure 2.27: Gopalan's diagram comparing the behavior of axial and polar vectors under time inversion ($1'$), spatial inversion ($\bar{1}$), and rotation inversion (1^Φ) symmetries. Reproduced from Fig. 1 in Ref. 144.

article.[65] Since then, other related schemes have been developed to explain how $\bar{1}'$ symmetry and ferrotoroidicity can be understood and integrated into the broader classifications of ferroics.

Gopalan and his colleagues Litvin and VanLeeuwen were the first to suggest an anti-symmetry operation of rotation reversal.[144, 145] In Gopalan's 2011 article published in *Nature Materials*, they present a rational for modeling the static rotational symmetry inherently present in structures such as chiral helices, tilted perovskites, or other motifs. They describe the rotation of each motif by the axial vector:

$$\Phi(\mathbf{r}) \sim \hat{\mathbf{r}}_i \times \hat{\mathbf{r}}'_i, \quad (2.20)$$

where Φ is the static rotation angle, and $\mathbf{r}_i$ are the vectors pointing towards the atomic positions. The operation 1^Φ reverses the sign of the rotation $\Phi \rightarrow -\Phi$ without translating the center of mass of the motif. This type of anti-translation is similar to time inversion ($1'$) in which the sense of the spin (up state or down state) is reversed. For all anti-translations, application of two successive operations results in the starting configuration (i.e. $1' \cdot 1' = 1$ and $1^\Phi \cdot 1^\Phi = 1$). They argue this scheme can be used to categorize toroidal magnetism, since the tensor terms for toroidization would vanish under time inversion or rotation inversion. In Table 1 of their paper, they also propose classifications for a number of other physical properties, including

“linear rotomagnetolectricity” and “rototorroidalmagnetism.” VanLeeuwen’s paper published three years later further developed this concept of rotation-reversal symmetry, and tabulated “double antisymmetry” groups from them.[145]

Spaldin’s 2013 article was discussed previously in Sec. 2.2. In that article, she and her coauthors discussed the symmetry of the LiMPO_4 series end members, and proposed they may actually be examples of materials with magnetoelectric monopoles. The conclusion of the article discusses whether toroidal moments can rightly be treated as a primary order parameter, or if toroidization is always a secondary order which occurs due to antiferromagnetic order or a structural transition. They therefore suggest that since a monopolization also breaks both spatial and time inversion symmetry, it may be a more suitable for completing the fundamental scheme for ferroics. The SHG techniques used by Fiebig and the others should also be able to detect monopolization. However, more recently in 2020 Spaldin co-authored a paper with Thöle and Keliri arguing the magnetoelectric toroidal moment is useful for describing the antiferromagnetic domains in magnetoelectric materials.[146] They specifically discuss the LiMPO_4 series—among other materials—and present their computations for determining the toroidal contribution to the magnetoelectric response. They also present a concise summary of the different contributions to the magnetoelectric multipole as a means of understanding the various contributions to the magnetoelectric effect.

The theoretical work of Cástan, Saxena, and their colleagues was also discussed previously, in Sec. 2.3.[80] They too proposed an alternate “diagram” from Van Aken’s.[58] They argued that since the net order of ferroelectrics, ferromagnets, and ferrtoroidics can all be described by vectors but ferroelastics cannot—ferroelastics are described by a tensor of rank two—then the fourth category should instead be another type of ferrotoroidic. They suggested distinguishing

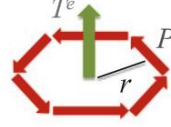
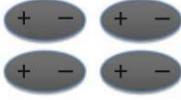
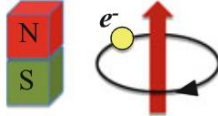
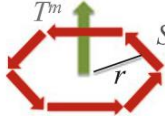
Space Time	Invariant	Change
Invariant	Ferrotoroidic [E] 	Ferroelectric 
Change	Ferromagnetic 	Ferrotoroidic [M] 

Figure 2.28: Cástan’s diagram comparing the behavior of vectorial ferroic properties under spatial and time inversion symmetries. Reproduced from Fig. 4.1 in Ref. 80.

electric ferrotoroidics and magnetic ferrotoroidics. Electric toroidal moments would be invariant under both spatial and time inversion symmetries, and thus represent the trivial case for symmetry. Cástan *et al.* emphasized they would not anticipate electric ferrotoroidal phase transitions to actually occur, but rather they argue it would be beneficial to have language for the null scenario.

In 2018, Saxena co-authored a paper with Cheong and several other colleagues on multiferroicity and other types of ferroic ordering. They also suggested that since ferroelastic order is described by a second-rank tensor, it should be replaced by an order parameter described by a vector. They proposed “ferro-rotational.” They cite the point symmetries for ferro-rotational order as $\bar{1}$, $2/m$, $\bar{3}$, $\bar{4}$, $\bar{6}$, $4/m$, and $6/m$. They listed candidate materials as $\text{NaBi}(\text{MoO}_4)_2$ (space group $I4_1/a$), PbMoO_4 (space group $I4_1/a$), $\text{Cu}_3\text{Nb}_2\text{O}_8$ ($P\bar{1}$), $\text{CaMn}_7\text{O}_{12}$ ($R\bar{3}$), and $\text{RbFe}(\text{MoO}_4)_2$ ($P\bar{3}$). Cheong also co-authored a paper with Jin a few years later presenting evidence for $\text{RbFe}(\text{MoO}_4)_2$ exhibiting ferro-rotational order.[148] They took very careful SHG measurements and were able to measure the clockwise and counterclockwise rotation of the domains, as well as the temperature dependence of the rotation.

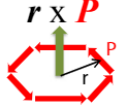
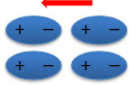
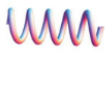
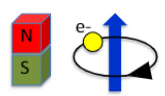
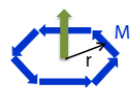
Space Inversion Time Reversal	Invariance	Change
Invariance	Ferro-rotational 	Ferro-electric  Ferro-chiral 
Change	Ferro-magnetic 	Ferro-toroidal $r \times M$ ($P \times M$) 

Figure 2.29: Cheong's diagram comparing the behavior of vectorial ferroic properties under spatial and time inversion symmetries. Reproduced from Fig. 1 in Ref. 147.

As a note, Talebi, Van Aken, and Guo recently published a comprehensive review of toroidal moments in electrodynamics in 2018.[149] It re-presents much of the underlying theory Sannikov and Dubovik originally proposed, but in light of the more recent work by Spaldin, Fiebig, Zimmerman, Popov, Van Aken, Tolédano, and the many others previously discussed.

While all of these proposed classification schemes are inspiring, as a chemist I found them all unhelpful. If my role as a chemist is to create new materials, I need some model for explaining how the structure relates to the function of the material. While possessing a certain point symmetry is a start, you cannot predict which phase a material will take. In solid state synthesis, you can only control the composition of the starting reagents and thermodynamic conditions for the synthesis. Structural modification is very challenging. And magnetic symmetry is even more difficult to tailor with chemical modification. Therefore, I sought to better understand how the chemical structure and magnetic structure could contribute to toroidal structure, so that rational modifications of a series of materials could be attempted to maximize the net toroidal moment in a material.

Chapter 3: A Magnetic Symmetry-Based Model for a Ferrotoroidal Lattice

This chapter is mostly yet-unpublished work, except for §3.5, which presents my contribution to Diethrich 2022.

Diethrich, T. J.; Gnewuch, S.; Dold, K. G.; Taddei, K. M.; Rodriguez, E. E. Tuning Magnetic Symmetry and Properties in the Olivine Series $\text{Li}_{1-x}\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$ through Selective Delithiation. *Chem. Mater.* **2022**, *34*, 5039–5053.

This chapter presents the rationale and methodology for defining a ferrotoroidal lattice. It begins (§3.1) by explaining the benefits of constructing a toroidal model using the conventional descriptions of magnetic space group symmetry. The next two sections (§3.2 & 3.3) argue the defining symmetry feature for a toroidal ring is $\bar{1}'$ and clarify that an axio-polar vector best models a toroidal moment. The following section (§3.4) continues the discussion of $\bar{1}'$ point symmetry to explain how one can distinguish ferrotoroidal, antiferrotoroidal, and non-toroidal point groups based upon the limiting groups. Section §3.5 explains in more detail how to determine the magnetic point group for a particular magnetic structure. This classification scheme for ferrotoroidicity is then used to identify sites of suitable symmetry to support a toroidal moment within a magnetic lattice (§3.6).

3.1: Introduction and Motivation for Modeling Toroidal Moments Using the Conventions of Magnetic Space Group Symmetry

The underlying premise behind chemical crystallography is that the arrangement of atoms in a crystal can be modeled like points in a point lattice. Likewise, a diffraction pattern of that crystal lattice can be interpreted using an appropriate vector lattice describing the distances and angles between the atoms. There are a number of excellent texts on chemical and magnetic crystallography. In this section, I summarize those details pertinent to the discussion of modeling ferrotoroidal lattices. My knowledge of crystallography and magnetic crystallography has been shaped by many articles, books, coursework, and workshops over the years—too numerous to ever cite. I do want to particularly mention the following references, which were particularly helpful when writing this section: [150, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160]. The wording herein is my own understanding of the material.

When working in real space, the infinite set of vectors $\mathbf{t}$ describing the translational symmetry of the lattice are described using a vector lattice T . A point lattice of the vector lattice is constructed by first defining positional vectors $\mathbf{x}_O$ with respect to a chosen origin X_O , and then using the translational vectors $\mathbf{t}$ of the vector lattice to describe the translational symmetry of the point lattice. There are an infinite number of possible point lattices for every vector lattice, since any point can be chosen as the origin. To describe the unit cell, a coordinate system is chosen specifying the origin and basis. By convention the lattice vectors are chosen as the basis vectors—unless Cartesian basis vectors are more appropriate. It is important to note that the point lattice is not the crystal lattice, which is composed of atoms in a periodic arrangement. Crystallographers

choose an appropriate vector and point lattice to describe the symmetric arrangement of atoms, but not all points within the point lattice are occupied by those atoms.

A point describes a site in the lattice, and its coordinates are defined with respect to a chosen origin—which itself is an arbitrarily chosen point. The periodic arrangement is best described by using as many symmetry elements as appropriate to simplify the description of the lattice. These symmetry elements are tabulated according to the conventions of group theory, and therefore every crystal lattice is assigned to a space group type. The space groups are organized according to the symmetry elements used to describe the periodic arrangement of the atoms in a lattice. For chemical crystallography, comparing atoms in a crystal lattice to points in a point lattice works very well.

However, in magnetic crystallography that situation is no longer sufficient to describe the symmetry in the material. When a material is in a paramagnetic state, each individual magnetic ion has a net magnetic moment, but those moments are not aligned in an ordered periodic arrangement. They are therefore said to possess time inversion symmetry. In other words, “up” and “down,” “right” and “left,” “+x” and “-x,” are indistinguishable. Furthermore, in magnetic crystallography if a site in a lattice possesses time inversion symmetry (notated with a prime such as $2'$) that means there cannot be a periodic ordering of net magnetic moments at that site. The individual magnetically-active atoms possess a magnetic moment, but the moments of the atoms in adjacent unit cells or at other equivalent positions in the lattice are not arranged in a periodic way.

Once a magnetic material has undergone a phase transition to an ordered magnetic state, the arrangement of the magnetic moments lowers the symmetry of the entire system. Therefore one would say symmetry has been lost (*i.e.* broken). This implies a magnetic material in the

paramagnetic state possesses more symmetry than an analogous crystal structure composed of non-magnetic atoms because the randomly ordered magnetic moments possess time inversion symmetry. The formal mathematical description is as follows:

If the crystallographic group (only considering the atoms) is described by Group $\mathcal{F}$, then the paramagnetic group is the direct product of $\mathcal{F}$ and $1'$:

$$\mathcal{F} 1' = \mathcal{F} \times 1'. \quad (3.1)$$

The paramagnetic group $\mathcal{F} 1'$ therefore has twice as many elements as $\mathcal{F}$. For example, if the symmetry elements of the crystallographic group were $\{2, \bar{1}\}$, then in the paramagnetic group they would be $\{2, \bar{1}, 2', \bar{1}'\}$. The redundant primed symmetry elements express the time inversion symmetry possessed in the paramagnetic state. No site in the lattice can permit a net ordered magnetic moment. In order for there to be the same number of symmetry elements for the magnetically ordered state below the magnetic phase transition as the chemical unit cell above the transition, the magnetically ordered state must be described by a subgroup $\mathcal{F}(\mathcal{D})$ with half the number of symmetry elements as $\mathcal{F} 1'$:

$$\mathcal{F}(\mathcal{D}) = \mathcal{D} + (\mathcal{F} - \mathcal{D} 1') \quad (3.2)$$

Note then that half of the symmetry elements will be unprimed, and the other half will be primed.

Whereas all lattice sites in the paramagnetic state forbade a net periodic arrangement of magnetic moments, net moments are now permitted on certain sites in the magnetically-ordered state. Each subgroup $\mathcal{F}(\mathcal{D})$ is a representation of one possible periodic arrangement of magnetic moments. For example, if one representation would have all the moments aligned along one crystallographic direction, that would be a ferromagnetic structure. If the representation would have the moments anti-aligned, the structure would be antiferromagnetic. Most magnetic phase transitions are second-order, where the ordering of the magnetic moments is the only change

in the symmetry and therefore energy of the system. If there is a concomitant structural distortion, that additional symmetry reduction is considered as well. Such first-order phase transitions would therefore have even fewer symmetry elements in the ordered state. When assigning a magnetic structure to a phase, all the possible subgroups are computed and the model which best fits the data is assumed to be the correct one. As a note: In practice sometimes two (or more) representations are needed to describe the magnetic order. For example, if the data demonstrates the moments are mostly aligned along one direction but canted by a small angle along another direction, the two representations together are used to describe the observed orientation.

A lattice is defined with both a basis and an origin. The basis is the lattice vectors. Any point could be chosen as the origin of the crystal lattice, but there are conventions for assigning the origin. In most cases, the site with the highest symmetry is chosen. In centrosymmetric space groups an inversion center is always chosen. These conventions make it easier to analyze the symmetry of a crystal lattice, and compare it to other crystal lattices. In other words, it is most practical to always choose one of the conventional origins for the space group. The only exception would be when choosing a different site would aid analysis of a phase transition or structural distortion.

In magnetic crystallography it is even more crucial to choose a consistent origin so that the phase transition from the paramagnetic to ordered magnetic state can be analyzed in a systematic manner. Typically it is easiest to have the magnetic lattice vectors coincide with the chemical lattice, unless a different basis is needed to fully describe the symmetry. In those cases, the magnetic basis vectors are always described with respect to the chemical basis using integer values of basis vectors whenever possible. For example, a magnetic basis of $(a, 2b, c)$ would indicate the magnetic unit cell is doubled along the b direction with respect to the chemical

unit cell. This method is sufficient for describing the magnetic symmetry for commensurate structures. In incommensurate structures, the basis cannot be described using integer values of basis vectors with respect to the chemical basis. The magnetic structures in this dissertation are commensurate and so this will not be discussed further here.

There are three general methods for describing the magnetic ordering in a magnetic material, each with their own benefits and limitations. They are magnetic space groups, representational analysis, and superspace formalism. The primary benefit of the magnetic space group approach is it corresponds to the crystal lattice as closely as possible whenever possible. The overall properties of a crystalline material are determined not just by the magnetic symmetry but by the structural symmetry of all the atoms in the crystal lattice. Therefore this approach is easiest to compare the chemical and magnetic structure models. However, it is more difficult to describe incommensurate magnetic order with this approach. Representational analysis describes the periodicity of the magnetic moments according to one or more propagation vectors and so is more directly applicable to incommensurate structures and analysis of reciprocal space. All commensurate representations have a corresponding magnetic space group, and so the analysis is very similar for those magnetic structures. The superspace approach does not consider the underlying crystal lattice at all, and enables analysis of magnetic ordering on any scale, including skyrmions.

In this work, I consider the magnetic symmetry using the magnetic space groups, since the symmetry of the entire crystal is crucial for creating a system with the permitted symmetry for ferrotoroidal order. In addition, it is simpler to ascertain where in the crystal structure the symmetry elements are lost (*i.e.* which symmetries are broken) across the magnetic phase transition. Their comparison is simpler because the magnetic unit cell is described with respect

to the chemical unit cell.

There are a number of underlying assumptions for how ordered toroidal moments would arise in a solid state material, which was discussed in detail in Chapter 2. The consensus for the criteria includes the following:

1. Toroidal moments must be invariant under space-time inversion ($\bar{I}'$), behaving neither as axial vectors nor as polar vectors but rather a different category.
2. The point group symmetries which permit a toroidal moment will also permit a linear magneto-electric effect.
3. A toroidal moment would be perpendicular to a “ring of spins,” like those found in antiferromagnetic structures.
4. Just as there is some reduction in symmetry associated with the magnetic ordering of the lattice, a toroidal phase transition would also lower the symmetry of the system. This ordering would be coexistent with the magnetic ordering.

Since magnetic moments are located on magnetic ions, they have defined sites within the crystal lattice. It logically follows that there must be specific sites for the toroidal moments as well. These sites must be invariant under space-time ($\bar{I}'$) inversion in order to permit a net toroidal moment. This site symmetry cannot permit a net magnetic moment, and so the magnetic and toroidal sites would be mutually exclusive. The toroidal sites must also be the center of a “ring of spins,” formed by an antiferromagnetic arrangement. Lastly, the toroidal moments must be perpendicular to the “ring of spins,” since this would be the lowest-energy configuration.

It would also logically follow that there must be an ordered toroidal lattice, whose symmetry is dictated by the ordering of the magnetic lattice. The toroidal lattice would coexist with the magnetic lattice, just as a magnetic lattice coexists with a crystal lattice with non-magnetic

ions. For these reasons, a toroidal lattice must be defined with respect to a magnetic lattice, and understood using the conventions of magnetic space group crystallography. The rest of this chapter is devoted to developing these arguments and explaining their implications.

3.2: Space-Time Inversion Symmetry ($\bar{1}'$)

In magnetic space groups and point groups, there is not only spatial inversion symmetry ($\bar{1}$) but also time inversion symmetry ($1'$) to consider. A “primed” symmetry element is invariant under time inversion symmetry. For example, when a two-fold rotational element is combined with the inversion element, a mirror plane results: $2_z \bar{1} = \bar{2}_{xy} = m_{xy}$. By convention $\bar{2}$ is notated as m , but $\bar{2}$ is equally correct. A similar convention is employed for time inversion. When a symmetry element is combined with time inversion, it is primed. For example, a two-fold rotational element combined with time inversion is notated: $2_z 1' = 2'_z$. Likewise, when spatial inversion is combined with time inversion, this is notated: $\bar{1} 1' = \bar{1}'$. Therefore it is referred to as space-time inversion.

Recall Ascher’s Table (Tab. 2.1) which was introduced in §2.1. Each of the irreducible representations of $\bar{1} 1'$ is related to a classification of ferroic ordering, which Schmid expanded to include toroidization in 2001.[13, 14, 15, 16, 45] According to that scheme, toroidization would be variant (indicated by -1) under $1'$ and $\bar{1}$ symmetries, but invariant under $\bar{1}'$.

A brief note on Tab. 2.1: it is not meaningful to have a point group of $1'$. The reason for this, is that it is not possible to assign any point in a magnetic lattice with only $1'$ symmetry. Any kind of inversion symmetry (*i.e.* improper rotation) is only meaningful through an inversion point, and so the notation $1 1'$ is more appropriate. This is because it specifies that the time

inversion is defined to be located at whichever location is specified for the identity element 1. Because of this, the representation invariant under time inversion is notated $\Gamma_{11'}$ and contains both the identity and the time inversion elements $\{1, 1'\}$ so that it has an order of 2 like the others. This analysis is based upon the point group tables presented in MPOINT on the Bilbao Crystallographic Server.[161]

In addition to being invariant under $(\bar{1}')$, a toroidal moment would be perpendicular to a “ring of spins” in an antiferromagnetic arrangement.[17, 18, 19, 20] To better understand space-time $(\bar{1}')$ inversion symmetry and how it relates to a “ring of spins,” first consider the symmetry elements of an ideal “ring” in two dimensions, a circle.

The origin of a circle, located at the center, is a fixed point. This means that when any of the symmetry operations of the circle act on that point, it will be invariant. There is an infinite rotation axis going through the origin, perpendicular to the plane of the circle (Fig. 3.1a). In addition, there are infinitely many mirror planes bisecting the circle, also perpendicular to the plane of the circle (Fig. 3.1b). The symmetry at the origin is therefore ∞_m , and is a site of inversion $(\bar{1})$. At any given point on the circle, the clockwise and counter-clockwise directions are equivalent. Because of this, there are also infinitely many perpendicular mirror planes bisecting the plane of the circle.

Now consider that same ring, but every point on the ring is a magnetic spin moment. First consider the scenario in which the clockwise and counter-clockwise directions are equivalent. The spins are perpendicular to the mirror planes (Fig. 3.1c). The points are depicted with a double-headed arrow, pointed along the ring. Both the “clockwise” and “counterclockwise” states are equivalent, so that the points are invariant under time inversion symmetry. If a point is spatially inverted through the origin of the ring, there is no inversion of the direction of the spins because both states are equivalent. Therefore the inversion center is now described by the

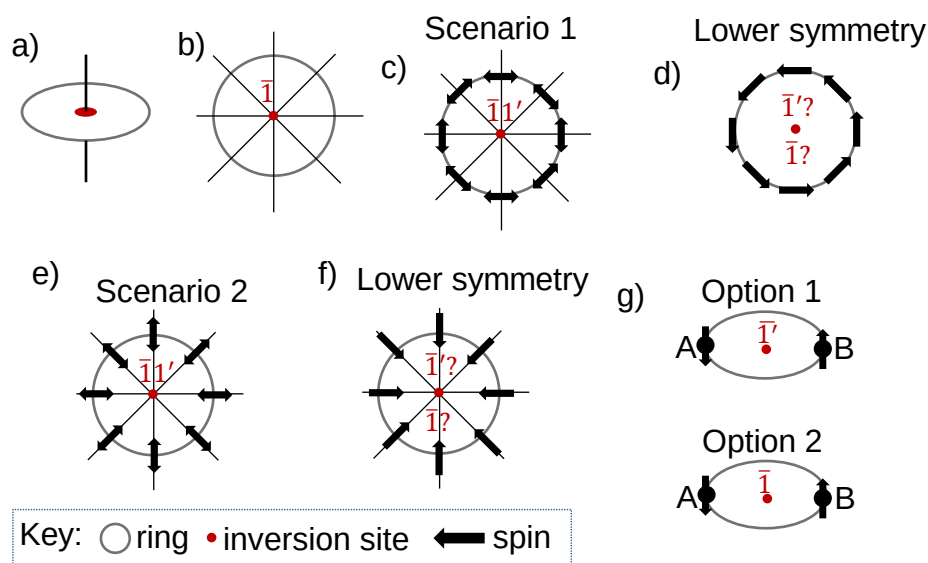


Figure 3.1: a) Depiction of an infinite rotation axis perpendicular to the plane of a circle, with the origin of the circle indicated as a large red dot. b) The same circle as in Fig. 3.1a, but oriented looking down the plane of the circle. The lines indicate the perpendicular mirror planes bisecting the plane of the circle. While there are an infinite number of these mirror planes, only four are depicted for clarity. c) Depiction of Scenario 1, in which the magnetic moments drawn as double-headed arrows are oriented perpendicular to the mirror planes. d) The same circle as in Fig. 3.1c, but now the arrows are single-headed. The reduction in symmetry leads to the loss of the perpendicular mirror planes. The $\bar{1}'?$ and $\bar{1}?$ labels signify the ambiguity when assigning the symmetry at the center of the circle. e) Depiction of Scenario 2, in which the magnetic moments are oriented parallel to the mirror planes. f) The same circle as in Fig. 3.1e, where the symmetry at the points along the circle have been reduced so that the magnetic moments are single-headed and oriented towards the center of the ring. g) Example of the two options for assigning the symmetry at the center between two anti-aligned magnetic moments (spin A and spin B) in a ring.

symmetry $\bar{1}1'$.

Now consider what happens to Scenario 1 when clockwise and counter-clockwise are no longer equivalent (Fig. 3.1d). Now the spins are depicted as single-headed arrows arranged head-to-tail. The infinite mirror planes perpendicular to the plane of the circle are lost. Therefore the symmetry at the origin of the ring is now *lower* than $\bar{1}1'$. There are two options for describing the resulting symmetry (Fig. 3.1g):

1. The points at sites opposite one another on the ring have their magnetic spins pointing in

opposite directions, making the symmetry at the origin $\bar{1}'$. The spatial inversion through the origin is combined with time inversion since the spins are reversed.

2. The points at sites opposite one another on the ring have their magnetic spins pointing in the *same* directions. At any point on the ring, they are pointing in the clockwise direction. Therefore, the symmetry at the origin is $\bar{1}$. The spins are not reversed when they pass through the inversion center.

Consider Scenario 2, where the spins are oriented parallel to the mirror planes (Fig. 3.1e).

The double-headed arrow signify that inwards and outwards are equivalent. Now consider that same ring with single-headed arrows (Fig. 3.1f). The symmetry is actually higher than the situation in Fig. 3.1d. Since the arrows were pointing along the ring, the mirror planes are retained. However, the symmetry of the points along the ring have still been lowered. Axial vectors are always used to indicate the symmetry has been lowered at a site, as explained in §3.1.

Regardless, the same two options are possible when assigning the symmetry at the origin. Either:

1. The spins opposite one another are pointed in *opposite* directions and therefore the symmetry at the origin is $\bar{1}'$.
2. The spins opposite one another are pointed in the the *same* direction (inwards) and the symmetry at the origin is $\bar{1}$.

The reason for these different interpretations is the different possible definitions for the “origin” of the system. If the entirety of the system is in fact only one ring of spins, it is intuitive to treat the center (*i.e.* origin) of the ring as the origin. Likewise, it is intuitive to assign the orientation of spins in Fig. 3.1d as “counter-clockwise.” Similarly, the spins pointed towards the center of the ring in Fig. 3.1f are “spin up,” since they are pointed towards the center. While this scheme is perfectly logical when considering point symmetry, it is invalid when considering a three-dimensional periodic system of repeating units, like a crystal structure.

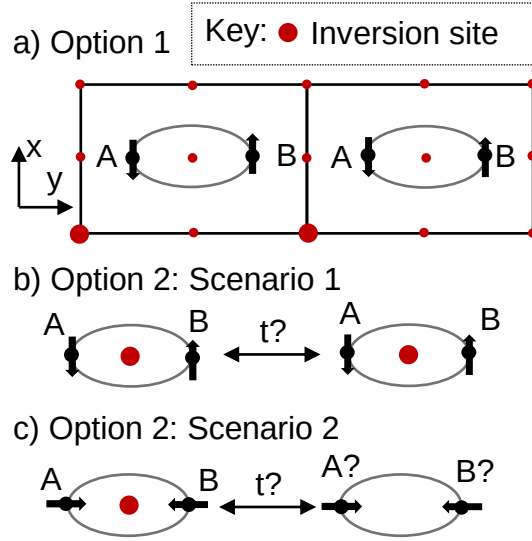


Figure 3.2: a) Simple depiction of a ring of two moments (spin A and spin B) within a two-dimensional lattice. The ring is oriented around a site of inversion symmetry. The origin of the lattice is separate from the center of the ring, indicated with a large red dot. The lattice basis defines spin A as “spin down” and spin B as “spin up.” There are multiple other inversion sites in the lattice, depicted as small red circles. This will be discussed in detail in §3.6. b) Example of two rings of spins with the origin defined as the center of the ring, and “spin down” defined as counter-clockwise. The black double-headed arrow and label “t?” signify there is no systematic way for defining the translational periodicity of the rings and the origins to one another. c) Similar situation to Fig. 3.2b, but “spin up” is defined as the moments pointed towards the center. In addition to the ambiguity assigning the translational periodicity, the directions of the spins in an adjacent ring is also ambiguous.

Consider Fig. 3.2, which is drawn in two-dimensions for clarity. It depicts the logical consequences when considering multiple rings composed of two spins (spin A and spin B) in space. In Fig. 3.2a, the center of the circle is drawn around a site of inversion symmetry, but there is a separate lattice origin and basis defining “spin up” and “spin down.” The origin is depicted with a large red dot. The other inversion sites in the lattice are depicted with smaller red dots. Since spin A and spin B are defined as being opposite, the symmetry at the center of the ring is $\bar{1}'$. This indicates not only are the locations of the atoms related by spatial inversion, but the direction of the moments are related by time inversion as well.

Fig. 3.2b & c depict the two possible scenarios when the origin is defined as the center

of the ring. In Fig. 3.2b, both spin A and spin B are equivalent because they are both oriented counter-clockwise. However, when considering another ring of spins, there is no intuitive way of assigning translational periodicity between the origins of the rings. A translational lattice must be assigned.

However, when creating a translational lattice there are inversion sites associated with the lattice itself, in addition to the inversion site between the spins. In short, whenever there is a site of inversion combined with a lattice translation, there will always be another site of inversion half-way in-between. This will not be discussed further here, since it will be discussed in detail in §3.6. For now, it is sufficient to point out that the symmetry of the entire lattice cannot be neglected, and so it is invalid to define the symmetry of the spins by the center of the unit cell.

Likewise, Fig. 3.2 depicts the ambiguity when “spin up” is defined as the center of a ring. If there is another ring, does that mean “spin up” is defined as pointing towards the center of the original ring? Do both rings have an origin? If so, is “spin up” being re-defined with the addition of each subsequent ring? What implications would that have for other atoms in the system which are not a part of the rings? These rhetorical questions are meant to demonstrate the significance of having one, defined origin for the entire system, separate from the center of the ring. The lattice origin and basis both function to define the inversion of the moments throughout the lattice, not just for the rings. In addition, the lattice defines the translational periodicity of the rings of magnetic ions, as well as any other non-magnetic atoms. The topic of toroidal lattices will be addressed again in §3.6.

3.3: Behavior of Axio-Polar Vectors

As mentioned in §3.1, axial vectors are used to represent a magnetic spin moment. The moment on a particular ion arises due to the electrons spinning around the nucleus. Therefore when the electrons spin in the opposite direction, the sign of the moment reverses. Therefore an axial vector best models both the direction of the moment, and the direction of the electrons orbiting the nucleus. A polar vector only describes the symmetry of a direction, like a displacement of a ion in a lattice distortion. Therefore they possess different symmetries and behave differently under symmetry operations.

The topic of a “third kind” of vector for toroidal moments was discussed both in §2.3 and §2.9. Many different kinds of vectors are used in the study of ferroics to describe various aspects of the physical properties and symmetries of the system. For example, consider ferromagnetic materials. The bulk crystal would have a net magnetization along a certain crystal direction which would be described by a vector. The magnetic moments are modeled as axial vectors to describe their behavior under time inversion symmetry. The microscopic orientation of the individual magnetic moments gives rise to the macroscopic direction of net magnetization. The expectation is that ferrotoroidal materials would have analogous phenomena. A macroscopic ferrotoroidal crystal would exhibit a net toroidization along a certain crystal direction. The net toroidization would be described by a polar vector. Likewise, the microscopic orientation of individual toroidal moments in the unit cell would give rise to the observed net toroidization in the bulk material. However, the time inversion symmetry requirements for toroidal moments is mutually exclusive to the requirements for magnetic moments.

Consider Tab. 3.1. This is a modification of Tab. 2.1 from §2.1 and inspired by Tab. 2.6

Table 3.1: Behavior of Vector Types under Inversion Symmetries.

Symmetry	Vector Type			
	axial	polar	axio-polar	trivial
identity	o	o	o	o
spatial inversion	o	∅	∅	o
time inversion	∅	o	∅	o
space-time inversion	∅	∅	o	o

Note: “∅” indicates the vector is variant under the symmetry, while “o” indicates invariance.

from §2.3 as well as Fig. 2.26, 2.27, 2.28, and 2.29 from §2.9. To avoid confusion from using so many “1” symbols throughout this discussion, “∅” indicates symmetry variance and “o” indicates invariance.

In this scheme, all types of vectors are defined to be invariant under the identity operation. In addition, there logically needs to be a trivial vector which is invariant under all four types of symmetry operations. This would best be modeled as a double-headed vector, as was used in Fig. 3.1 and 3.2. The inspiration for using a double-headed arrow was from the work on magnetic point group visualizations by Marc de Graef.[162, 163] Spatial inversion is any improper symmetry operation (*e.g.* $\bar{1}$), time inversion is any proper primed symmetry operation (*e.g.* $2'$), and space-time inversion is an improper primed symmetry operation (*e.g.* $\bar{1}'$).

The scheme treats polar and axial vectors in a similar way to net polarization and net magnetization in Fig. 2.26 from §2.9. A polar vector reverses direction under spatial inversion and is invariant under time inversion. This is because a polar vector itself is not symmetric from both directions, as opposed to a point which is symmetric from any direction. An axial vector reverses direction under time inversion and is invariant under spatial inversion. This may seem counter-intuitive, but the reason for this is that the symmetry of an axial vector includes the rotational direction of the vector, such as the rotation of the electrons around the nucleus to form

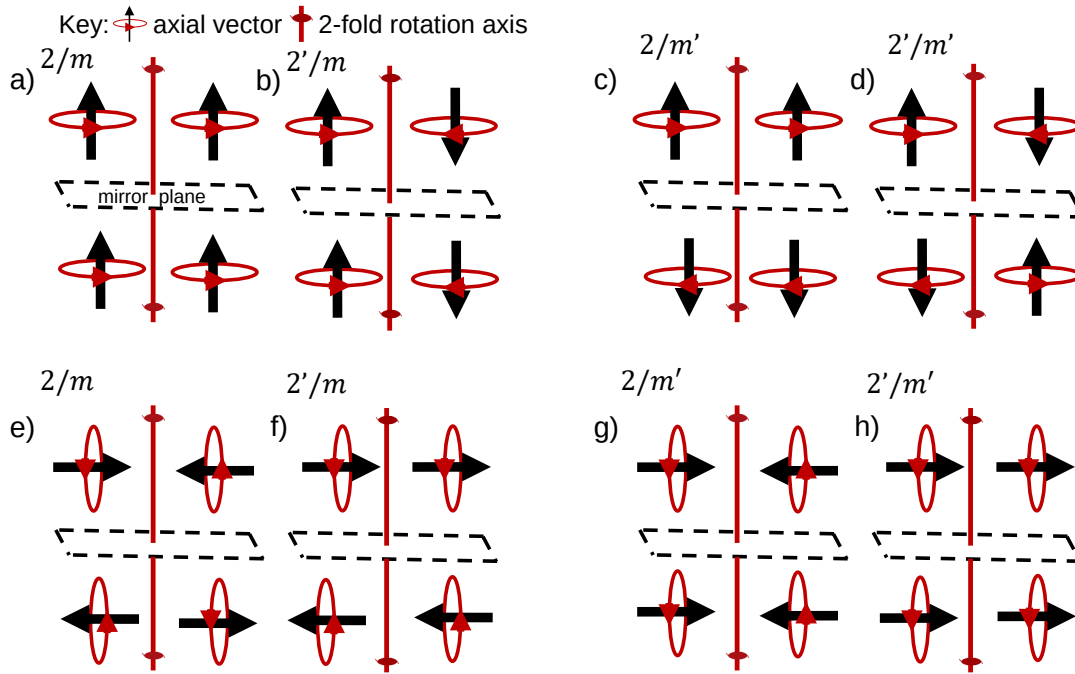


Figure 3.3: a-d) Transformation of axial vectors aligned parallel to the 2-fold rotation axis in the magnetic point groups: a) $2/m$, b) $2'/m$, c) $2/m'$, d) $2'/m'$. e-f) Transformation of axial vectors aligned parallel to the mirror plane in the magnetic point groups: e) $2/m$, f) $2'/m$, g) $2/m'$, h) $2'/m'$.

a magnetic moment. As a result, an axial vector behaves differently under spatial inversion than a polar vector.

Axio-polar vectors would model toroidal moments, since they behave similarly to polar vectors under spatial inversion, but are complementary to the behavior of axial vectors under time inversion. Axial vectors are invariant under time inversion, but reverse under space-time inversion. Axio-polar vectors exhibit the opposite behavior. Therefore the point groups of symmetry elements permitting a net magnetic moment (as in ferromagnets) would be complementary and mutually exclusive to point groups permitting a net toroidal moment.

Fig. 3.3 and 3.4 demonstrate the mutually exclusive behavior of ferromagnetic and ferrotoroidal point groups. As discussed in §3.2, the intersection point between a 2-fold rotation axis and a mirror plane will be a site of inversion symmetry. In Fig. 3.3 the symmetry of the intersection

point is $\bar{1}$. Therefore the direction of the axial moments are pointed in the same direction in quadrants 1 & 3, and quadrants 2 & 4. In Fig. 3.3b, the inversion point now has the symmetry $\bar{1}'$ since one of the symmetry elements are primed. Therefore the axial moments are oriented in opposite directions in quadrants 1 & 3, and quadrants 2 & 4. Fig. 3.3c-h are included for the sake of completeness. They demonstrate that the absolute configuration of the axial moments depends both upon the point group, and whether the moments are oriented parallel to the 2-fold rotation axis, or parallel to the mirror plane. For example, if the moments are aligned parallel to the 2-fold rotation axis, the configuration is ferromagnetic in the point group $2/m$. However, if the moments are aligned parallel to the mirror plane, the configuration is only ferromagnetic in the point group $2'/m'$. It is therefore imperative to not only consider the point symmetry in a system, but also the absolute orientation of the moments relative to the symmetry elements to accurately assess if a configuration is ferromagnetic or antiferromagnetic.

Recall Tab. 3.1, and the discussion of axio-polar vectors. An axio-polar vector would be variant under spatial inversion and time inversion but invariant under space-time inversion. Fig. 3.4 demonstrates the transformations of the axio-polar vectors under the same magnetic point groups as in Fig. 3.3. Consider first Fig. 3.4a. Since an axio-polar vector *is* variant under spatial inversion $\{\bar{1}\}$, the transformation of the vectors is the same as it would be for polar vectors with this configuration. Notice how this configuration is antiferromagnetic, whereas for the axial vectors this configuration was ferromagnetic. Likewise, Fig. 3.4e gives the same configuration as if the vectors were simply polar vectors. The difference between axio-polar vectors and polar vectors is that polar vectors are invariant under time inversion symmetry $\{11', \bar{1}'\}$ and therefore it would give the same vector transformations for $2'/m$, $2/m'$, and $2'/m'$ as for $2/m$. This is not the case for axio-polar vectors. Notice the axio-polar vectors will give the same four combinations of

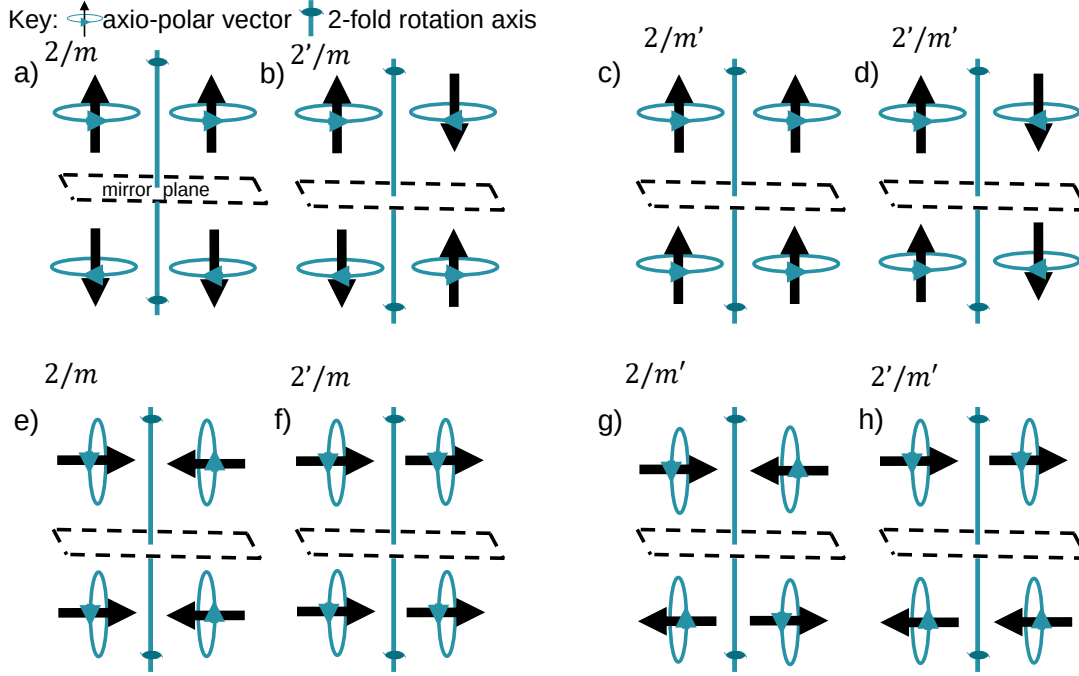


Figure 3.4: a-d) Transformation of axio-polar vectors aligned parallel to the 2-fold rotation axis in the magnetic point groups: a) $2/m$, b) $2'/m$, c) $2/m'$, d) $2'/m'$. e-f) Transformation of axio-polar vectors aligned parallel to the mirror plane in the magnetic point groups: e) $2/m$, f) $2'/m$, g) $2/m'$, h) $2'/m'$.

vector transformations as for axial vectors, but with different point groups. This is because while axial vectors are invariant under spatial inversion ($\bar{1}$) and variant under space-time inversion ($\bar{1}'$), the opposite is true of axio-polar vectors. Tab. 3.2 summarizes the transformations of axial and axio-polar vectors under spatial ($\bar{1}$) and space-time ($\bar{1}'$) inversion symmetries. Notice they are complementary and mutually exclusive.

An important implication of this is that sites of space-time ($\bar{1}'$) inversion forbid a magnetic moment (*i.e.* an axial vector) on them, but permit a toroidal moment (*i.e.* an axio-polar vector) and *vice versa*. This means it is forbidden by symmetry for a toroidal moment to occur on a site with a magnetic moment on it. Furthermore, since sites of $\bar{1}'$ symmetry are defined by an anti-aligned configuration of magnetic moments, toroidal moments may only occur in lattices with an antiferromagnetic arrangement of magnetic moments.

Table 3.2: Comparison of the Transformations of Axial and Axio-polar Vectors under the Magnetic Point Groups $2/m$, $2'/m$, $2/m'$, and $2'/m'$.

Magnetic Point Group	Inversion Site Symmetry	Vector Type	
		axial	axio-polar
$2/m$	$\bar{1}$	o	ø
$2'/m$	$\bar{1}'$	ø	o
$2/m'$	$\bar{1}'$	ø	o
$2'/m'$	$\bar{1}$	o	ø

Note: “ø” indicates the vector is variant under the symmetry, while “o” indicates invariance.

A brief note before concluding this section: Mathematically an axial vector is defined as being the cross product of two polar vectors. In essence, the two polar vectors approximate a “rotation direction” because they define if the system is right- or left-handed. The cross product of an axial vector and a polar vector is a polar vector mathematically. However, in this application analyzing magnetic symmetry it is pertinent to distinguish a “regular” polar vector from a polar vector which is a cross product of an axial and polar vector. Therefore calling it an axio-polar vector is useful for clarity. In §2.3 I mentioned that the results of MTENSOR from the Bilbao Crystallographic Server are consistent when computing the tensors for a “polar toroidal moment.” A better term is “axio-polar toroidal moment” since it specifies more clearly that it is variant under time inversion symmetry ($11'$) like an axial vector, and is variant under spatial inversion symmetry ($\bar{1}$) like a polar vector.

3.4: Ferrotoroidal and Antiferrotoroidal, and Non-Ferrotoroidal point groups

Tab. 2.3, Tab. 2.4, and Tab. 2.5 from §2.3 list various magnetic point groups which are associated with ferrotoroidic order. None of them agree. The purpose of this section is to demonstrate a rational classification system for designating which magnetic point groups would

permit ferrotoroidal order.

It is important to clarify these point groups are not formally the same as the point group of a space group (crystallographic point groups). In space groups, symmetry operations can have both rotational (R_i) and translational (τ_i) components, as well as a translational component due to the lattice (t_n) such as in centered cells. To determine the point group of a space group, all the operations of the space group $\{R_i|\tau_i+t_n\}$ are taken and all the translational components are set to zero $\tau_i+t_n=0$. Only the rotational components are considered, so that any screw or glide operations are treated as simple rotational and mirror operations. This notational method is called Seitz notation.

According to the Neumann Principle, the symmetry of the point group dictates the symmetry of the physical properties. While going from space group to point group for such analysis is trivial, going backwards from point group to space group is not. This is a challenging problem when attempting to design a functional material from a crystal chemistry perspective.

In crystallographic space groups all of the point symmetry elements are *not necessarily* overlapping. The translational symmetry elements define where exactly the symmetry elements are located within a lattice. Furthermore, any kind of improper symmetry (*i.e.* $\bar{1}$ and $\bar{1}'$) is defined around an inversion site. Thus, to understand where exactly an entity would be invariant under space-time ($\bar{1}'$) inversion symmetry, the translational symmetry must also be considered. In addition, in order for an entity to be invariant under a symmetry operation, it needs to be located *on* that symmetry element. Therefore, in order for toroidal moments to be invariant under space-time ($\bar{1}'$) inversion symmetry, those moments *must* occur on sites with $\bar{1}'$ symmetry. It could be possible for the site to have higher symmetry, but it must still have $\bar{1}'$ as a minimal subgroup.

In the case of inversion symmetry in a lattice, there will always be a point of inversion at the intersection point between a rotation and screw axis with even order (*e.g.* 2, 2₁, 4₂, 6) and a perpendicular mirror or glide plane (*e.g.* 2/*m*, 4/*n*, 6₃/*m*). As a mathematical example, consider multiplying the matrices for 2_z and *m*_{xy} in an orthogonal basis:

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \bar{1}. \quad (3.3)$$

The result is an inversion matrix.

These situations are trivial to identify because the full Hermann-Mauguin space group symbols always indicate the perpendicular mirror or glide planes present. For example, in *C*2/*c* they occur where the two-fold rotation axes intersect with the perpendicular glide planes. These positions are always considered high-symmetry points (*i.e.* special positions) and assigned a Wyckoff letter, making identifying and specifying these locations trivial. In addition, rotoinversion axes of odd order (*i.e.* $\bar{1}$ and $\bar{3}$) also imply the presence of points of inversion. Their identification is also trivial. After reviewing the Hermann-Mauguin space group symbol, consult the list of special positions listed for that space group type.

Just as the intersection of certain symmetry elements in chemical space groups leads to sites of spatial inversion ($\bar{1}$), there will also be sites of space-time inversion ($\bar{1}'$) in certain magnetic space groups. These will occur in lattices wherever rotoinversion axes of odd order are primed (*i.e.* $\bar{3}$). They will also occur at the intersection of rotational axes of even order and mirror or glide planes perpendicular to them, but only when *one* of those symmetry elements is primed.

For example, at the intersection of $2'_z$ and m_{xy} :

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}' \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}' = \bar{1}'. \quad (3.4)$$

The result is that the symmetry at the site of intersection is not just spatial inversion ($\bar{1}$), but rather space-time inversion ($\bar{1}'$). If both $2'_z$ and m'_{xy} are primed:

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}' \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}' = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \bar{1}. \quad (3.5)$$

The result is *not* space-time inversion ($\bar{1}'$), but rather *only* spatial inversion ($\bar{1}$). Recall from §3.1, the magnetic space groups which describe an ordered magnetic system (*e.g.* ferromagnetic or antiferromagnetic) will have half of the symmetry elements of the paramagnetic model. Specifically, half of its symmetry elements will be primed, and the other half will not, according to Eq. 3.2. Each possible representation will have a different combination of primed and unprimed symmetry elements. Therefore, each will produce a different combination of spin orientations, as was demonstrated in §3.3.

Recall from §2.3 the point groups which permit the various ferroic orders can be determined by considering the subgroups of the limiting group for each type. Tab. 2.6 indicates the limiting groups proposed by Saxena for each type, including ferrotoroidic order.[77, 78] According to Saxena's work, the limiting group for ferromagnetic order is $\frac{\infty}{m} \frac{2'}{m'} \frac{2'}{m'}$, and for ferrotoroidic order is $\frac{\infty}{m'} \frac{2}{m} \frac{2}{m}$.

Recall from §3.2 that $\frac{\infty}{m}$ indicates there is a site of spatial inversion ($\bar{1}$) at the intersection between the rotation axis and mirror plane. In a similar way, $\frac{\infty}{m'}$ indicates the presence of

space-time inversion ($\bar{1}'$). Therefore, ferrotoroidic order is associated with possessing sites of space-time inversion ($\bar{1}'$) symmetry. This is logically consistent scheme for classifying toroidal moments and the axio-polar vectors which model them, since they are both invariant under space-time inversion ($\bar{1}'$).

In contrast, the necessary ordering for ferromagnetic order includes $\frac{2'}{m}$. Recall from §3.3 that the intersection between a primed 2-fold axis ($2'$) and a perpendicular primed mirror plane (m') is a site of spatial inversion ($\bar{1}$). This is because the product of time inversion and space-time inversion is spatial inversion ($1' \bar{1}' = \bar{1}$). Therefore ferromagnetic ordering is associated with invariance under spatial inversion ($\bar{1}$).

Before continuing, it is worth noting that Saxena proposed the limiting group for ferroelectric order is $\frac{\infty}{m'} \frac{2'}{m} \frac{2'}{m}$. [77, 78] It is not intuitive to consider ferroelectric order—characterized by the loss of spatial inversion—with time inversion symmetry. Ferroelectric materials do not need to possess any magnetically-active ions, and therefore magnetic moments. Likewise, ferroelastic materials do not fit well into any classification scheme for magnetic point groups. It is perhaps more useful to consider limiting groups for magnetic point groups in terms of types of magnetic ordering—paramagnetic, ferromagnetic, antiferromagnetic, ferrotoroidic, antiferrotoroidic, etc. There is another reason for the logical incoherence as well: Recall from Fig.3.3 in §3.3 that the assignment of ferromagnetic and antiferromagnetic arrangements is dependent upon the orientation of the magnetic moments relative to the symmetry elements. If the limiting group analysis were considered again, but using point groups which specified the directions of the symmetry elements in the point group, as Litvin did when computing toroidal tensors in Ref. 67, a more unified and consistent classification scheme could be achieved. However, I am leaving that work to qualified theoretical physicists and mathematicians to pursue.

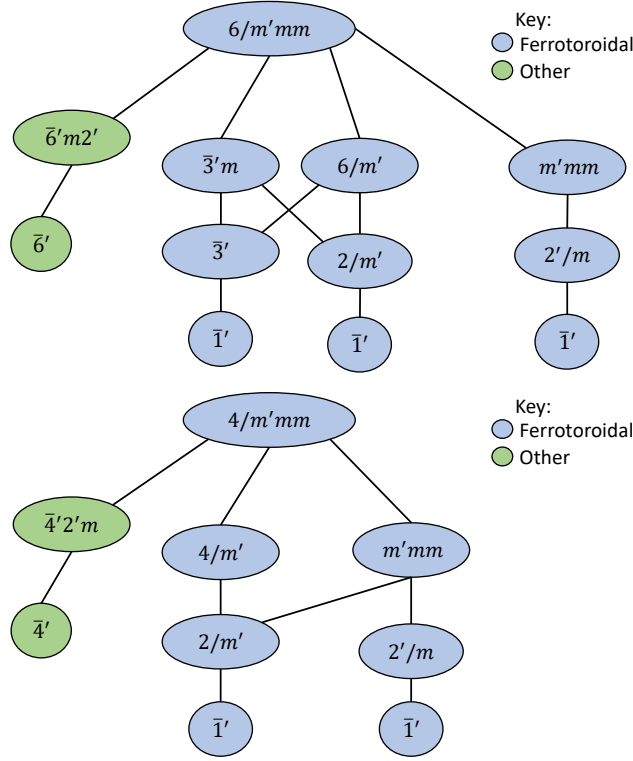


Figure 3.5: Group-subgroup trees where the maximal supergroups are $6/m'mm$ and $4/m'mm$

It is not possible to consider point groups with infinite rotational axes, since the maximum axes order in crystallography is 4 and 6. In addition, point groups are written in shorthand. For example, $6/mmm$ is shorthand for $\frac{6}{m} \frac{2}{m} \frac{2}{m}$. Therefore, if we were to consider the maximal subgroups of $\frac{\infty}{m'} \frac{2}{m} \frac{2}{m}$ to be $4/m'mm$ and $6/m'mm$, we would also need to consider the maximal subgroup $\frac{\infty}{m'} \frac{2'}{m} \frac{2'}{m}$ since the full symbols for those two point groups are actually $\frac{4}{m'} \frac{2'}{m} \frac{2'}{m}$ and $\frac{6}{m'} \frac{2'}{m} \frac{2'}{m}$. This is because the magnetic point groups $\frac{4}{m'} \frac{2}{m} \frac{2}{m}$ or $\frac{4}{m'} \frac{2}{m} \frac{2}{m}$ do not exist.

Fig. 3.5 presents the group-subgroup trees for $4/m'mm$ and $6/m'mm$. Notice, all the blue-colored point groups are the same ten point groups from Tab. 2.4 which Schmid determined would permit both a spontaneous toroidal moment, and a linear magneto-electric effect. The minimal (*e.g.* lowest-symmetry) point group for all of them is $\bar{1}'$. This is crucial from a crystal-chemistry perspective, because it means that those symmetry elements both *must* and *will* always

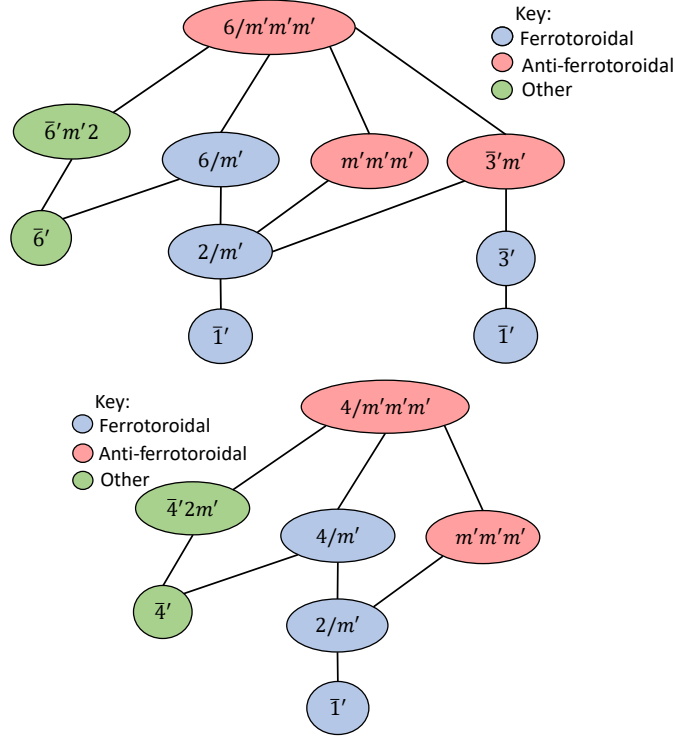


Figure 3.6: Group-Subgroup trees where the maximal supergroups are $6/m'm'm'$ and $4/m'm'm'$ be present, even with other symmetry elements present within the crystal. The green-colored subgroups are labeled “other.” Recall from §3.4 that rotoinversion axes of odd order ($\bar{1}$ and $\bar{3}$) result in centers of inversion in a lattice. Rotoinversion axes of even order ($\bar{2} = m$, $\bar{4}$, and $\bar{6}$) do not. Notice that in the group-subgroup tree, $\bar{1}'$ is *not* the minimal point group symmetry for these “other” groups. Rather, the minimal symmetry is $\bar{4}'$ and $\bar{6}'$, which are both non-centrosymmetric and therefore not compatible with a ring of spins.

The groups $6/m'mm$ and $4/m'mm$ are not the only point groups with $\bar{1}'$ as a minimal subgroup. Consider now the group-subgroup trees for $\frac{6}{m'} \frac{2}{m'} \frac{2}{m'}$ and $\frac{4}{m'} \frac{2}{m'} \frac{2}{m'}$, presented in Fig. 3.6. They also include point groups whose lowest point group symmetry is $\bar{1}'$. The six blue-colored point groups appeared in the trees from Fig. 3.5. However, the point groups colored pink are a different category. They all have the defining symmetry elements of an even-numbered rotation

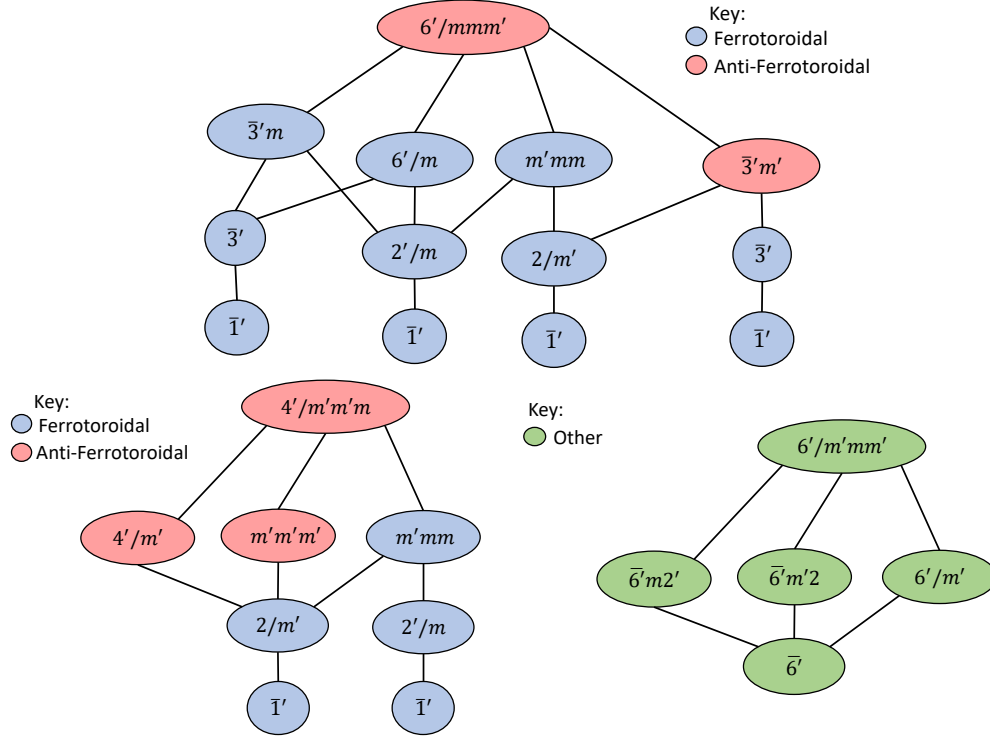


Figure 3.7: Group-Subgroup trees where the maximal supergroups are $6'/mmm'$, $4'/m'm'm$, and $6'/m'mm'$

axis perpendicular to a primed mirror plane (e.g. $\frac{2}{m'}$, $\frac{4}{m'}$, $\frac{6}{m'}$), where there will always be a site of $\bar{1}'$ at the intersection between the rotation axis and mirror plane. However, the additional symmetry elements cause the formation of multiple rings of spins which are themselves anti-aligned with one another. Therefore the final arrangement would be antiferrotoroidal. An example of this will be demonstrated in §4.1 by comparing configurations with the point groups mmm' (ferrotoroidal) and $m'm'm'$ (antiferrotoroidal). It is important to be aware this can only be observed in three-dimensional space and not in a one-dimensional system around a single point. This is because the orientation of the magnetic spins relative to the orientations of the symmetry elements is also imperative, as demonstrated in §3.3. Fig. 3.7 includes the remaining anti-ferrotoroidal group-subgroup trees.

The final group-subgroup tree presented in Fig. 3.7 is distinctive because it contains only

Table 3.3: Classifications of the Point Groups Labeled “Other” in Tab. 3.4

Point Group	Permitted Ref. 60		Permitted Ref. 67
	EH^a	T^b	T
$\bar{6}'$	$\bigcirc^c$	$\bigcirc$	$\bigcirc$
$\bar{4}'$	$\bigcirc$	$\bigcirc$	$\bigcirc$
$6'/m'mm'$	$\otimes^d$	$\otimes$	$\otimes$
$6'/m'$	$\otimes$	$\otimes$	$\otimes$
$\bar{6}'m2'$	$\bigcirc$	$\bigcirc$	$\bigcirc$
$\bar{6}'m'2$	$\bigcirc$	$\otimes$	$\otimes$
$\bar{4}'2'm$	$\bigcirc$	$\bigcirc$	$\bigcirc$

^aEH = linear magnetoelectric effect

^bT = net toroidal moment (net toroidization)

^c $\bigcirc$ = “is permitted” ^d $\otimes$ = “is not permitted”

green-colored (non-toroidal) point groups. This tree was included for the sake of completeness because it contained $\bar{6}'$ as a minimal subgroup, and the maximal supergroup $6'/m'mm'$ contained similar symmetry elements to others included in this work. However, as indicated in Tab. 3.3, the point groups $6'/m'mm'$, $6'/m'$, and $\bar{6}'m'2$ all do not permit a net ordering of toroidal moments, according to both Schmid’s and Litvin’s analyses.[60, 67] There is no analogous group-subgroup tree for $\bar{4}'$. Previously I mentioned the point groups $\bar{4}'$ and $\bar{6}'$ are non-centrosymmetric but $\bar{4}'2'm$, $\bar{6}'m'2$, and $\bar{6}'m2'$ are all non-centrosymmetric as well. They not only do not have $\bar{1}$ as a minimal subgroup, but not even $\bar{1}$. The point groups $\bar{6}'/m'mm'$ and $6'/m'$ are centrosymmetric, because they have $\bar{1}$ as minimal symmetry. But that is not the necessary symmetry for a ring of spins (§3.2). Therefore, those point groups are incompatible with ferrotoroidicity as defined and studied in three-dimensional solid state materials.

Table 3.3 compares the categorization of the seven “other” point groups to the classifications given by Schmid in 2008,[60] and Litvin in that same year.[67] Both references agree that $6'/m'$, $6'/m'mm'$, and $\bar{6}'m'2$ cannot permit a net toroidal moment. Note that $\bar{6}'m'2$ allows the linear

Table 3.4: Ferrotoroidal and Anti-ferrotoroidal Point Groups.

Point Group Category	Permitted Point Groups	
Ferrotoroidal	$\bar{1}'$	mmm'
	$2'/m$	$2/m'$
	$4/m'$	$4/m'mm$
	$6/m'$	$6/m'mm$
	$\bar{3}'$	$\bar{3}'m$
Antiferrotoroidal	$m'm'm'$	$4'/m'$
	$4'/m'm'm$	$4'/m'm'm'$
	$6'/mmm'$	$6'/m'm'm'$
		$\bar{3}'m'$
Other (Non-toroidal) ^a	$\bar{6}'$	$\bar{4}'$
	$6'/m'mm'$	$6'/m'$
	$\bar{6}'m2'$	$\bar{6}'m'2$
		$\bar{4}'2'm$

^aSee Tab. 3.3 for designations of the point groups in this category.

magnetoelectric effect, meaning that it is a necessary but insufficient condition for ferrotoroidicity. Indeed, the effect in and of itself is not a measurement of ferrotoroidicity. Coincidentally both phenomena have similar symmetry restrictions.

Tab. 3.4 is a summary of the point groups included in the three categories presented in this section for ease of reference.

Before concluding this section, I also wanted to mention the predicted direction for a net toroidal moment, given the magnetic point symmetry of the crystal. I had not found this explicitly stated in any reference, and so I compiled Tab. 3.5. The monograph *Symmetry and Magnetism* by Birss was particularly helpful for understanding the directions for the magnetoelectric tensor components.[151] The toroidal moment directions were mentioned by Kornev in Tab. 1 in Ref. 32, which was included as Tab. 2.2 in §2.1. The Bilbao Crystallographic Server has a program called MTENSOR currently under development, which computes a great number

Table 3.5: Symmetry parameters of the toroidal moment in centrosymmetric subgroups of $mmm1'$

P.G. ^a	Tensor ^b	T.M. Dir. ^c
$m'm'm'$	$\begin{bmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{bmatrix}$	n/a^d
$m'mm$	$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha_{yz} \\ 0 & \alpha_{zy} & 0 \end{bmatrix}$	$\mathbf{T}_x$
$mm'm$	$\begin{bmatrix} 0 & 0 & \alpha_{xz} \\ 0 & 0 & 0 \\ \alpha_{zx} & 0 & 0 \end{bmatrix}$	$\mathbf{T}_y$
mmm'	$\begin{bmatrix} 0 & \alpha_{xy} & 0 \\ \alpha_{yx} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$	$\mathbf{T}_z$

^aShubnikov point group

^bMagneto-electric tensor

^cToroidal moment direction

^dNot applicable (symmetry forbidden)

of different physical property tensors based upon a selected magnetic point group.[75] However, it only chooses the point group in the default setting. For example, it only computes the physical property tensor for $m'mm$, not $mm'm$ or mmm' .

The interpretation of the Tab. 3.5 is as follows: if the magnetoelectric effect is allowed in the off-diagonal components along a given plane (*e.g.* the xy plane), then the toroidal moment would be along the axis perpendicular to that plane (*e.g.* along the z axis). Note, however, this table only includes the point groups associated with $Pnma1'$, or $mmm1'$ because those are associated with LiCoPO_4 and analogous olivine materials. Indeed, Ref. 32 was a paper studying the linear magnetic effect in LiCoPO_4 . This table will be referred to again in §4.1 when discussing toroidal moments in materials with the olivine structure type.

Table 3.6: Symmetry parameters of the toroidal moment in centrosymmetric subgroups of $2/m1'$

P.G. ^a	Tensor ^b	T.M. Dir. ^c
$2_x/m'_x$	$\begin{bmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & \alpha_{yz} \\ 0 & \alpha_{zy} & \alpha_{zz} \end{bmatrix}$	$\mathbf{T}_x$
$2'_x/m_x$	$\begin{bmatrix} 0 & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & 0 & 0 \\ \alpha_{zx} & 0 & 0 \end{bmatrix}$	$\mathbf{T}_{yz}$
$2_y/m'_y$	$\begin{bmatrix} \alpha_{xx} & 0 & \alpha_{xz} \\ 0 & \alpha_{yy} & 0 \\ \alpha_{zx} & 0 & \alpha_{zz} \end{bmatrix}$	$\mathbf{T}_y$
$2'_y/m_y$	$\begin{bmatrix} 0 & \alpha_{xy} & 0 \\ \alpha_{yx} & 0 & \alpha_{yz} \\ 0 & \alpha_{zy} & 0 \end{bmatrix}$	$\mathbf{T}_{xz}$
$2_z/m'_z$	$\begin{bmatrix} \alpha_{xx} & \alpha_{xy} & 0 \\ \alpha_{yx} & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{bmatrix}$	$\mathbf{T}_z$
$2'_z/m_z$	$\begin{bmatrix} 0 & 0 & \alpha_{xz} \\ 0 & 0 & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & 0 \end{bmatrix}$	$\mathbf{T}_{xy}$

^a Shubnikov point group

^b Magneto-electric tensor

^c Toroidal moment direction

Tab. 3.6 is the same analysis as Tab. 3.5, but for the subgroups of $2/m1'$. This is the symmetry for materials with the pyroxene structure type, which will be examined in detail in §4.9. For now, note that the toroidal moment would be predicted to occur perpendicular to the off-diagonal terms. For example, in the case of $2'_y/m_y$, this would allow a net toroidal component along the x and z plane. The expectation would be that the magnitude of the off-diagonal magneto-electric components would be proportional to the angle of the toroidal moment. For

example, if $\alpha_{xy} \gg \alpha_{zy}$, then the expectation would be that the component $\mathbf{T}_z \gg \mathbf{T}_x$.

Note that it is imperative to know along which direction the two-fold rotation axis is oriented for a particular structure, as the predicted toroidal moment directions depends upon it. For example, the program MTENSOR on the Bilbao Crystallographic Server uses the $2_y/m'_y$ and $2'_y/m_y$ forms of the point groups.[75] Litvin used $2_z/m'_z$ and $2'_z/m_z$ in Ref. [67], as included in Tab. 2.5 of §2.3. I determined the forms for $2_x/m'_x$ and $2'_x/m_x$ through process of elimination and pattern recognition based upon the others.

3.5: Determining a Magnetic Subgroup

Before moving the discussion from point symmetry to space group symmetry, there are a few technical details to explain. In order to identify new candidates for ferrotoroidicity, it is vital to be able to identify the magnetic point group of the magnetic space group. What complicates this is there are several methods for determining magnetic structures, which I mentioned in §3.1. Irreducible representations and magnetic space groups are the two most commonly used. They are in agreement when the determined structure is described by one representation, since every representation is assigned to a magnetic space group. However, often the magnetic structure is more complicated. The structure may be described by more than one representation, or there may be a reduction in symmetry which the authors who reported the structure failed to express using the conventions of either methodology.

In this section, I will describe the methodology I used to address a situation which my colleague Timothy Diethrich brought to me. He had performed neutron powder diffraction for $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ ($x = 0.2, 0.3, 0.5$) and $\text{Li}_{1-x}\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$ ($x = 0.2, 0.3, 0.4, 0.5, 0.6$). He was

uncertain how to determine the magnetic space group for his delithiated materials, since he needed two representations to best model his neutron powder diffraction pattern data. He also did not know how to determine the magnetic point group from it, nor how to determine if it was a ferrotoroidal candidate. My contribution to his work was ultimately published in Ref. 164.

The first step is to determine all the irreducible representations for the parent paramagnetic group, in this case $Pnma1'$. Each representation is associated with a particular Magnetic Space Group. There are two user-friendly resources for obtaining this information.

The first is SARA_h web Representational Analysis software created by Andrew Wills, available from his research group web page at <http://fermat.chem.ucl.ac.uk/spaces/willsgroup/> last updated June 2018 at the time of writing.[165] The benefit of the web-based version is it is less prone to software bugs from computer operating system upgrades.¹ SARA_h has several especially useful features. One is that all of the mathematics are presented for the computation. Another is that the basis vector tables are outputted in LaTeX format, which can be easily copy and pasted into supplemental material when drafting a publication. There is also a downloadable program called SARA_h Refine which integrates with the Refinement Software FullProf (and GSAS - now obsolete) to assist in testing the possible magnetic models with one's neutron diffraction refinement.[166]

Alternatively, one can use the program k-SUBGROUPSMAG from the Bilbao Crystallographic Server, available at the web page <https://www.cryst.ehu.es/>.[161, 167] There are a team of researchers in the Materials Laboratory at the University of Basque County, Spain who maintain and develop all the programs on the Bilbao Crystallographic Server. There are also additional features available

¹It does, however, currently operate off of Professor Will's MacBook Pro in his office. Therefore, if it happens to not be working at the moment, try again in a few hours or the next day. He does not have the funding for a private server. He explained this to the participants at a workshop/summer school I attended.

Table 3.7: Magnetic symmetry associated with the eight irreducible representations of the parent paramagnetic space group $Pnma1'$. Reproduced with minor labeling edits from Tab. 3 in Ref. [175]. It is similar to Tab. 1 in Ref. [164].

I.R. ^a	M.S.G. ^b	M.P.G. ^c	B.V. ^d	M.O. ^e
Γ_1^+	$Pnma$	mmm	G_y	AFM
Γ_2^+	$Pn'm'a$	$m'm'm$	$G_x + F_z$	FM
Γ_3^+	$Pnm'a'$	$mm'm'$	$F_x + G_z$	FM
Γ_4^+	$Pn'ma'$	$m'mm'$	F_y	FM
Γ_1^-	$Pn'm'a'$	$m'm'm'$	$A_x + C_z$	AFM
Γ_2^-	$Pnma'$	mmm'	A_y	AFM
Γ_3^-	$Pn'ma$	$m'mm$	C_y	AFM
Γ_4^-	$Pnm'a$	$mm'm$	$C_x + A_z$	AFM

^aIrreducible Representation, superscript (+) indicates gerade, superscript (-) indicates ungerade with respect to spatial inversion symmetry ($\bar{1}$); ^bMagnetic Space Group; ^cMagnetic Point Group; ^dBasis Vectors of the spin modes, which are defined as ($F = \uparrow\uparrow\uparrow\uparrow$), ($G = \uparrow\downarrow\uparrow\downarrow$), ($C = \uparrow\uparrow\downarrow\downarrow$), and ($A = \uparrow\downarrow\downarrow\uparrow$) for the four magnetic atoms. The subscripts x , y , and z define along which crystallographic direction the moments are parallel. ^eMagnetic Order; AFM = antiferromagnetic, FM = ferromagnetic

for selecting only certain subgroups, like those compatible with certain kinds of phase transitions or physical properties. This is particularly helpful when working with a parent space group which gives dozens of possible magnetic subgroups. The software is also actively being integrated into the Refinement Software GSAS-II.[168]

As a note: The popular refinement software JANA has the Magnetic Space group tables integrated into its software package as well.[169, 170] I have limited experience with the software, having only done a few tutorials with it and so will not mention more here. Likewise the refinement software TOPAS-Academic has the capability of performing magnetic refinement using manually scripted macros in “launch mode” and the software ISODISTORT.[171, 172] The software ISODISTORT performs similar calculations to SARAh and k-SUBGROUPSMAG but is not as user-friendly.[173, 174]

Regardless of which software package is chosen, the process is the same. Indicate the

parent paramagnetic group, the propagation vector, and the location of the coordinate positions of the magnetic atoms. The positions are important because if they are located on a special position it can restrict the results. In this example, the iron or manganese ion is located on the $4c$ site. The propagation vector coincides with the unit cell, and so $k = 0,0,0$. A summary of the results are given in Tab. 3.7. Note that different programs will give different indices for each Γ representation. For example, SARA_h will report $\Gamma_1, \Gamma_2, \dots, \Gamma_8$, but they may be in a different order than another program. I adopted the gerade/ungerade superscripts used by Kornev in Ref. 32, which was included as Tab. 2.2 in §2.1. It is helpful to know at a glance which subgroups contain $\bar{1}$ as an element (gerade), and which contain $\bar{1}'$ (ungerade). Note, my indices do not match the ones from Ref. 164. Throughout the rest of this section refer to Tab. 3.7 for the labeling scheme. Be advised, the vector spin mode labels F , G , C , and A are defined based upon the order that the first, second, third, and fourth atomic coordinates are listed. This labeling scheme was used by E. F. Bertaut, and presented in his seminal article on Representational Analysis of Magnetic Structures published in 1968.[176] Therefore I use it here, since it succinctly describes the spin pattern in a system with four magnetic atoms and is therefore relevant to olivine and pyroxene. However, different software programs may list the four coordinates in different orders, and G , C , and A may differ in different research articles. Diethrich defined the sites in this order: M1 $[x, y, z]$, M2 $[(-x + 1/2), (-y + 1), (z - 1/2)]$, M3 $[(-x + 1), (y + 1/2)]$, and M4 $[(x + 1/2), (-y + 1/2), (-z + 3/2)]$.

After determining all the possible magnetic models, each of these models are tested in whichever refinement software is being used to analyze the neutron diffraction data. Diethrich used FullProf and SARA_h Refine.[164] The $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ ($x = 0.2, 0.3, 0.5$) all had the same magnetic structure as LiFePO_4 , $Pnma'$, with the basis vector A_y corresponding to Γ_2^- . Therefore

that analysis was trivial because its point group is mmm' , which permits ferrotoroidicity. The $\text{Li}_{1-x}\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$ ($x = 0.2, 0.3, 0.4, 0.5, 0.6$) series, however, was more complex. Fitting with Γ_2^- alone did not produce a satisfactory fit for the refinement model. For the first two compositions ($\text{Li}_{1-x}\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$ ($x = 0.2, 0.3$)), Diethrich obtained the best fit after adding a small contribution from basis vector A_z from Γ_4^- . The remaining compositions ($\text{Li}_{1-x}\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$ ($x = 0.4, 0.5, 0.6$)) showed no evidence of the A_y mode from Γ_2^- . Instead, the best fit was obtained by combining the A_x mode from Γ_1^- and the G_y mode from Γ_1^+ .

While combining Basis Vector modes from different representations is a perfectly legitimate way of describing a magnetic structure, unfortunately one cannot rightly call the results $\Gamma_1^- + \Gamma_1^+$ or $Pn'm'a' + Pnma$, for example. This would imply there are a total of 16 symmetry elements, eight from each. The correct descriptor would be a subgroup of the two groups, and contain the symmetry elements which are shared by each.

To perform this analysis, I created Fig. 3.8. There were four irreducible representations used in Diethrich's analysis: Γ_1^+ , Γ_1^- , Γ_2^- , and Γ_4^- . I then looked up the point symmetry elements in each corresponding magnetic space group. For brevity, I assigned each a numeral, with the key located in the bottom left corner of the figure (*e.g.* 3 corresponds to 2_y). If that element is primed, the numeral is primed (*e.g.* 3' corresponds to $2'_y$). Next, I determined the four symmetry elements in common for each representation. To determine which magnetic point group they corresponded to, I first consulted §2.3 of the International Tables of Crystallography Vol. A1.[177] Under the table for $Pnma$, there are seven possible *translationengleiche* subgroups listed, with their corresponding symmetry elements and any basis transformation or origin shift if applicable. My assumption is the same process would be pertinent for magnetic space groups as well, but also including the primed symmetry elements.

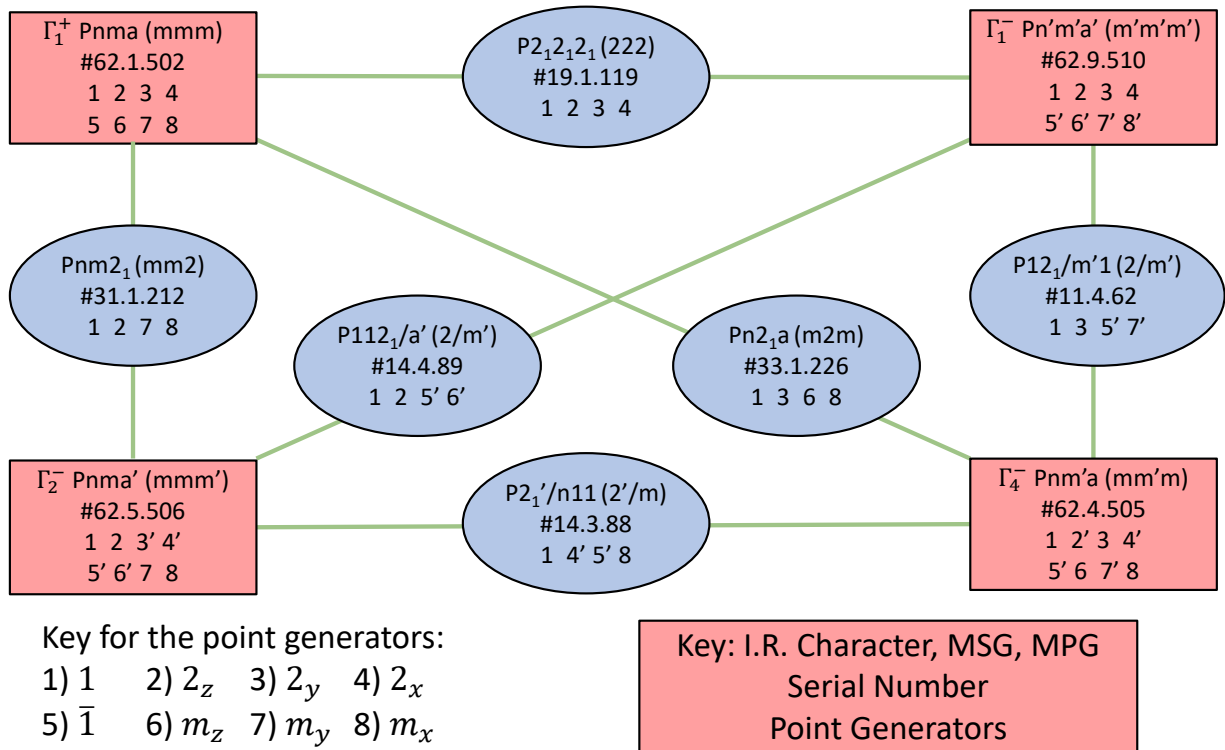


Figure 3.8: Subgroup Diagram for $Pnma$, $Pn'm'a'$, $Pnma'$, and $Pnm'a$. Reproduced with labeling edits from Fig. S19 from Ref. 164.

Tab. 3.8 is a Character table of how the sixteen primed and unprimed symmetry elements of the parent paramagnetic group $Pnma1'$ split into the eight irreducible representations. The symbol “1” indicates the element is present in the given representation, while the symbol “–1” indicates it is absent. Notice how none of the representations contain the element $1'$, since this symmetry element cannot exist on its own. Also note, the Γ_1^+ representation contains only non-primed elements. The other seven representations have four primed and four non-primed elements. In addition, if the representation has a certain type of primed element, (e.g. $2'_z$), then the “sister” non-primed element (e.g. 2_z) will not be included in the representation.

Referring back to Fig. 3.8, the four elements shared by Γ_1^- and Γ_1^+ are 1, 2, 3, and 4 (1 , 2_z , m_y , and m_x respectively). These correspond to $P2_12_12_1$ with an origin shift of 0,0,1/4. However,

Table 3.8: Character table for the irreducible representations of $Pnma1'$ from k-SUBGROUPSMAG on the Bilbao Crystallographic Server

Γ	1	2_z	2_y	2_x	$\bar{1}$	m_z	m_y	m_x	$1'$	$2'_z$	$2'_y$	$2'_x$	$\bar{1}'$	m'_z	m'_y	m'_x
Γ_1^+	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1
Γ_2^+	1	1	-1	-1	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1
Γ_3^+	1	-1	-1	1	1	-1	-1	1	-1	1	1	-1	-1	1	1	-1
Γ_4^+	1	-1	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1
Γ_1^-	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1
Γ_2^-	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1	1	1	-1	-1
Γ_3^-	1	-1	-1	1	-1	1	1	-1	-1	1	1	-1	1	-1	-1	1
Γ_4^-	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1	1	-1	1	-1

since it is imperative that the magnetic and structural unit cells are the same, the origin is *not* shifted in this circumstance. I then consulted the Three-Dimensional Magnetic Space Group Tables,[178] and determined the numbered index and magnetic point group. The point group is 222 and so it is non-ferrotoroidal.

The four elements shared by Γ_2^- and Γ_4^- are 1, 4', 5', and 8 (1 , $2'_z$, $\bar{1}'$, and m_x respectively). These correspond to $P2'_1/n11$ with a basis transformation of $(-\mathbf{b}, \mathbf{a}, \mathbf{b} + \mathbf{c})$. However, for the magnetic and structural unit cells to be the same, the basis is *not* transformed in this case. The magnetic point group is $(2/m')$ and is ferrotoroidal. Note, it has $\bar{1}'$ as a symmetry element.

Table 3.9 is a summary of the results for all eight materials Diethrich studied.

It was sufficient for Diethrich to simply identify if the materials had the necessary symmetry to be a ferrotoroidal candidate, based upon the point symmetry. However, in order to move ferrotoroidal theory beyond the confines of point symmetry, it is necessary to next carefully consider how the symmetric motif of a ring of spins can exist in a three-dimensional lattice.

Table 3.9: Magnetic symmetry for various $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ and $\text{Li}_{1-x}\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$ compositions determined by Diethrich *et al.* Ref. [164] Reproduced from Tab. 2 in Ref. [164].

Composition		B.V. ^a	MSG ^b	MPG ^c	FTO ^d
$\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$	$x = 0.2$	A_y	$Pnma'$	$m'mm$	yes
	$x = 0.3$	A_y	$Pnma'$	$m'mm$	yes
	$x = 0.4$	A_y	$Pnma'$	$m'mm$	yes
$\text{Li}_{1-x}\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$	$x = 0.2$	$A_y + A_z$	$P2'_1/n11$	$2'/m$	yes
	$x = 0.3$	$A_y + A_z$	$P2'_1/n11$	$2'/m$	yes
	$x = 0.4$	$A_x + G_y$	$P2_12_12_1$	222	no
	$x = 0.5$	$A_x + G_y$	$P2_12_12_1$	222	no
	$x = 0.6$	$A_x + G_y$	$P2_12_12_1$	222	no

^aBasis Vector Components of the spin modes, defined as ($G = \uparrow\downarrow\uparrow\downarrow$) and ($A = \uparrow\downarrow\downarrow\uparrow$) for the four magnetic atoms. The subscripts x , y , and z define along which crystallographic direction the moments are parallel. ^bMagnetic Space Group; ^cMagnetic Point Group; ^dPermits Ferrotoroidal Order (yes or no)

3.6: Ferrotoroidal Lattice

To summarize what has been discussed thus far:

- §3.2 explained how anti-aligned spins would by definition have a site of space-time inversion ($\bar{1}'$) between them. The alignment of the spins would be defined by the origin and basis of the lattice.
- §3.3 described the behavior of axial vectors, polar vectors, and axio-polar vectors under inversion symmetries. The orientation of the spins in relation to the orientation of the symmetry elements ultimately defined whether a configuration was considered ferromagnetic or antiferromagnetic. Toroidal moments can co-exist in a magnetic lattice in an antiferromagnetic arrangement on the sites of $\bar{1}'$, where magnetic moments are forbidden.
- §3.4 explained that inversion sites occur in a lattice at the intersection between rotation or screw axes of even order, and perpendicular mirror or glide planes.

This section (§3.6) brings all these concepts together to discuss how to construct a toroidal

lattice, answering the crucial questions of where the toroidal moments will occur, how many will be present, and how to determine their orientation and arrangement.

In §3.2 I explained the origins of the rings of spins would be sites of $\bar{1}'$, but did not indicate where or how many of these sites would occur in a magnetic lattice. I will continue that discussion here. Let us begin by first considering how axial vectors behave in a lattice under various inversion symmetries. Consider a one-dimensional unit cell. Entities within the unit cell can be oriented along three-dimensions, but for the sake of simplicity there are only lattice translations along one direction. In addition, since this work is presented on two-dimensional paper, the magnetic moments will be drawn in the xy plane, even though the analysis is valid when they are oriented in all three dimensions.

We begin with Fig. 3.9a. It depicts a periodic arrangement of an axial vector x . The rectangle defines the unit cell, with the origin depicted as a black dot. Since the symmetry at the origin is only the identity operation (1), the only remaining symmetry in the system to describe how to map from the vector x in the unit cell to the identical one in the next is a lattice translation $+t$ along the x -axis. Formally, we would say the mapping $\{1|t\}$ maps x onto x in the adjacent unit cell. This notation is called Seitz notation. It is a shorthand method which indicates the rotational component of the operation on the left (in this case 1), and the translational component on the right (in this case the lattice translation t).

Now consider Fig. 3.9b. Now the origin is a site of spatial inversion ($\bar{1}$) symmetry. Therefore instead of only one axial vector per unit cell, there must now be two vectors. An inversion center is always defined to be halfway in-between the two (or more) entities related by inversion. Following that same logic the converse must also be true: if an inversion point exists, there must be two (or more) entities related by inversion around that site. As discussed in §3.3,

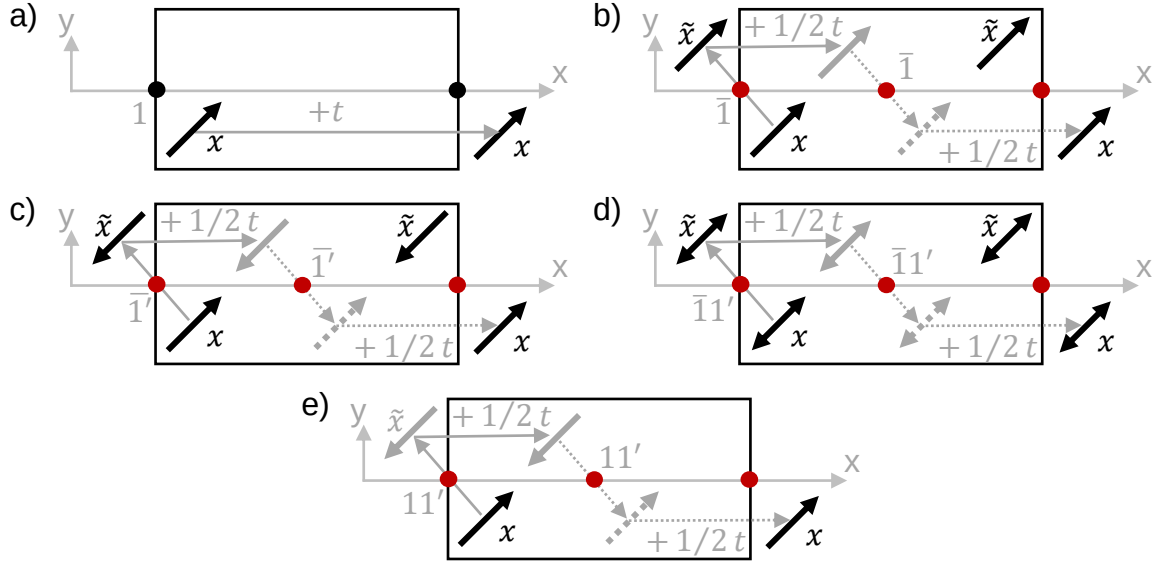


Figure 3.9: Depictions of five one-dimensional unit cells with different origin symmetries. a) A periodic arrangement of an axial vector x . The pattern is positioned within a one-dimensional box with dimensions t . b) A depiction of the operation $\{\bar{I}|1/2t\}$ on x , resulting in $\tilde{x}$. The red circles indicate the sites of spatial inversion ($\bar{I}$). The entity must be inverted and translated by half a unit cell two times in order to end at the original position in the adjacent unit cell. This requires there to be a second site of inversion at $1/2t$. c) A similar arrangement to Fig. 3.9a, but the origin is now a site of $\bar{I}'$ symmetry. d) In this diagram the symmetry at the origin is $\bar{I}1'$ and the vectors are depicted as double-headed arrows to describe their invariance under $\bar{I}1'$. e) Diagram with the origin symmetry $11'$. Only one vector per unit cell is depicted in black since there is no spatial inversion present.

an axial vector will not reverse direction under spatial inversion ($\bar{I}$). Therefore, both spins are pointed in the same direction. Formally, $\{\bar{I}|0\}$ maps x onto $\tilde{x}$.

Fig. 3.9c-e are the same analysis as Fig. 3.9b, but with the mappings for $\{\bar{I}'|0\}$, $\{\bar{I}1'|0\}$, and $\{11'|0\}$, respectively. Note that if this analysis were performed with axio-polar vectors, Fig. 3.9a & 3.9d would be the same, but the results of Fig. 3.9b & 3.9c would be switched. The axio-polar vectors would have anti-aligned moments around a $\bar{I}$ site, but parallel moments around a $\bar{I}'$ site, since the behavior of axio-polar vectors under $\bar{I}$ and $\bar{I}'$ is the opposite of axial vectors.

Notice how in Fig. 3.9b-e there are actually two inversion sites per unit cell: one at the origin and the other in the middle of the unit cell, at $+1/2t$. That is because this second inversion

site must also exist. There must always be a way of using the mappings of the symmetry elements of the system to take any chosen position, such as x and generate the other equivalent positions. It is not valid to simply take every position and simply apply $\{1|t\}$. That would be treating the symmetry as if the space group was $P1$. While this is technically functional, it does not utilize the symmetry of the system. Instead, we want to determine how to map x onto x in the adjacent unit cell, using the mappings of the symmetry elements of the system.

Consider the example in Fig. 3.9b, and the operation $\{\mathbf{M}|\mathbf{m}\} = \{\bar{1}|1/2t\}$. The mapping of x by $\{\mathbf{M}|\mathbf{m}\}$ is depicted with solid light grey arrows. Now the vector has been inverted and translated half a unit cell. Then apply this operation again. This second mapping is indicated with dotted light grey arrows. The final position is the same as x but in the adjacent unit cell. Mathematically, $\{\mathbf{M}|\mathbf{m}\} \{\mathbf{M}|\mathbf{m}\} = \{\mathbf{MM}|\mathbf{Mm} + \mathbf{m}\}$. Therefore $\{\bar{1}|1/2t\} \{\bar{1}|1/2t\} = \{1|t\}$, which is the same location but translated over one unit cell. Therefore if you are at an inversion point, and translate over one unit cell in any basis direction, there will be a second site of inversion halfway in-between. For example, in a simple unit cell like $P\bar{1}$, there would be a total of $2^3 = 8$ inversion sites.

This simple reality has great significance when constructing a three-dimensional lattice with a desired point symmetry, with a structural motif with a desired point symmetry. If you have a simple symmetric motif, like a ring of spins, you cannot simply construct a lattice by taking that motif and translating it along three dimensions. You will be overlooking the other symmetry elements in the lattice imposed on the structure.

It was the theoreticians who first proposed using the center of the unit cell as the “origin” of the ring of spins. In §2.1 & §2.2 I discussed Ref. 29, 63, and 64. All use the “center of the unit cell” as an arbitrary starting point for the “ring of spins” motif, and assume in a periodic

structure like a crystal lattice, that motif would be repeated in the same manner in all three dimensions. However, when one attempts to apply that method to an actual crystal structure, it fails to unambiguously define the rings of spins.

Recall Fig. 2.7 from §2.2, reproduced from Ref. 58. The authors were attempting to construct a toroidal “ring of spins” for LiCoPO_4 . The origin of the ring was chosen as the “center of the unit cell.” Coincidentally, that location is an inversion center because the space group $Pnma$ for the structure of LiCoPO_4 is centrosymmetric. Yet there was no discussion in the article about the underlying inversion symmetry present. The authors also incorrectly identified the direction of the net toroidal moment.

Also recall Fig. 2.25 from §2.7 reproduced from Ref. 138. The authors re-examined LiCoPO_4 , but again failed to recognize the inversion symmetry present. They recognized that there were pairs of magnetic moments related by the same distance between one another, but failed to understand those geometric relationships were a constraint imposed by the symmetry of the structure. Furthermore, they did not identify the spins which were related by inversion to one another, and would have been equidistant from one another along all three dimensions, not just down the z axis.

The method was also inadequate for the pyroxene $\text{LiFeSi}_2\text{O}_6$ discussed in §2.6. Fig. 2.14 from Ref. 115 has the direction of the toroidal moment indicated as four individual toroidal moments located on the same sites as the magnetic moments. Fig. 2.17 from Ref. 116 makes no attempt to indicate a location for the toroidal moment, but rather indicates the general direction of the net toroidal moment.

It is clear, that to unambiguously define the “rings of spins” in a lattice, several criteria must be met:

- The magnetic point group must have a minimal subgroup of $\bar{1}'$, listed in Tab. 3.4.
- The toroidal moments are only allowed to exist on the sites of $\bar{1}'$ symmetry. These occur at the intersection of rotational axes of even order and mirror or glide planes perpendicular to them, when one and only one of those symmetry elements is primed. They also occur at primed rotoinversion axes of odd order (*i.e.* $\bar{3}$).
- The toroidal moments will be perpendicular to the magnetic moments, and the r vectors should be drawn from the center of inversion to the anti-aligned magnetic moments related by inversion around that site. The “rings” are therefore every pair of r vectors.

In §4.1 & §4.9 will present detailed examples with real crystal structures. But first, I will describe this method with our simple one-dimensional unit cell used in Fig. 3.9.

Consider Fig. 3.10a. This is the same magnetic structure as Fig. 3.9c, with the black magnetic moments anti-aligned and located at sites x and $\tilde{x}$. The minimal point symmetry of the lattice is $\bar{1}'$, so the point symmetry is suitable. The $\bar{1}'$ sites are already identified, as red circles. The first set of r and $\tilde{r}$ vectors are drawn in blue, centered about the $\bar{1}'$ site at $x = 0$. The second set of r vectors are centered about the site at $x = 1/2$. Since the magnetic moments are drawn in the xy plane, the toroidal moments will be perpendicular, oriented along the z axis. Fig. 3.10b & 3.10c depict the rings in blue, and the toroidal moments in green. In Fig. 3.10b, the toroidal moment pointing along $+z$ is marked $\odot$, and along $-z$ is marked $\otimes$. While the length of $r_2 < r_1$, the angle between r_1 and the magnetic moment at x is greater, and so the magnitude of the toroidal moment will be greater at site $x = 0$ than $x = 1/2$. Fig. 3.10c is the same as Fig. 3.10b, but oriented along the xz axis to emphasize the orientation of the toroidal moments. The black arrows are the magnetic moments in the xy plane. The blue lines are the rings of spins in the xy plane.

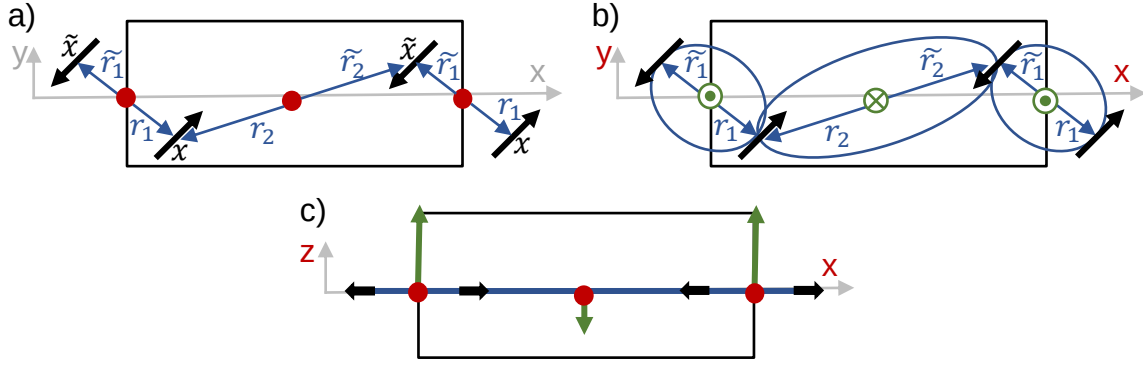


Figure 3.10: Toroidal lattice within a one-dimensional antiferromagnetic lattice. a) Two anti-aligned black magnetic moments at sites x and $\tilde{x}$, with the blue vectors r_1 and $\tilde{r}_1$ oriented from the red $\bar{1}'$ inversion site to the magnetic moments. b) The same magnetic lattice as in Fig. 3.10a, but with the ring of spins drawn as blue circles, and the green toroidal moments drawn as $\odot$ for the moment pointing in the $+z$ direction, and $\otimes$ for the $-z$ direction. The green toroidal moments are covering the red inversion sites. c) The same toroidal lattice as Fig. 3.10c, but oriented along the xz axis to emphasize the green toroidal moments and red inversion sites. The black arrows are in the black magnetic moments and blue toroidal rings in the xy plane.

The toroidal lattice in Fig. 3.10b & 3.10c demonstrate several features which will be discussed more in subsequent sections (§4.1 & §4.9). Each ring of spins will have a toroidal moment associated with it. All the toroidal moments will not necessarily be oriented in the same direction. The net toroidal moment would be the vector sum of all the individual magnetic moments.

While a useful first example, since Fig. 3.10 is a one-dimensional lattice, it is not possible to show how ferrotoroidal versus antiferrotoroidal structures could arise. Therefore, we proceed to the olivine and pyroxene structure examples in Chapter 4.

Chapter 4: Toroidal Structure in Antiferromagnetic Materials with Olivine and Pyroxene Structure Types

This chapter is entirely yet-unpublished work.

This chapter presents a method for modeling a ferrotoroidal lattice from a crystal lattice containing magnetically ordered ions. This methodology is applied to selected olivine (§4.1-§4.8) and pyroxene (§4.9-§4.12) magnetic structures to predict ferrotoroidal, antiferrotoroidal, and non-toroidal structures. The results are then compared and a general discussion of the utility of this method follows (§4.13).

4.1: Toroidal Structure in the Olivine Structure Type

The most intensely studied candidate ferrotoroidic material is LiCoPO_4 , which has the olivine structure type with the space group $Pnma$. Therefore the first example for constructing a toroidal lattice will be the olivine structure type. This section will begin with describing the structure type, and demonstrate a systematic method for defining the r vectors around the $\bar{1}'$ sites. This method will be applied to not only LiCoPO_4 , but also to analogous transition metal orthophosphates with diverse magnetic symmetries. The toroidal structures will then be compared and classified.

The first step is to examine the magnetic space group and associated point group. The

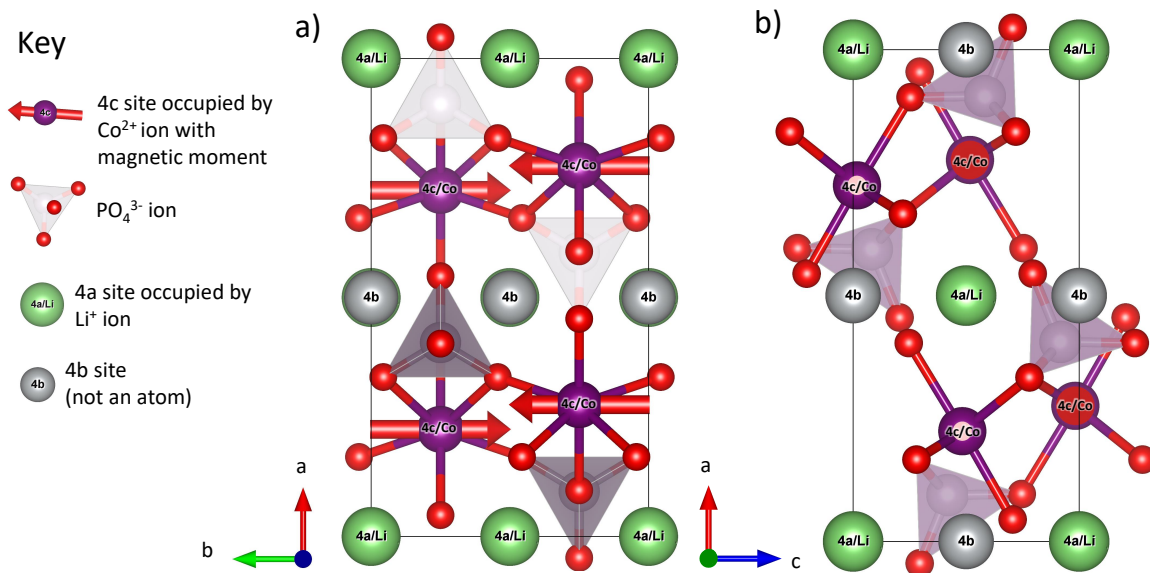


Figure 4.1: Magnetic Structure of LiCoPO_4 , viewed along the c axis (a) and the b axis (b).

magnetic structure for LiCoPO_4 was discussed in §2.1 and presented in Fig. 2.5. It is presented again in Fig. 4.1. As a reminder, the magnetic space group is $Pnma'$. We then consult Part 2 of the Magnetic Group Tables compiled by Litvin, which is available free of charge from the IUCr website.[178] To navigate quickly through this 11,976 page document, skip to page 2441 where the Three-Dimensional Magnetic Space Group Tables begin. Scroll down a few pages and select “62 $Pnma$.” The document is hyperlinked and so it will advance to page 2451 where all the serial numbers for all the possible magnetic space groups are listed for that specific crystallographic space group. Selecting “62.5.506 $Pnma'$ ” will advance to the pertinent table on page 3469.

The heading for $Pnma'$ indicates the short international symbol for the magnetic point group is mmm' , and the full international symbol for the magnetic space group is $P2_1'/n2_1'/m2_1/a'$. Note, the point group is one of the ten listed in Tab. 3.4 from §3.4 which permits a ferrotoroidal arrangement. A summary of the Wyckoff positions, their symmetries, and their coordinates are given in Tab. 4.1. We see there are eight coordinates with the symmetry $\bar{1}'$, at the $4a$ and $4b$ sites.

Table 4.1: Wyckoff letters in the crystallographic space group $Pnma'$, along with their multiplicities, site symmetries and coordinates. An index has been assigned to each coordinate for ease of communication.

Mult.	Wyck.	Sym.	Index	Coordinates
8	d	1	d1	x, y, z
			d2	$\bar{x} + \frac{1}{2}, \bar{y}, z + \frac{1}{2}$
			d3	$\bar{x}, y + \frac{1}{2}, \bar{z}$
			d4	$x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} + \frac{1}{2}$
			d5	$\bar{x}, \bar{y}, \bar{z}$
			d6	$x + \frac{1}{2}, y, \bar{z} + \frac{1}{2}$
			d7	$x, \bar{y} + \frac{1}{2}, z$
			d8	$\bar{x} + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$
4	c	m	c1	$x, \frac{1}{4}, z$
			c2	$x + \frac{1}{2}, \frac{1}{4}, \bar{z} + \frac{1}{2}$
			c3	$\bar{x}, \frac{3}{4}, \bar{z}$
			c4	$\bar{x} + \frac{1}{2}, \frac{3}{4}, z + \frac{1}{2}$
4	b	$\bar{1}'$	b1	$0, 0, \frac{1}{2}$
			b2	$\frac{1}{2}, \frac{1}{2}, 0$
			b3	$0, \frac{1}{2}, \frac{1}{2}$
			b4	$\frac{1}{2}, 0, 0$
4	a	$\bar{1}'$	a1	$0, 0, 0$
			a2	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
			a3	$0, \frac{1}{2}, 0$
			a4	$\frac{1}{2}, 0, \frac{1}{2}$

(The multiplicity indicates the number of coordinates for that given letter classification.) Note that in Tab. 4.1 each coordinate has been given an index which is the Wyckoff letter followed by a sequential numeral. These indices will be referred to throughout this section. They are not to be confused with the Wyckoff Positions, referred to by the multiplicity and Wyckoff letter. For example, $4c$ refers to all four of the c coordinates collectively, while $c4$ refers to one specific coordinate of the $4c$ site. In the structure of LiCoPO_4 , the $4a$ site is occupied by Li^+ ions, and the $4c$ site is occupied by Co^{2+} ions. Their positions are depicted in Fig. 4.1. The figure also

depicts the $4b$ site, indicated by grey circles. It is important to emphasize, $4b$ is *not* occupied by any atom in LiCoPO_4 . In fact, the $4b$ site is not occupied in *any* olivine materials discussed.

The next step in the process is constructing the sets of r vectors. To explicitly define all the individual vectors in a particular system, I will use the notation $\mathbf{r}_\alpha^\beta$. For each individual $\mathbf{r}$ vector, α is the index of the magnetic atom, and β is the index of the inversion site. Refer to Tab. 4.1 for the indices.

Since all materials with an olivine structure have an orthorhombic lattice, the crystallographic coordinates a , b , and c correspond to the Cartesian directions x , y , and z respectively. Note, care must be taken when considering a non-orthonormal crystal lattice, since the equations used for defining a toroidal moment are applicable in a Cartesian system. An example calculation is given below for defining $\mathbf{r}_{c1}^{b4}$ and $\mathbf{r}_{c3}^{b4}$:

$$\mathbf{r}_{c1}^{b4} = \begin{pmatrix} x \\ \frac{1}{4} \\ z-1 \end{pmatrix} - \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \\ 0 \end{pmatrix} = \begin{pmatrix} x - \frac{1}{2} \\ -\frac{1}{4} \\ z-1 \end{pmatrix} \quad (4.1)$$

Note how -1 was added to the z component of the $c1$ coordinate. This is because the $c1$ coordinate closest to the $b4$ coordinate is in the adjacent unit cell. Therefore to have the numerical value of the coordinate be within the range $0 - 1$, this adjustment must be made. A similar adjustment is made for the x component of the $c3$ coordinate in the next computation:

$$\mathbf{r}_{c3}^{b4} = \begin{pmatrix} -x+1 \\ \frac{3}{4} \\ -z+1 \end{pmatrix} - \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \\ 0 \end{pmatrix} = \begin{pmatrix} -(x - \frac{1}{2}) \\ +\frac{1}{4} \\ -(z-1) \end{pmatrix} \quad (4.2)$$

The $\mathbf{r}_\alpha^\beta$ vectors are intentionally expressed using the general expressions for the coordinates

(listed in Tab. 4.1). This is to aid comparison between structurally analogous materials. Note how the two vectors are related by inversion, since they are centered about a $b4$ coordinate. These and the remaining vectors are listed in Tab. 4.2.

Note, if applying this method to a new structure, it is helpful to use a crystal structure viewing program (*e.g.* VESTA or CrystalMaker®)[179, 180] to search for all the bond distances between the inversion sites and the magnetic atoms. First, hide all atoms except for the magnetic ions, and any ions of the $\bar{1}'$ inversion sites. If the inversion site is not occupied, such as the $4b$ site in LiCoPO_4 , use the software to place a “dummy” atom on the unoccupied site to facilitate this analysis. In addition, give each inversion site and magnetic ion site a unique coordinate, such as those listed in Tab. 4.1. To do this, you may first need to “remove the symmetry” of the unit cell, artificially using the space group $P1$. Then prompt the program to search for all the bond distances between the inversion sites and the magnetic atoms. The magnetic ions related by inversion around a particular inversion site will have the same bond distance. This makes finding the $\mathbf{r}_\alpha^\beta$ vectors a simple task.

To verify each $\mathbf{r}_\alpha^\beta$ vector is correctly defined, replace the general coordinate expressions with the values of x , y , and z used for that particular crystal structure analyzed in the software. The length of the vector will equal the bond length exactly, if done correctly. However, recall that the r vectors are expressed in terms of fractional coordinates, which are intentionally unit-less. Therefore, to compute the distance of the vector, you must first convert to units of length using the unit cell parameters.

Table 4.2: Definitions of the $\mathbf{r}_\alpha^\beta$ vectors centered about the $4a$ and $4b$ sites for the toroidal moments in the olivine structure with the space group $Pnma$

$\mathbf{r}_{c1}^{a1} = \begin{pmatrix} +x \\ +\frac{1}{4} \\ +(z-1) \end{pmatrix}$	$\mathbf{r}_{c2}^{a1} = \begin{pmatrix} +(x-\frac{1}{2}) \\ +\frac{1}{4} \\ -(z-\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{c1}^{b1} = \begin{pmatrix} +x \\ +\frac{1}{4} \\ +(z-\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{c2}^{b1} = \begin{pmatrix} +(x-\frac{1}{2}) \\ +\frac{1}{4} \\ -(z-1) \end{pmatrix}$
$\mathbf{r}_{c3}^{a1} = \begin{pmatrix} -x \\ -\frac{1}{4} \\ -(z-1) \end{pmatrix}$	$\mathbf{r}_{c4}^{a1} = \begin{pmatrix} -(x-\frac{1}{2}) \\ -\frac{1}{4} \\ +(z-\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{c3}^{b1} = \begin{pmatrix} -x \\ -\frac{1}{4} \\ -(z-\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{c4}^{b1} = \begin{pmatrix} -(x-\frac{1}{2}) \\ -\frac{1}{4} \\ +(z-1) \end{pmatrix}$
$\mathbf{r}_{c1}^{a2} = \begin{pmatrix} +(x-\frac{1}{2}) \\ +\frac{1}{4} \\ +(z-\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{c2}^{a2} = \begin{pmatrix} +x \\ +\frac{1}{4} \\ -(z-1) \end{pmatrix}$	$\mathbf{r}_{c1}^{b2} = \begin{pmatrix} +(x-\frac{1}{2}) \\ +\frac{1}{4} \\ +(z-1) \end{pmatrix}$	$\mathbf{r}_{c2}^{b2} = \begin{pmatrix} +x \\ +\frac{1}{4} \\ -(z-\frac{1}{2}) \end{pmatrix}$
$\mathbf{r}_{c3}^{a2} = \begin{pmatrix} -(x-\frac{1}{2}) \\ -\frac{1}{4} \\ -(z-\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{c4}^{a2} = \begin{pmatrix} -x \\ -\frac{1}{4} \\ +(z-1) \end{pmatrix}$	$\mathbf{r}_{c3}^{b2} = \begin{pmatrix} -(x-\frac{1}{2}) \\ -\frac{1}{4} \\ -(z-1) \end{pmatrix}$	$\mathbf{r}_{c4}^{b2} = \begin{pmatrix} -x \\ -\frac{1}{4} \\ +(z-\frac{1}{2}) \end{pmatrix}$
$\mathbf{r}_{c1}^{a3} = \begin{pmatrix} +x \\ -\frac{1}{4} \\ +(z-1) \end{pmatrix}$	$\mathbf{r}_{c2}^{a3} = \begin{pmatrix} +(x-\frac{1}{2}) \\ -\frac{1}{4} \\ -(z-\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{c1}^{b3} = \begin{pmatrix} +x \\ -\frac{1}{4} \\ +(z-\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{c2}^{b3} = \begin{pmatrix} +(x-\frac{1}{2}) \\ -\frac{1}{4} \\ -(z-1) \end{pmatrix}$
$\mathbf{r}_{c3}^{a3} = \begin{pmatrix} -x \\ +\frac{1}{4} \\ -(z-1) \end{pmatrix}$	$\mathbf{r}_{c4}^{a3} = \begin{pmatrix} -(x-\frac{1}{2}) \\ +\frac{1}{4} \\ +(z-\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{c3}^{b3} = \begin{pmatrix} -x \\ +\frac{1}{4} \\ -(z-\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{c4}^{b3} = \begin{pmatrix} -(x-\frac{1}{2}) \\ +\frac{1}{4} \\ +(z-1) \end{pmatrix}$
$\mathbf{r}_{c1}^{a4} = \begin{pmatrix} +(x-\frac{1}{2}) \\ -\frac{1}{4} \\ +(z-\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{c2}^{a4} = \begin{pmatrix} +x \\ -\frac{1}{4} \\ -(z-1) \end{pmatrix}$	$\mathbf{r}_{c1}^{b4} = \begin{pmatrix} +(x-\frac{1}{2}) \\ -\frac{1}{4} \\ +(z-1) \end{pmatrix}$	$\mathbf{r}_{c2}^{b4} = \begin{pmatrix} +x \\ -\frac{1}{4} \\ -(z-\frac{1}{2}) \end{pmatrix}$
$\mathbf{r}_{c3}^{a4} = \begin{pmatrix} -(x-\frac{1}{2}) \\ +\frac{1}{4} \\ -(z-\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{c4}^{a4} = \begin{pmatrix} -x \\ +\frac{1}{4} \\ +(z-1) \end{pmatrix}$	$\mathbf{r}_{c3}^{b4} = \begin{pmatrix} -(x-\frac{1}{2}) \\ +\frac{1}{4} \\ -(z-1) \end{pmatrix}$	$\mathbf{r}_{c4}^{b4} = \begin{pmatrix} -x \\ +\frac{1}{4} \\ +(z-\frac{1}{2}) \end{pmatrix}$

An example calculation for a structure of LiCoPO_4 is given below, where $x = 0.2758$ and $z = 0.983$.

$$\mathbf{r}_{c1}^{b4} = \begin{pmatrix} x - \frac{1}{2} \\ -\frac{1}{4} \\ z - 1 \end{pmatrix} = \begin{pmatrix} 0.2758 - \frac{1}{2} \\ -\frac{1}{4} \\ 0.983 - 1 \end{pmatrix} = \begin{pmatrix} -0.2242 \\ -\frac{1}{4} \\ -0.017 \end{pmatrix} \quad (4.3)$$

Recall that $\mathbf{r}_{c3}^{b4}$ will be the inverse of $\mathbf{r}_{c1}^{b4}$.

$$\mathbf{r}_{c3}^{b4} = \begin{pmatrix} -(x - \frac{1}{2}) \\ +\frac{1}{4} \\ -(z - 1) \end{pmatrix} = \begin{pmatrix} -(0.2758 - \frac{1}{2}) \\ +\frac{1}{4} \\ -(0.983 - 1) \end{pmatrix} = \begin{pmatrix} +0.2242 \\ \frac{1}{4} \\ +0.017 \end{pmatrix} \quad (4.4)$$

Next, convert to units of angstrom using the unit cell parameters, which are: $a = 10.1877\text{\AA}$, $b = 5.9073\text{\AA}$, and $c = 4.6891\text{\AA}$. Since the unit cell is orthogonal, the unit cell transformation is as follows:

$$\begin{aligned} \hat{x} &= \Delta x \times a \\ \hat{y} &= \Delta y \times b \\ \hat{z} &= \Delta z \times c \end{aligned} \quad (4.5)$$

Then length is determined by the equation below:

$$\text{length} = \sqrt{(\hat{x})^2 + (\hat{y})^2 + (\hat{z})^2} \quad (4.6)$$

For $\mathbf{r}_{c1}^{b4}$ the computation is as follows:

$$\begin{aligned} \Delta x &= -0.2242 & \Delta y &= -\frac{1}{4} & \Delta z &= -0.017 \\ \hat{x} &= \Delta x \times a = -0.2242 \times 10.1877\text{\AA} = -2.2841\text{\AA} \\ \hat{y} &= \Delta y \times b = -0.25 \times 5.9073\text{\AA} = -1.477\text{\AA} \\ \hat{z} &= \Delta z \times c = -0.017 \times 4.6891\text{\AA} = -0.07971\text{\AA} \end{aligned} \quad (4.7)$$

$$\sqrt{(\hat{x})^2 + (\hat{y})^2 + (\hat{z})^2} = \sqrt{(-2.282\text{\AA})^2 + (-1.477\text{\AA})^2 + (-0.07971\text{\AA})^2} = 2.721\text{\AA}$$

And for $\mathbf{r}_{c3}^{b4}$ the computation is:

$$\begin{aligned}\Delta x &= +0.2242 & \Delta y &= +\frac{1}{4} & \Delta z &= +0.017 \\ \hat{x} &= \Delta x \times a = +0.2242 \times 10.1877\text{\AA} = -2.2841\text{\AA} \\ \hat{y} &= \Delta y \times b = +0.25 \times 5.9073\text{\AA} = -1.477\text{\AA} \\ \hat{z} &= \Delta z \times c = +0.017 \times 4.6891\text{\AA} = -0.07971\text{\AA}\end{aligned}\tag{4.8}$$

$$\sqrt{(\hat{x})^2 + (\hat{y})^2 + (\hat{z})^2} = \sqrt{(-2.282\text{\AA})^2 + (-1.477\text{\AA})^2 + (-0.07971\text{\AA})^2} = 2.721\text{\AA}$$

Both vectors give the same length. The length agrees with the length computed in my crystal structure viewer software. Therefore the magnitudes of the $\mathbf{r}_{\alpha}^{\beta}$ vector components are correctly defined.

One final check must be done to verify the $\mathbf{r}_{\alpha}^{\beta}$ vectors before continuing. Return to your preferred crystal structure viewing software and ensure the positive/negative directions of the $\mathbf{r}_{\alpha}^{\beta}$ components are correctly defined. This is done most easily by turning on the bonds between the inversion site and magnetic ion site of interest. Remember that the vectors point from the inversion site to the magnetic ion site. By comparing to the coordinate axis for the unit cell, it is easy to ensure you have correctly defined each $\mathbf{r}_{\alpha}^{\beta}$ vector to be pointed along the correct “x/a,” “y/b,” or “z/c” direction, or if the orientation of one or more components needs to be reversed.

In addition to each $\mathbf{r}_{\alpha}^{\beta}$ vector, each individual moment vector $\mathbf{m}^{\alpha}$ must also be defined. These are based upon the spin modes of the basis vectors for each irreducible representation, as defined in Tab. 4.3. Note, the basis vectors are different than in Tab. 3.7 from §3.5. The four atom positions are defined according to Tab. 4.1, instead of Ref. [164]. Therefore A and C have been interchanged compared to Tab. 3.7.

Table 4.3: Magnetic symmetry associated with the eight irreducible representations of the parent paramagnetic space group $Pnma1'$. Minor label changes to the Basis Vectors from Tab. 3.7. Macroscopic Properties from Tab. 2.2 in §2.1, originally from Ref. 32.

I.R. ^a	M.S.G. ^b	M.P.G. ^c	B.V. ^d	M.O. ^e	M.P.D. ^f
Γ_1^+	$Pnma$	mmm	G_y	AFM	
Γ_2^+	$Pn'm'a$	$m'm'm$	$G_x + F_z$	FM	$\mathbf{M}_z$
Γ_3^+	$Pnm'a'$	$mm'm'$	$F_x + G_z$	FM	$\mathbf{M}_x$
Γ_4^+	$Pn'ma'$	$m'mm'$	F_y	FM	$\mathbf{M}_y$
Γ_1^-	$Pn'm'a'$	$m'm'm'$	$C_x + A_z$	AFM	
Γ_2^-	$Pnma'$	mmm'	C_y	AFM	$\mathbf{T}_z$
Γ_3^-	$Pn'ma$	$m'mm$	A_y	AFM	$\mathbf{T}_x$
Γ_4^-	$Pnm'a$	$mm'm$	$A_x + C_z$	AFM	$\mathbf{T}_y$

^aIrreducible Representation, superscript (+) indicates gerade, superscript (-) indicates ungerade with respect to spatial inversion symmetry ($\bar{1}$); ^bMagnetic Space Group; ^cMagnetic Point Group; ^dBasis Vectors of the spin modes, which are defined as ($F = \uparrow\uparrow\uparrow\uparrow$), ($G = \uparrow\downarrow\uparrow\downarrow$), ($C = \uparrow\uparrow\downarrow\downarrow$), and ($A = \uparrow\downarrow\downarrow\uparrow$) for the four magnetic atoms. The subscripts x , y , and z define along which crystallographic direction the moments are parallel. ^eMagnetic Order; AFM = antiferromagnetic, FM = ferromagnetic ^fMacroscopic Property Direction; $\mathbf{M}$ = net magnetic moment and $\mathbf{T}$ = net toroidal moment

In the following sections (§4.2–§4.7), the individual toroidal vectors and net toroidal moment per unit cell will be computed for various magnetic structures. Tab. 4.3 will be a useful reference throughout these sections.

4.2: Example defining $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$ using Γ_2^-

Tab. 4.4 lists the $\mathbf{m}^\alpha$ vector as C_y for Γ_2^- . The individual spin components of the basis vectors are notated as s_x where x are Cartesian axes directions. It should be noted, this is the same magnetic structure as LiFePO_4 , $t\text{-NaPO}_4$, and several compositions of lithiated $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ ($x = 0.2, 0.3, 0.4$).[2, 10, 164]

Table 4.4: Definitions of the $\mathbf{m}^\alpha$ vectors for the spin modes C_y of Γ_2^-

$\mathbf{m}^\alpha$	Spin Mode Components
$\mathbf{m}^{c1}$	$+s_y$
$\mathbf{m}^{c2}$	$+s_y$
$\mathbf{m}^{c3}$	$-s_y$
$\mathbf{m}^{c4}$	$-s_y$

The next step is to construct the equations defining each individual toroidal moment using Eq. 2.11 from §2.2, which is restated here with my notation for easy reference:

$$\mathbf{t}_\gamma = \frac{1}{2} \sum_{\beta} \mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha. \quad (4.9)$$

The individual toroidal moments ($\mathbf{t}_\gamma$) are defined using the relevant $\mathbf{r}_\alpha^\beta$ vectors from Tab. 4.2 and $\mathbf{m}^\alpha$ vectors listed in Tab. 4.4. The expressions for $\mathbf{t}_\gamma$ are given below. Note, all four expressions for a given Wyckoff Position are numbered collectively for brevity.

$$\begin{aligned} \mathbf{t}_{a1} &= \frac{1}{2} \sum_{a1} \mathbf{r}_\alpha^{a1} \times \mathbf{m}^\alpha = [\mathbf{r}_{c1}^{a1} \times \mathbf{m}^{c1}] + [\mathbf{r}_{c3}^{a1} \times \mathbf{m}^{c3}] + [\mathbf{r}_{c2}^{a1} \times \mathbf{m}^{c2}] + [\mathbf{r}_{c4}^{a1} \times \mathbf{m}^{c4}] \\ \mathbf{t}_{a2} &= \frac{1}{2} \sum_{a2} \mathbf{r}_\alpha^{a2} \times \mathbf{m}^\alpha = [\mathbf{r}_{c1}^{a2} \times \mathbf{m}^{c1}] + [\mathbf{r}_{c3}^{a2} \times \mathbf{m}^{c3}] + [\mathbf{r}_{c2}^{a2} \times \mathbf{m}^{c2}] + [\mathbf{r}_{c4}^{a2} \times \mathbf{m}^{c4}] \\ \mathbf{t}_{a3} &= \frac{1}{2} \sum_{a3} \mathbf{r}_\alpha^{a3} \times \mathbf{m}^\alpha = [\mathbf{r}_{c1}^{a3} \times \mathbf{m}^{c1}] + [\mathbf{r}_{c3}^{a3} \times \mathbf{m}^{c3}] + [\mathbf{r}_{c2}^{a3} \times \mathbf{m}^{c2}] + [\mathbf{r}_{c4}^{a3} \times \mathbf{m}^{c4}] \\ \mathbf{t}_{a4} &= \frac{1}{2} \sum_{a4} \mathbf{r}_\alpha^{a4} \times \mathbf{m}^\alpha = [\mathbf{r}_{c1}^{a4} \times \mathbf{m}^{c1}] + [\mathbf{r}_{c3}^{a4} \times \mathbf{m}^{c3}] + [\mathbf{r}_{c2}^{a4} \times \mathbf{m}^{c2}] + [\mathbf{r}_{c4}^{a4} \times \mathbf{m}^{c4}] \end{aligned} \quad (4.10)$$

$$\begin{aligned} \mathbf{t}_{b1} &= \frac{1}{2} \sum_{b1} \mathbf{r}_\alpha^{b1} \times \mathbf{m}^\alpha = [\mathbf{r}_{c1}^{b1} \times \mathbf{m}^{c1}] + [\mathbf{r}_{c3}^{b1} \times \mathbf{m}^{c3}] + [\mathbf{r}_{c2}^{b1} \times \mathbf{m}^{c2}] + [\mathbf{r}_{c4}^{b1} \times \mathbf{m}^{c4}] \\ \mathbf{t}_{b2} &= \frac{1}{2} \sum_{b2} \mathbf{r}_\alpha^{b2} \times \mathbf{m}^\alpha = [\mathbf{r}_{c1}^{b2} \times \mathbf{m}^{c1}] + [\mathbf{r}_{c3}^{b2} \times \mathbf{m}^{c3}] + [\mathbf{r}_{c2}^{b2} \times \mathbf{m}^{c2}] + [\mathbf{r}_{c4}^{b2} \times \mathbf{m}^{c4}] \\ \mathbf{t}_{b3} &= \frac{1}{2} \sum_{b3} \mathbf{r}_\alpha^{b3} \times \mathbf{m}^\alpha = [\mathbf{r}_{c1}^{b3} \times \mathbf{m}^{c1}] + [\mathbf{r}_{c3}^{b3} \times \mathbf{m}^{c3}] + [\mathbf{r}_{c2}^{b3} \times \mathbf{m}^{c2}] + [\mathbf{r}_{c4}^{b3} \times \mathbf{m}^{c4}] \\ \mathbf{t}_{b4} &= \frac{1}{2} \sum_{b4} \mathbf{r}_\alpha^{b4} \times \mathbf{m}^\alpha = [\mathbf{r}_{c1}^{b4} \times \mathbf{m}^{c1}] + [\mathbf{r}_{c3}^{b4} \times \mathbf{m}^{c3}] + [\mathbf{r}_{c2}^{b4} \times \mathbf{m}^{c2}] + [\mathbf{r}_{c4}^{b4} \times \mathbf{m}^{c4}] \end{aligned} \quad (4.11)$$

To compute the cross product of $\mathbf{r} \times \mathbf{m}$, recall the following from grade school mathematics:

$$\mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha = (\mathbf{r}_y \mathbf{m}_z - \mathbf{r}_z \mathbf{m}_y) \hat{\mathbf{i}} + (\mathbf{r}_z \mathbf{m}_x - \mathbf{r}_x \mathbf{m}_z) \hat{\mathbf{j}} + (\mathbf{r}_x \mathbf{m}_y - \mathbf{r}_y \mathbf{m}_x) \hat{\mathbf{k}} \quad (4.12)$$

This expression can be quickly simplified by considering the basis vector spin components. For example, for Γ_2^- , there is only a y-component to $\mathbf{m}$. Therefore the expression becomes:

$$\begin{aligned}\mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha &= (\cancel{\mathbf{r}_y \mathbf{m}_z} - \mathbf{r}_z \mathbf{m}_y) \hat{\mathbf{i}} + (\cancel{\mathbf{r}_z \mathbf{m}_x} - \cancel{\mathbf{r}_x \mathbf{m}_z}) \hat{\mathbf{j}} + (\mathbf{r}_x \mathbf{m}_y - \cancel{\mathbf{r}_y \mathbf{m}_x}) \hat{\mathbf{k}} \\ \mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha &= -(\mathbf{r}_z \mathbf{m}_y) \hat{\mathbf{i}} + (\mathbf{r}_x \mathbf{m}_y) \hat{\mathbf{k}}\end{aligned}\quad (4.13)$$

Then Eq. 4.13 can be substituted into Eq. 4.10 & 4.11. An example calculation for $\mathbf{t}_{a1}$ is given below:

$$\begin{aligned}\mathbf{r}_{c1}^{a1} \times \mathbf{m}^{c1} &= -\mathbf{m}_y(z-1) \hat{\mathbf{i}} + \mathbf{m}_y(x) \hat{\mathbf{k}} = -\mathbf{m}_y(z) \hat{\mathbf{i}} + \mathbf{m}_y \hat{\mathbf{i}} + \mathbf{m}_y(x) \hat{\mathbf{k}} \\ \mathbf{r}_{c3}^{a1} \times \mathbf{m}^{c3} &= -(-\mathbf{m}_y)(-z+1) \hat{\mathbf{i}} + (-\mathbf{m}_y)(-x) \hat{\mathbf{k}} = -\mathbf{m}_y(z) \hat{\mathbf{i}} + \mathbf{m}_y \hat{\mathbf{i}} + \mathbf{m}_y(x) \hat{\mathbf{k}} \\ \mathbf{r}_{c2}^{a1} \times \mathbf{m}^{c2} &= -\mathbf{m}_y(-z+1/2) \hat{\mathbf{i}} + \mathbf{m}_y(x-1/2) \hat{\mathbf{k}} = \mathbf{m}_y(z) \hat{\mathbf{i}} - (1/2)\mathbf{m}_y \hat{\mathbf{i}} + \mathbf{m}_y(x) \hat{\mathbf{k}} - (1/2)\mathbf{m}_y \hat{\mathbf{k}} \\ \mathbf{r}_{c4}^{a1} \times \mathbf{m}^{c4} &= -(-\mathbf{m}_y)(z-1/2) \hat{\mathbf{i}} + (-\mathbf{m}_y)(-x+1/2) \hat{\mathbf{k}} = \mathbf{m}_y(z) \hat{\mathbf{i}} - (1/2)\mathbf{m}_y \hat{\mathbf{i}} + \mathbf{m}_y(x) \hat{\mathbf{k}} - (1/2)\mathbf{m}_y \hat{\mathbf{k}} \\ \mathbf{t}_{a1} &= \frac{1}{2} \sum_{a1} 2[-\mathbf{m}_y(z) \hat{\mathbf{i}} + \mathbf{m}_y \hat{\mathbf{i}} + \mathbf{m}_y(x) \hat{\mathbf{k}}] + 2[\mathbf{m}_y(z) \hat{\mathbf{i}} - (1/2)\mathbf{m}_y \hat{\mathbf{i}} + \mathbf{m}_y(x) \hat{\mathbf{k}} - (1/2)\mathbf{m}_y \hat{\mathbf{k}}] \\ \mathbf{t}_{a1} &= \cancel{-\mathbf{m}_y(z) \hat{\mathbf{i}}} + \mathbf{m}_y \hat{\mathbf{i}} + \mathbf{m}_y(x) \hat{\mathbf{k}} + \cancel{\mathbf{m}_y(z) \hat{\mathbf{i}}} - (1/2)\mathbf{m}_y \hat{\mathbf{i}} + \mathbf{m}_y(x) \hat{\mathbf{k}} - (1/2)\mathbf{m}_y \hat{\mathbf{k}} \\ \mathbf{t}_{a1} &= (1/2)\mathbf{m}_y \hat{\mathbf{i}} + 2(x)\mathbf{m}_y \hat{\mathbf{k}} - (1/2)\mathbf{m}_y \hat{\mathbf{k}}\end{aligned}\quad (4.14)$$

The same process is done for the individual toroidal moments on the other $\bar{1}'$ sites, giving:

$$\begin{aligned}\mathbf{t}_{a2} &= -(1/2)\mathbf{m}_y \hat{\mathbf{i}} + (2x)\mathbf{m}_y \hat{\mathbf{k}} - (1/2)\mathbf{m}_y \hat{\mathbf{k}} \\ \mathbf{t}_{a3} &= \mathbf{t}_{a1} \\ \mathbf{t}_{a4} &= \mathbf{t}_{a2} \\ \mathbf{t}_{b1} &= -(1/2)\mathbf{m}_y \hat{\mathbf{i}} + (2x)\mathbf{m}_y \hat{\mathbf{k}} - (1/2)\mathbf{m}_y \hat{\mathbf{k}} \\ \mathbf{t}_{b2} &= (1/2)\mathbf{m}_y \hat{\mathbf{i}} + (2x)\mathbf{m}_y \hat{\mathbf{k}} - (1/2)\mathbf{m}_y \hat{\mathbf{k}} \\ \mathbf{t}_{b3} &= \mathbf{t}_{b1} \\ \mathbf{t}_{b4} &= \mathbf{t}_{b2}\end{aligned}\quad (4.15)$$

Note, the results for the $\mathbf{t}_a$ sites are the same as for the $\mathbf{t}_b$ sites, just with a different pattern of

positive and negative coefficients. This is because the a sites and b sites are numerically similar, just shifted spatially by $(0, 0, \frac{1}{2})$ (Tab. 4.1). Also, note the similarity between the $\mathbf{r}_\alpha^\beta$ vectors in Tab. 4.2. The reason $\mathbf{t}_{a3} = \mathbf{t}_{a1}$ is because this is an antiferromagnetic configuration. Sites $a3$ and $a1$ are spatially related by inversion, making their $\mathbf{r}_\alpha^\beta$ vectors inverses of one another (*e.g.* $x, 1/4, z-1$ is the inverse of $-x, -1/4, -z+1$). In addition, the $\mathbf{m}^\alpha$ vectors are inverses of one another (*e.g.* $+\mathbf{m}_y$ is the inverse of $-\mathbf{m}_y$). Therefore in the calculation of $\mathbf{t}_{a3}$, the cross products of $\mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha$ are the same since a negative times a negative equals a positive. The same is true for $\mathbf{t}_{a4}$ and $\mathbf{t}_{a2}$, $\mathbf{t}_{b1}$ and $\mathbf{t}_{b3}$, and $\mathbf{t}_{b4}$ and $\mathbf{t}_{b2}$.

The net toroidal moment per unit cell ($\mathbf{T}_{net}$) is calculated using Eq. 2.12 from §2.2, restated here:

$$\mathbf{T} = \frac{1}{2V} \sum_i \mathbf{r}_i \times \mathbf{m}_i$$

The variable V is the volume of the unit cell. For an orthorhombic unit cell, $V = abc$. Since the individual toroidal moments were already computed, this can be rewritten more generally:

$$\mathbf{T}_{net} = \frac{1}{V} \sum_\gamma \mathbf{t}_\gamma \quad (4.16)$$

At this point, there are three choices for how to proceed. Recall, there is still no concrete experimental evidence for the existence of individual toroidal moments. So from this point forward, the theory would have to be informed by experimental evidence. Are the toroidal moments on all eight of the $\bar{1}'$ sites? The a sites are occupied with lithium ions in LiCoPO_4 and its analogs (*e.g.* LiFePO_4 , etc.). Does that mean a toroidal moment cannot exist on that site, and so there are only individual moments on the b sites? And what would that mean for partially delithiated materials such as $\text{Li}_{0.8}\text{Fe}_{0.2}\text{Mn}_{0.8}\text{PO}_4$? In other words, is $\mathbf{T}_{net}$ best computed as $\mathbf{T}_a$, $\mathbf{T}_b$, or $\mathbf{T}_{a+b}$? Each are given below for Γ_2^- , for comparison:

$$\mathbf{T}_a = \frac{(8x)\mathbf{m}_y \hat{\mathbf{k}} - (2)\mathbf{m}_y \hat{\mathbf{k}}}{abc} = \frac{8(x-1/4)\mathbf{m}_y \hat{\mathbf{k}}}{abc}$$

$$\begin{aligned}\mathbf{T}_b &= \frac{(8x)\mathbf{m}_y \hat{\mathbf{k}} - (2)\mathbf{m}_y \hat{\mathbf{k}}}{abc} = \frac{8(x - 1/4)\mathbf{m}_y \hat{\mathbf{k}}}{abc} \\ \mathbf{T}_{a+b} &= \frac{(16x)\mathbf{m}_y \hat{\mathbf{k}} - (4)\mathbf{m}_y \hat{\mathbf{k}}}{abc} = \frac{16(x - 1/4)\mathbf{m}_y \hat{\mathbf{k}}}{abc}\end{aligned}\tag{4.17}$$

Since $\mathbf{T}_a = \mathbf{T}_b$, as long as a consistent method is chosen for comparing different materials, the analysis will be consistent. Any of the three options can be validly chosen, from a symmetry perspective. I personally believe the toroidal moments would only exist at the b sites, since they are unoccupied. In my naivete, it seems reasonable that neutrons could interact with a toroidal moment. With that said, I would be easily convinced by experimental evidence demonstrating otherwise. Materials such as $\text{Li}_{0.8}\text{Fe}_{0.2}\text{Mn}_{0.8}\text{PO}_4$ certainly pose many questions. Would there be a toroidal moment at every a site not occupied by a lithium ion? And is it even possible to diffract from a site which does not contain an atom?

In any case, the interpretation of either $\mathbf{T}_a$, $\mathbf{T}_b$, or $\mathbf{T}_{a+b}$ is that the net toroidal moment will have only a component along the $\hat{\mathbf{k}}$ direction, which corresponds to the z axis. Note, this result is consistent with the predicted direction listed in Tab. 3.5 & 4.3.

The following sections (§4.3–4.7) report the $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$ expressions for the other magnetic structures observed in transition metal orthophosphate materials with the olivine structure. The full algebraic manipulations will not be demonstrated for each one, for the sake of brevity. Note that since the chemical structures are all analogous to one another, the sets of expressions for $\mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha$ labeled Eq. 4.10 & 4.11 in §4.2 are the same in each of the following examples as well. At the conclusion of this section (§4.8), the magnetic and toroidal structures will be compared for all the pertinent transition metal orthophosphate materials. This will be followed by a general discussion of the utility of the toroidal structure model.

4.3: Determining $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$ using Γ_4^-

This section reports the expressions $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$ for LiNiPO_4 . Its magnetic structure is $Pnm'a$ (point group = $mm'm$), [47, 81] which corresponds to Γ_4^- in Tab. 4.3. The structure can be referenced in the Magnetic Space Group tables under index number 62.4.505.[178] Its full international symbol for the magnetic space group is $P2'_1/n2_1/m'2'_1/a$. The $4a$ and $4b$ Wyckoff Positions have the site symmetry $\bar{1}'$, and the $4c$ Wyckoff Positions have the symmetry m' . This differs from $Pnma'$, where the site symmetry of the $4c$ site was m .

The $\mathbf{m}^\alpha$ vectors used to compute $\mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha$ are given in Tab. 4.5.

Table 4.5: Definitions of the $\mathbf{m}^\alpha$ vectors for the spin modes $A_x + C_z$ of Γ_4^-

$\mathbf{m}^\alpha$	Spin Mode Components
$\mathbf{m}^{c1}$	$+s_x + s_z$
$\mathbf{m}^{c2}$	$-s_x + s_z$
$\mathbf{m}^{c3}$	$-s_x - s_z$
$\mathbf{m}^{c4}$	$+s_x - s_z$

Since the spin modes for Γ_4^- do not have a y-component, Eq. 4.12 can be simplified as follows:

$$\begin{aligned}\mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha &= (\mathbf{r}_y \mathbf{m}_z - \mathbf{r}_z \mathbf{m}_y) \hat{\mathbf{i}} + (\mathbf{r}_z \mathbf{m}_x - \mathbf{r}_x \mathbf{m}_z) \hat{\mathbf{j}} + (\mathbf{r}_x \mathbf{m}_y - \mathbf{r}_y \mathbf{m}_x) \hat{\mathbf{k}} \\ \mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha &= (\mathbf{r}_y \mathbf{m}_z) \hat{\mathbf{i}} + (\mathbf{r}_z \mathbf{m}_x - \mathbf{r}_x \mathbf{m}_z) \hat{\mathbf{j}} - (\mathbf{r}_y \mathbf{m}_x) \hat{\mathbf{k}}\end{aligned}\quad (4.18)$$

Substituting Eq. 4.18 into Eq. 4.10 & 4.11 gives the following expressions for $\mathbf{t}_\gamma$:

$$\mathbf{t}_{a1} = (1/2)\mathbf{m}_z \hat{\mathbf{i}} + (2z)\mathbf{m}_x \hat{\mathbf{j}} - (3/2)\mathbf{m}_x \hat{\mathbf{j}} - (2x)\mathbf{m}_z \hat{\mathbf{j}} + (1/2)\mathbf{m}_z \hat{\mathbf{j}} \quad (4.19)$$

$$\mathbf{t}_{a2} = \mathbf{t}_{a1}$$

$$\mathbf{t}_{a3} = (-1/2)\mathbf{m}_z \hat{\mathbf{i}} + (2z)\mathbf{m}_x \hat{\mathbf{j}} - (3/2)\mathbf{m}_x \hat{\mathbf{j}} - (2x)\mathbf{m}_z \hat{\mathbf{j}} + (1/2)\mathbf{m}_z \hat{\mathbf{j}}$$

$$\mathbf{t}_{a4} = \mathbf{t}_{a3}$$

$$\mathbf{t}_{b1} = (1/2)\mathbf{m}_z \hat{\mathbf{i}} + (2z)\mathbf{m}_x \hat{\mathbf{j}} - (3/2)\mathbf{m}_x \hat{\mathbf{j}} - (2x)\mathbf{m}_z \hat{\mathbf{j}} + (1/2)\mathbf{m}_z \hat{\mathbf{j}} \quad (4.20)$$

$$\mathbf{t}_{b2} = \mathbf{t}_{b1}$$

$$\mathbf{t}_{b3} = (-1/2)\mathbf{m}_z \hat{\mathbf{i}} + (2z)\mathbf{m}_x \hat{\mathbf{j}} - (3/2)\mathbf{m}_x \hat{\mathbf{j}} - (2x)\mathbf{m}_z \hat{\mathbf{j}} + (1/2)\mathbf{m}_z \hat{\mathbf{j}}$$

$$\mathbf{t}_{b4} = \mathbf{t}_{b3}$$

Substituting Eq. 4.19 & 4.20 into Eq. 4.16 gives:

$$\begin{aligned} \mathbf{T}_a &= \frac{2(4z-3)\mathbf{m}_x \hat{\mathbf{j}} + 2(-4x+1)\mathbf{m}_z \hat{\mathbf{j}}}{abc} \\ \mathbf{T}_b &= \frac{2(4z-3)\mathbf{m}_x \hat{\mathbf{j}} + 2(-4x+1)\mathbf{m}_z \hat{\mathbf{j}}}{abc} \\ \mathbf{T}_{a+b} &= \frac{4(4z-3)\mathbf{m}_x \hat{\mathbf{j}} + 4(-4x+1)\mathbf{m}_z \hat{\mathbf{j}}}{abc} \end{aligned} \quad (4.21)$$

Just like in §4.2, $\mathbf{T}_a = \mathbf{T}_b$ and so either $\mathbf{T}_a$, $\mathbf{T}_b$, or $\mathbf{T}_{a+b}$ could be validly used for analysis.

In all three cases, the net toroidal moment is allowed along the $\hat{\mathbf{j}}$ direction, which corresponds to the y axis. This result is consistent with the predicted direction listed in Tab. 3.5 & 4.3.

4.4: Determining $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$ using Γ_1^-

This section reports the expressions $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$ for LiMnPO_4 . Its magnetic structure is $Pn'm'a'$ (point group = $m'm'm'$), [87, 181] which corresponds to Γ_1^- , according to the scheme in Tab. 4.3. Recall, $m'm'm'$ is classified as an antiferrotoroidal point group in Tab. 3.4 in §3.4. The structure can be referenced in the Magnetic Space Group tables under index number 62.9.510.[178] Its full international symbol for the magnetic space group is $P2_1/n'2_1/m'2_1/a'$. The 4a and 4b Wyckoff Positions have the site symmetry $\bar{1}'$, and the 4c site has the symmetry m' .

The $\mathbf{m}^\alpha$ vectors used to compute $\mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha$ are given in Tab. 4.6.

Table 4.6: Definitions of the $\mathbf{m}^\alpha$ vectors for the spin modes $C_x + A_z$ of Γ_1^-

$\mathbf{m}^\alpha$	Spin Mode Components
$\mathbf{m}^{c1}$	$+s_x + s_z$
$\mathbf{m}^{c2}$	$+s_x - s_z$
$\mathbf{m}^{c3}$	$-s_x - s_z$
$\mathbf{m}^{c4}$	$-s_x + s_z$

Since the spin modes for Γ_1^- do not have a y-component, Eq. 4.18 is used.

Substituting Eq. 4.18 into Eq. 4.10 & 4.11 gives the following expressions for $\mathbf{t}_\gamma$:

$$\mathbf{t}_{a1} = -(1/2)\mathbf{m}_x \hat{\mathbf{j}} - (1/2)\mathbf{m}_z \hat{\mathbf{j}} - (1/2)\mathbf{m}_x \hat{\mathbf{k}} \quad (4.22)$$

$$\mathbf{t}_{a2} = +(1/2)\mathbf{m}_x \hat{\mathbf{j}} + (1/2)\mathbf{m}_z \hat{\mathbf{j}} - (1/2)\mathbf{m}_x \hat{\mathbf{k}}$$

$$\mathbf{t}_{a3} = -(1/2)\mathbf{m}_x \hat{\mathbf{j}} - (1/2)\mathbf{m}_z \hat{\mathbf{j}} + (1/2)\mathbf{m}_x \hat{\mathbf{k}}$$

$$\mathbf{t}_{a4} = +(1/2)\mathbf{m}_x \hat{\mathbf{j}} + (1/2)\mathbf{m}_z \hat{\mathbf{j}} + (1/2)\mathbf{m}_x \hat{\mathbf{k}}$$

$$\mathbf{t}_{b1} = +(1/2)\mathbf{m}_x \hat{\mathbf{j}} - (1/2)\mathbf{m}_z \hat{\mathbf{j}} - (1/2)\mathbf{m}_x \hat{\mathbf{k}} \quad (4.23)$$

$$\mathbf{t}_{b2} = -(1/2)\mathbf{m}_x \hat{\mathbf{j}} + (1/2)\mathbf{m}_z \hat{\mathbf{j}} - (1/2)\mathbf{m}_x \hat{\mathbf{k}}$$

$$\mathbf{t}_{b3} = +(1/2)\mathbf{m}_x \hat{\mathbf{j}} - (1/2)\mathbf{m}_z \hat{\mathbf{j}} + (1/2)\mathbf{m}_x \hat{\mathbf{k}}$$

$$\mathbf{t}_{b4} = -(1/2)\mathbf{m}_x \hat{\mathbf{j}} + (1/2)\mathbf{m}_z \hat{\mathbf{j}} + (1/2)\mathbf{m}_x \hat{\mathbf{k}}$$

Substituting Eq. 4.22 & 4.23 into Eq. 4.16 gives:

$$\mathbf{T}_a = \mathbf{T}_b = \mathbf{T}_{a+b} = 0 \quad (4.24)$$

Since there are individual $\mathbf{t}_\gamma$ components which together cancel to produce no net toroidal moment per unit cell, this configuration is antiferrotoroidal. This will be discussed further in §4.8.

4.5: Determining $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$ using Γ_2^+

This section reports the expressions $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$ for a delithiated form of LiCoPO_4 , specifically $\text{Li}_{0.2}\text{CoPO}_4$. Its magnetic structure is $Pn'm'a$ (point group = $m'm'm$),[9] which corresponds to Γ_2^+ , according to the scheme in Tab. 4.3. The structure can be referenced in the Magnetic Space Group tables under index number 62.6.507.[178] Its full international symbol for the magnetic space group is $P2'_1/n'2'_1/m'2_1/a$. The $4a$ and $4b$ Wyckoff Positions have the site symmetry $1'$ (*not* $\bar{1}'$), and the $4c$ site has the symmetry m' .

The $\mathbf{m}^\alpha$ vectors used to compute $\mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha$ are given in Tab. 4.7.

Table 4.7: Definitions of the $\mathbf{m}^\alpha$ vectors for the spin modes $G_x + F_z$ of Γ_2^+

$\mathbf{m}^\alpha$	Spin Mode Components
$\mathbf{m}^{c1}$	$+s_x + s_z$
$\mathbf{m}^{c2}$	$-s_x + s_z$
$\mathbf{m}^{c3}$	$+s_x + s_z$
$\mathbf{m}^{c4}$	$-s_x + s_z$

Since the spin modes for Γ_2^+ do not have a y-component, Eq. 4.18 is used.

Substituting Eq. 4.18 into Eq. 4.10 & 4.11 gives the following expressions for $\mathbf{t}_\gamma$:

$$\mathbf{t}_{a1} = \mathbf{t}_{a2} = \mathbf{t}_{a3} = \mathbf{t}_{a4} = \mathbf{t}_{b1} = \mathbf{t}_{b2} = \mathbf{t}_{b3} = \mathbf{t}_{b4} = 0 \quad (4.25)$$

Therefore it follows that:

$$\mathbf{T}_a = \mathbf{T}_b = \mathbf{T}_{a+b} = 0. \quad (4.26)$$

This is a non-toroidal configuration. Since the components of $\mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha$ cancel, there are no individual toroidal moments. As an example, the computation for $\mathbf{t}_{a1}$ is given below:

$$\begin{aligned} \mathbf{r}_{c1}^{a1} \times \mathbf{m}_{c1} &= +(1/4)\mathbf{m}_z \hat{\mathbf{i}} + (z)\mathbf{m}_x \hat{\mathbf{j}} - \mathbf{m}_x \hat{\mathbf{j}} - (x)\mathbf{m}_z \hat{\mathbf{j}} - (1/4)\mathbf{m}_x \hat{\mathbf{k}} \\ \mathbf{r}_{c2}^{a1} \times \mathbf{m}_{c2} &= +(1/4)\mathbf{m}_z \hat{\mathbf{i}} + (z)\mathbf{m}_x \hat{\mathbf{j}} - (1/2)\mathbf{m}_x \hat{\mathbf{j}} - (x)\mathbf{m}_z \hat{\mathbf{j}} + (1/2)\mathbf{m}_z \hat{\mathbf{j}} + (1/4)\mathbf{m}_x \hat{\mathbf{k}} \end{aligned}$$

$$\begin{aligned}
\mathbf{r}_{c3}^{a1} \times \mathbf{m}_{c3} &= -(1/4)\mathbf{m}_z \hat{\mathbf{i}} - (z)\mathbf{m}_x \hat{\mathbf{j}} + \mathbf{m}_x \hat{\mathbf{j}} + (x)\mathbf{m}_z \hat{\mathbf{j}} + (1/4)\mathbf{m}_x \hat{\mathbf{k}} \\
\mathbf{r}_{c4}^{a1} \times \mathbf{m}_{c4} &= -(1/4)\mathbf{m}_z \hat{\mathbf{i}} - (z)\mathbf{m}_x \hat{\mathbf{j}} + (1/2)\mathbf{m}_x \hat{\mathbf{j}} + (x)\mathbf{m}_z \hat{\mathbf{j}} - (1/2)\mathbf{m}_z \hat{\mathbf{j}} - (1/4)\mathbf{m}_x \hat{\mathbf{k}} \\
\mathbf{t}_{a1} &= \frac{1}{2} \sum_{a1} [\mathbf{r}_{c1}^{a1} \times \mathbf{m}_{c1}] + [\mathbf{r}_{c2}^{a1} \times \mathbf{m}_{c2}] + [\mathbf{r}_{c3}^{a1} \times \mathbf{m}_{c3}] + [\mathbf{r}_{c4}^{a1} \times \mathbf{m}_{c4}] \\
\mathbf{t}_{a1} &= 0
\end{aligned} \tag{4.27}$$

Notice how the coefficients for each $\mathbf{r}_{\alpha}^{\beta} \times \mathbf{m}_{\alpha}$ alternate between positive and negative so that when added together, the sum is zero for $\mathbf{t}_{a1}$. A similar scenario happens for $\mathbf{t}_{a2}$, $\mathbf{t}_{a3}$, $\mathbf{t}_{a4}$, $\mathbf{t}_{b1}$, $\mathbf{t}_{b2}$, $\mathbf{t}_{b3}$, and $\mathbf{t}_{b4}$.

It is logically self-consistent that Γ_2^+ would be non-toroidal because it is associated with a net ferromagnetic moment along the z axis (See Tab. 4.3). Ferrotoroidicity is only compatible with antiferromagnetic spin configurations, as discussed in §3.3.

4.6: Determining $\mathbf{t}_{\gamma}$ and $\mathbf{T}_{net}$ using individual basis vectors from Γ_1^- and Γ_1^+

This section reports the expressions $\mathbf{t}_{\gamma}$ and $\mathbf{T}_{net}$ for delithiated forms of LiFePO_4 and $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$: $\text{Fe}^{3+}\text{PO}_4$ and $\text{Li}_{1-x}\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$ ($x = 0.4, 0.5, 0.6$). Its magnetic structure is $P2_12_12_1$ (point group = 222), [10, 164] which corresponds to a magnetic structure described by the C_x basis vector from Γ_1^- and the G_y basis vector from Γ_1^+ , according to the scheme in Tab. 4.3. The magnetic structure can be referenced in the Magnetic Space Group tables under index number 19.1.119. [178] Its full international symbol for the magnetic space group of this composite magnetic structure is $P2_12_12_1$. This magnetic space group does not have any special positions. However, recall that the chemical structure is still $Pnma$, and the $4a$ and $4b$ sites still exist, with their associated m and $\bar{1}$ spatial symmetry.

The $\mathbf{m}^{\alpha}$ vectors used to compute $\mathbf{r}_{\alpha}^{\beta} \times \mathbf{m}^{\alpha}$ are given in Tab. 4.8.

Table 4.8: Definitions of the $\mathbf{m}^\alpha$ vectors for the G_y spin mode of Γ_1^+ and the C_x spin mode of Γ_1^-

$\mathbf{m}^\alpha$	Spin Mode Components
$\mathbf{m}^{c1}$	$+s_x + s_y$
$\mathbf{m}^{c2}$	$+s_x - s_y$
$\mathbf{m}^{c3}$	$-s_x + s_y$
$\mathbf{m}^{c4}$	$-s_x - s_y$

Since the spin modes used do not have a z -component, Eq. 4.12 can be simplified as follows:

$$\begin{aligned}\mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha &= (\mathbf{r}_y \mathbf{m}_z - \mathbf{r}_z \mathbf{m}_y) \hat{\mathbf{i}} + (\mathbf{r}_z \mathbf{m}_x - \mathbf{r}_x \mathbf{m}_z) \hat{\mathbf{j}} + (\mathbf{r}_x \mathbf{m}_y - \mathbf{r}_y \mathbf{m}_x) \hat{\mathbf{k}} \\ \mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha &= -(\mathbf{r}_z \mathbf{m}_y) \hat{\mathbf{i}} + (\mathbf{r}_z \mathbf{m}_x) \hat{\mathbf{j}} + (\mathbf{r}_x \mathbf{m}_y - \mathbf{r}_y \mathbf{m}_x) \hat{\mathbf{k}}\end{aligned}\quad (4.28)$$

Substituting Eq. 4.28 into Eq. 4.10 & 4.11 gives the following expressions for $\mathbf{t}_\gamma$:

$$\mathbf{t}_{a1} = -(1/2)\mathbf{m}_x \hat{\mathbf{j}} - (1/2)\mathbf{m}_x \hat{\mathbf{k}} \quad (4.29)$$

$$\mathbf{t}_{a2} = +(1/2)\mathbf{m}_x \hat{\mathbf{j}} - (1/2)\mathbf{m}_x \hat{\mathbf{k}}$$

$$\mathbf{t}_{a1} = -(1/2)\mathbf{m}_x \hat{\mathbf{j}} + (1/2)\mathbf{m}_x \hat{\mathbf{k}}$$

$$\mathbf{t}_{a1} = +(1/2)\mathbf{m}_x \hat{\mathbf{j}} + (1/2)\mathbf{m}_x \hat{\mathbf{k}}$$

$$\mathbf{t}_{b1} = +(1/2)\mathbf{m}_x \hat{\mathbf{j}} - (1/2)\mathbf{m}_x \hat{\mathbf{k}} \quad (4.30)$$

$$\mathbf{t}_{b2} = -(1/2)\mathbf{m}_x \hat{\mathbf{j}} - (1/2)\mathbf{m}_x \hat{\mathbf{k}}$$

$$\mathbf{t}_{b3} = +(1/2)\mathbf{m}_x \hat{\mathbf{j}} + (1/2)\mathbf{m}_x \hat{\mathbf{k}}$$

$$\mathbf{t}_{b4} = -(1/2)\mathbf{m}_x \hat{\mathbf{j}} + (1/2)\mathbf{m}_x \hat{\mathbf{k}}$$

Substituting Eq. 4.29 & 4.30 into Eq. 4.16 gives:

$$\mathbf{T}_a = \mathbf{T}_b = \mathbf{T}_{a+b} = 0 \quad (4.31)$$

This is the same scenario as Γ_1^- in §4.4. Since Γ_1^+ *does* have individual $\mathbf{t}_\gamma$ vectors, it is *not* non-toroidal like Γ_2^+ from §4.5. Rather, since the sum of the individual $\mathbf{t}_\gamma$ vectors is zero, there

is no *net* toroidal moment per unit cell. Therefore, this is an antiferrotoroidal configuration. This will be discussed further in §4.8.

4.7: Determining $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$ using individual basis vectors from Γ_2^- and Γ_4^-

This section reports the expressions $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$ for $\text{Li}_{1-x}\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$ ($x = 0.2, 0.3$). Its magnetic structure is $P2'_1/n$ (point group = $2'/m$), [164] which corresponds to a magnetic structure described by the C_y basis vector from Γ_2^- and the C_z basis vector from Γ_4^- , according to the scheme in Tab. 4.3. The point group $2'/m$ is classified as a ferrotoroidal point group in Tab. 3.4 of §3.4. The structure can be referenced in the Magnetic Space Group tables under index number 14.3.88. [178] Its full international symbol for the magnetic space group of this composite magnetic structure is $P2'_1/n11$. According to the conventions of the subgroup transformation from $Pnma$ to $P2_1/n$, the $4a$ and $4b$ inversion sites split into four sites: $2a$, $2b$, $2c$, and $2d$. Each of those sites have the same eight coordinates, and the site symmetry remains $\bar{1}'$. Just as with the example in §4.6, recall that the chemical structure remains $Pnma$.

The $\mathbf{m}^\alpha$ vectors used to compute $\mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha$ are given in Tab. 4.9.

Table 4.9: Definitions of the $\mathbf{m}^\alpha$ vectors for the C_y spin mode of Γ_2^- and the C_z spin mode of Γ_4^-

$\mathbf{m}^\alpha$	Spin Mode Components
$\mathbf{m}^{c1}$	$+s_y + s_z$
$\mathbf{m}^{c2}$	$+s_y + s_z$
$\mathbf{m}^{c3}$	$-s_y - s_z$
$\mathbf{m}^{c4}$	$-s_y - s_z$

Since the spin modes used do not have an x -component, Eq. 4.12 can be simplified as follows:

$$\mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha = (\mathbf{r}_y \mathbf{m}_z - \mathbf{r}_z \mathbf{m}_y) \hat{\mathbf{i}} + (\mathbf{r}_z \mathbf{m}_x - \mathbf{r}_x \mathbf{m}_z) \hat{\mathbf{j}} + (\mathbf{r}_x \mathbf{m}_y - \mathbf{r}_y \mathbf{m}_x) \hat{\mathbf{k}}$$

$$\mathbf{r}_\alpha^\beta \times \mathbf{m}^\alpha = (\mathbf{r}_y \mathbf{m}_z - \mathbf{r}_z \mathbf{m}_y) \hat{\mathbf{i}} - (\mathbf{r}_x \mathbf{m}_z) \hat{\mathbf{j}} + (\mathbf{r}_x \mathbf{m}_y) \hat{\mathbf{k}} \quad (4.32)$$

Substituting Eq. 4.32 into Eq. 4.10 & 4.11 gives the following expressions for $\mathbf{t}_\gamma$:

$$\mathbf{t}_{a1} = +(1/2)\mathbf{m}_z \hat{\mathbf{i}} + (1/2)\mathbf{m}_y \hat{\mathbf{i}} + 2(-x + 1/4)\mathbf{m}_z \hat{\mathbf{j}} + 2(x - 1/4)\mathbf{m}_y \hat{\mathbf{k}} \quad (4.33)$$

$$\mathbf{t}_{a2} = +(1/2)\mathbf{m}_z \hat{\mathbf{i}} - (1/2)\mathbf{m}_y \hat{\mathbf{i}} + 2(-x + 1/4)\mathbf{m}_z \hat{\mathbf{j}} + 2(x - 1/4)\mathbf{m}_y \hat{\mathbf{k}}$$

$$\mathbf{t}_{a3} = -(1/2)\mathbf{m}_z \hat{\mathbf{i}} + (1/2)\mathbf{m}_y \hat{\mathbf{i}} + 2(-x + 1/4)\mathbf{m}_z \hat{\mathbf{j}} + 2(x - 1/4)\mathbf{m}_y \hat{\mathbf{k}}$$

$$\mathbf{t}_{a4} = -(1/2)\mathbf{m}_z \hat{\mathbf{i}} + (1/2)\mathbf{m}_y \hat{\mathbf{i}} + 2(-x + 1/4)\mathbf{m}_z \hat{\mathbf{j}} + 2(x - 1/4)\mathbf{m}_y \hat{\mathbf{k}}$$

$$\mathbf{t}_{b1} = +(1/2)\mathbf{m}_z \hat{\mathbf{i}} - (1/2)\mathbf{m}_y \hat{\mathbf{i}} + 2(-x + 1/4)\mathbf{m}_z \hat{\mathbf{j}} + 2(x - 1/4)\mathbf{m}_y \hat{\mathbf{k}} \quad (4.34)$$

$$\mathbf{t}_{b2} = +(1/2)\mathbf{m}_z \hat{\mathbf{i}} + (1/2)\mathbf{m}_y \hat{\mathbf{i}} + 2(-x + 1/4)\mathbf{m}_z \hat{\mathbf{j}} + 2(x - 1/4)\mathbf{m}_y \hat{\mathbf{k}}$$

$$\mathbf{t}_{b3} = -(1/2)\mathbf{m}_z \hat{\mathbf{i}} - (1/2)\mathbf{m}_y \hat{\mathbf{i}} + 2(-x + 1/4)\mathbf{m}_z \hat{\mathbf{j}} + 2(x - 1/4)\mathbf{m}_y \hat{\mathbf{k}}$$

$$\mathbf{t}_{b4} = -(1/2)\mathbf{m}_z \hat{\mathbf{i}} + (1/2)\mathbf{m}_y \hat{\mathbf{i}} + 2(-x + 1/4)\mathbf{m}_z \hat{\mathbf{j}} + 2(x - 1/4)\mathbf{m}_y \hat{\mathbf{k}}$$

Notice, the coefficients for the terms $(1/2)\mathbf{m}_z \hat{\mathbf{i}}$ and $(1/2)\mathbf{m}_y \hat{\mathbf{i}}$ alternate between positive and negative, so they cancel when computing $\mathbf{T}_a$, $\mathbf{T}_b$, and $\mathbf{T}_{a+b}$. They are given below:

$$\begin{aligned} \mathbf{T}_a &= \frac{8(-x + 1/4)\mathbf{m}_z \hat{\mathbf{j}} + 8(x - 1/4)\mathbf{m}_y \hat{\mathbf{k}}}{abc} \\ \mathbf{T}_b &= \frac{8(-x + 1/4)\mathbf{m}_z \hat{\mathbf{j}} + 8(x - 1/4)\mathbf{m}_y \hat{\mathbf{k}}}{abc} \\ \mathbf{T}_{a+b} &= \frac{16(-x + 1/4)\mathbf{m}_z \hat{\mathbf{j}} + 16(x - 1/4)\mathbf{m}_y \hat{\mathbf{k}}}{abc} \end{aligned} \quad (4.35)$$

This corresponds to a ferrotoroidal configuration, where the toroidal component can have components along both the y and z axis. This is consistent with the classification scheme in Tab. 3.4 & 3.6 of §3.4. Note that in Fig. 3.8 of §3.5, the four point generators for $P2'_1/n11$ were 1, 4', 5', and 8 (corresponding to 1, 2'_x, $\bar{1}'$, and m_x). Therefore the magnetic point group specifically is $2'_x/m_x$. According to Tab. 3.6, the predicted direction for the toroidal moment is $\mathbf{T}_{yz}$.

4.8: Comparison of the Magnetic and Toroidal Structures in Various Transition Metal Orthophosphate Materials with the Olivine Structure Type

In order to calculate $\mathbf{T}_{net}$, the variables used in the appropriate $\mathbf{T}_{net}$ expression must first be obtained from the reported neutron powder diffraction refinement. Unfortunately, unlike single crystal refinement, there is no standard for what must be contained in the .cif (crystallographic information file). There is not even a requirement that a .cif be submitted in supplemental/supporting information with the paper. As a result, magnetic refinements are not reported in a consistent format in publications. Because of this, there were a few references I encountered where the volume of the unit cell was not reported, only the unit cell parameters. Therefore both in this section and in §4.12 I will begin by presenting the method to compute the volume with propagated error.

The formula for the volume of the unit cell (V) for an orthorhombic lattice is:

$$V = abc \quad (4.36)$$

where a , b , and c are the lattice parameters.

The formula for the propagation of error for multiplication is:

$$\frac{\Delta V}{V} = \sqrt{\left(\frac{\Delta a}{a}\right)^2 + \left(\frac{\Delta b}{b}\right)^2 + \left(\frac{\Delta c}{c}\right)^2} \quad (4.37)$$

where Δ indicates the error in the variable.

For the olivine materials, Ref. 10 did not report the refined volume of the unit cell for LiFePO_4 or FePO_4 . An example calculation for LiFePO_4 is given here. The reported lattice parameters were: $a = 10.3377(5)$, $b = 6.0112(2)$, and $c = 4.6950(2)$.

$$V = (10.3377 \text{ \AA})(6.0112 \text{ \AA})(4.6950 \text{ \AA})$$

$$V = 291.7566 \text{ \AA}^3$$

$$\Delta V = V \times \sqrt{\left(\frac{0.0005}{10.3377}\right)^2 + \left(\frac{0.0002}{6.0112}\right)^2 + \left(\frac{0.0002}{4.6950}\right)^2}$$

$$\Delta V = 0.02116$$

Since b and c have only 5 significant figures, the final computed volume is 291.76(2) $\text{\AA}^3$.

On the next page is a table summarizing the magnetic symmetry and refined structural variables which will be used to compute $\mathbf{T}_{net}$. It is a useful reference for the rest of this section.

Table 4.10: Summary of the magnetic symmetry and refined magnetic structure in various olivine analogs

Composition	B.V. ^a	M.S.G. ^b	P.G. ^c	$\mathbf{m}_x$ (μ_B)	$\mathbf{m}_y$ (μ_B)	$\mathbf{m}_z$ (μ_B)	χ^d	z^e	Vol. ^f ($\text{\AA}^3$)	Ref. ^g
LiCoPO ₄	C_y	$Pnmd'$	mmm'	n.a. ^h	3.28(4)	n.a.	0.2758(7)	0.983(2)	282.20(1)	[175]
LiFePO ₄	C_y	$Pnmd'$	mmm'	n.a.	4.19(5)	n.a.	0.2822(2)	0.9738(5)	291.76(2)	[10]
<i>t</i> -NaFePO ₄	C_y	$Pnmd'$	mmm'	n.a.	4.55(5)	n.a.	0.2875(3)	0.9853(6)	317.94(1)	[2]
LiFe _{0.4} Mn _{0.6} PO ₄	C_y	$Pnmd'$	$m'mm$	n.a.	4.00(4)	n.a.	n.r. ⁱ	n.r.	293.09(2)	[164]
LiFe _{0.3} Mn _{0.7} PO ₄	C_y	$Pnmd'$	$m'mm$	n.a.	3.80(3)	n.a.	n.r.	n.r.	295.11(1)	[164]
LiFe _{0.2} Mn _{0.8} PO ₄	C_y	$Pnmd'$	$m'mm$	n.a.	3.58(4)	n.a.	n.r.	n.r.	296.28(1)	[164]
LiNiPO ₄	$A_x + C_z$	$Pnm'a$	$mm'm$	n.d. ^j	n.a.	2.8(1)	0.2761(1)	0.9812(5)	278.07(4)	[47]
LiMnPO ₄	$C_x + A_z$	$Pn'm'd'$	$m'm'm'$	4.28(3)	n.a.	n.d.	0.2795(6)	0.976(1)	300.45(1)	[175]
Li _{0.2} CoPO ₄	$G_x + F_z$	$Pn'm'a$	$m'm'm$	3.1(1)	n.a.	n.d.	0.2684(5)	0.944(1)	264.50(3)	[9]
FePO ₄	$C_x + G_y + A_z$	$P2_12_12_1$	222	4.06(2)	0.90(6)	n.d.	0.2755(2)	0.9482(5)	266.99(4)	[10]
Li _{0.4} Fe _{0.6} Mn _{0.4} PO ₄	$C_x + G_y + A_z$	$P2_12_12_1$	222	4.13(6)	0.7(1)	n.d.	n.r.	n.r.	287.35(2)	[164]
Li _{0.5} Fe _{0.5} Mn _{0.5} PO ₄	$C_x + G_y + A_z$	$P2_12_12_1$	222	4.30(3)	0.59(3)	n.d.	n.r.	n.r.	288.97(1)	[164]
Li _{0.6} Fe _{0.4} Mn _{0.6} PO ₄	$C_x + G_y + A_z$	$P2_12_12_1$	222	3.46(3)	0.86(6)	n.d.	n.r.	n.r.	293.18(1)	[164]
Li _{0.7} Fe _{0.3} Mn _{0.7} PO ₄	$A_x + C_y + C_z$	$P2'_1/n11$	2'/ <i>m</i>	n.d.	3.49(6)	1.32(6)	n.r.	n.r.	293.42(3)	[164]
Li _{0.8} Fe _{0.2} Mn _{0.8} PO ₄	$A_x + C_y + C_z$	$P2'_1/n11$	2'/ <i>m</i>	n.d.	3.19(5)	2.64(6)	n.r.	n.r.	295.33(3)	[164]

^a Basis Vectors; ^b Magnetic space group; ^c Magnetic point group; ^d χ = fractional coordinate at the 4c site; ^e z = fractional coordinate at the 4c site; ^f Refined unit cell volume; ^g References(s) for magnetic structure; ^h n.a. = not allowed by symmetry; ⁱ n.r. = not reported; ^j n.d. = not detected, the refined error was larger than the (very small) refined moment

The final step in the process is inputting the refined parameters from Tab. 4.10 into the appropriate expression for $\mathbf{T}_{net}$. The first example will be for olivine materials the magnetic structure Γ_2^- . The formula for $\mathbf{T}_{net}$ for Γ_2^- is Eq. 4.17 from §4.2, restated here with minor formatting edits for convenience:

$$\mathbf{T}_{a+b} = \frac{(16 \mathbf{m}_y)(x - 1/4)\hat{\mathbf{k}}}{V}$$

An example calculation will be presented with the data for LiCoPO₄ from Ref. 175. The relevant refinement values are listed here, taken from Tab. 4.17: $x = 0.2758(7)$, $\mathbf{m}_y = 3.28(4) \mu_B$, and $V = 282.20(1) \text{ \AA}^3$.

$$\mathbf{T}_{a+b} = \frac{(16 \times 3.28 \mu_B)(0.2758 - 1/4)\hat{\mathbf{k}}}{282.20 \text{ \AA}^3} \quad (4.38)$$

$$\mathbf{T}_{a+b} = 0.00479796 \mu_B / \text{\AA}^3 \hat{\mathbf{k}}$$

$$\mathbf{T}_{a+b} = 4.79796 \mu_B / \text{nm}^3 \hat{\mathbf{k}}$$

The final value is expressed per nm^3 for ease of comparison and interpretation between other computed $\mathbf{T}_{net}$ values in this series of materials.

For computing the error in $\mathbf{T}_{net}$, only the error in the magnetic moments and volume will be used. The fractional coordinates are used in an expression with values which have infinite significant figures (e.g. 16, 1/4). The expressions themselves come about from the symmetry of the system, and the geometric arrangement of the r vectors. In addition, the dominant contribution to the error in the individual magnetic moments would be from the error in the magnetic moments. The dominant term contributing to the net toroidal moment is the volume term. Therefore it seems the best to estimate the error for the net toroidal moment using the error in the magnetic moment and volume terms alone, and disregard the error in the fractional coordinates. Indeed, having performed the calculation both ways, the error from the fractional coordinates did not impact

the final answer, after rounding to the nearest significant digit. This was also true for the other calculations for $\mathbf{T}_{net}$ presented in this chapter. Therefore the same methodology will be used with the rest of the examples in the chapter.

$$\Delta \mathbf{T}_{net} = \mathbf{T}_{net} \times \sqrt{\left(\frac{\Delta \mathbf{m}_y}{\mathbf{m}_y}\right)^2 + \left(\frac{\Delta V}{V}\right)^2}$$

$$\Delta \mathbf{T}_{net} = 0.00479796 \times \sqrt{\left(\frac{0.04}{3.28}\right)^2 + \left(\frac{0.01}{282.20}\right)^2}$$

$$\Delta \mathbf{T}_{net} = 0.00005851 \mu_B/\text{\AA}^3$$

$$\Delta \mathbf{T}_{net} = 0.05851 \mu_B/\text{nm}^3$$

Since the variable $\mathbf{m}_y$ has 3 significant figures, the final answer is $\mathbf{T}_{net} = 4.80(6) \mu_B/\text{nm}^3 \hat{\mathbf{k}}$. This corresponds to a net toroidal moment along the z crystallographic axis. This value along with the computed $\mathbf{T}_{net}$ for LiFePO_4 and $t\text{-NaFePO}_4$ are included in Tab. 4.11.

The next example will be for LiNiPO_4 with the magnetic structure Γ_4^- . The formula for $\mathbf{T}_{net}$ is Eq. 4.21 from §4.3, restated here with minor formatting edits for convenience:

$$\mathbf{T}_{a+b} = \frac{(4 \mathbf{m}_x)(4z-3)\hat{\mathbf{j}} + (4 \mathbf{m}_z)(-4x-1)\hat{\mathbf{j}}}{V}$$

The calculation will be presented with the data for LiNiPO_4 from Ref. 47. The relevant refinement values are listed here, taken from Tab. 4.10: $x = 0.2761(1)$, $z = 0.9812(5)$, $\mathbf{m}_z = 2.8(1) \mu_B$, $\mathbf{m}_x$ = not detected, and $V = 278.07(4) \text{\AA}^3$. Since $\mathbf{m}_x$ was not detected, that term is effectively zero.

Therefore Eq. 4.21 can be simplified further to the following:

$$\mathbf{T}_{a+b} = \frac{(4 \mathbf{m}_z)(-4x-1)\hat{\mathbf{j}}}{V}$$

$$\mathbf{T}_{a+b} = \frac{(4 \times 2.8 \mu_B)(-4 \times 0.2761 - 1)\hat{\mathbf{j}}}{278.07 \text{\AA}^3}$$

$$\mathbf{T}_{a+b} = -0.00420498 \mu_B/\text{\AA}^3 \hat{\mathbf{j}}$$

The negative sign does not have any particular meaning in this context, so the absolute value will be used for the rest of the calculations.

$$\mathbf{T}_{a+b} = 4.20498 \mu_B/\text{nm}^3 \hat{\mathbf{j}}$$

$$\Delta \mathbf{T}_{net} = \mathbf{T}_{net} \times \sqrt{\left(\frac{\Delta \mathbf{m}_z}{\mathbf{m}_z}\right)^2 + \left(\frac{\Delta V}{V}\right)^2}$$

$$\Delta \mathbf{T}_{net} = 0.00420498 \times \sqrt{\left(\frac{0.1}{2.8}\right)^2 + \left(\frac{0.04}{278.07}\right)^2}$$

$$\Delta \mathbf{T}_{net} = 0.00017137 \mu_B/\text{\AA}^3$$

$$\Delta \mathbf{T}_{net} = 0.17137 \mu_B/\text{nm}^3$$

Since the variable $\mathbf{m}_z$ has two significant figures, the final computed value is $\mathbf{T}_{net} = 4.2(2) \mu_B/\text{nm}^3 \hat{\mathbf{j}}$. This corresponds to a net toroidal moment along the y crystallographic axis.

The remaining values for $\mathbf{T}_{net}$ in Tab. 4.11 were either zero because the configuration was anti-ferrotoroidal, not computed because the material was non-toroidal, or not computed because insufficient refinement parameters were reported. This was the case for all of the lithiated and delithiated $\text{Li}_x\text{Fe}_{1-x}\text{Mn}_x\text{PO}_4$ series from Ref. 164. Figures of the refinements were included in the supplemental information, but neither .cif files nor tables of refined parameters were included in the publication.

The significance of the results of Tab. 4.11 is that LiFePO_4 has the largest computed toroidal moment. Thus far LiFePO_4 has not been explored as a candidate for ferrotoroidicity. Our research group was the first to propose it as a candidate material based upon its similar chemical and magnetic structure to LiCoPO_4 , but had no reason to expect it could be a superior candidate than LiCoPO_4 . This is particularly exciting because our research group has been able

Table 4.11: Summary of the toroidal order in various olivine analogs

Composition	T.O. ^a	$\mathbf{T}_{net}$ (μ_B/nm^3)	$\mathbf{T}_{xyz}^b$
LiCoPO ₄	FTO	4.80(6)	$\mathbf{T}_z$
LiFePO ₄	FTO	7.40(6)	$\mathbf{T}_z$
<i>t</i> -NaFePO ₄	FTO	8.59(5)	$\mathbf{T}_z$
LiFe _{0.4} Mn _{0.6} PO ₄	FTO	n.c. ^c	$\mathbf{T}_z$
LiFe _{0.3} Mn _{0.7} PO ₄	FTO	n.c.	$\mathbf{T}_z$
LiFe _{0.2} Mn _{0.8} PO ₄	FTO	n.c.	$\mathbf{T}_z$
LiNiPO ₄	FTO	4.2(2)	$\mathbf{T}_y$
LiMnPO ₄	AFTO	0	0
Li _{0.2} CoPO ₄	non	non	non
FePO ₄	AFTO	0	0
Li _{0.4} Fe _{0.6} Mn _{0.4} PO ₄	AFTO	0	0
Li _{0.5} Fe _{0.5} Mn _{0.5} PO ₄	AFTO	0	0
Li _{0.6} Fe _{0.4} Mn _{0.6} PO ₄	AFTO	0	0
Li _{0.7} Fe _{0.3} Mn _{0.7} PO ₄	FTO	n.c.	$\mathbf{T}_{yz}$
Li _{0.8} Fe _{0.2} Mn _{0.8} PO ₄	FTO	n.c.	$\mathbf{T}_{yz}$

^a Toroidal Order: AFTO = antiferrotoroidal, FTO = ferrotoroidal, non = non-toroidal; ^b $\mathbf{T}_{xyz}$ = allowed toroidal moment direction(s); ^c n.c. = not computed, need more data

to synthesize large single crystals of LiFePO₄, suitable for magneto-electric measurements and single crystal neutron experiments.

The other exciting result of the model is a detailed understanding of how an anti-ferrotoroidal material would be possible. By modeling individual toroidal moments at individual sites in the unit cell, the symmetry of the chemical and magnetic structure provides the model for where those toroidal moments are repeated and how they are oriented. By following the logical process for determining which symmetries would allow the toroidal moments to be aligned, the symmetries for them being anti-aligned are determined as well.

Fig. 4.2 & 4.3 depict for the first time a microscopic model for the location and orientation of individual toroidal moments in LiCoPO₄ and LiMnPO₄. Note that the individual toroidal

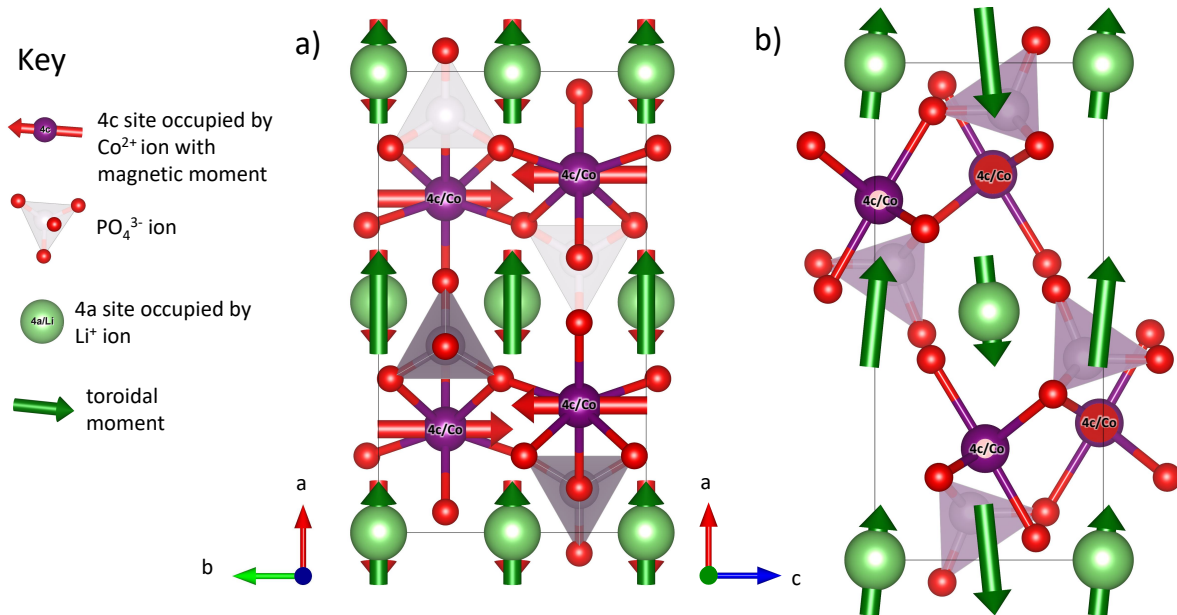


Figure 4.2: Ferrotoroidal Structure of LiCoPO_4 , viewed along the c axis (a) and the b axis (b).

moments are not co-linear with one another. Yet in the case of LiCoPO_4 , the net sum of the individual moments is along one direction, as predicted. Likewise, the net sum of the individual moments for LiMnPO_4 is zero. Just as such an arrangement of magnetic moments is called "antiferromagnetic," such an arrangement of toroidal moments is logically called "antiferrotoroidal."

Antiferrotoroidal order was discussed briefly in §2.2. Recall that Fig. 2.9 was Spaldin, Fiebig, and Mostovoy's depiction for how they anticipated YMnO_3 would be antiferrotoroidal. They suggested there would be three ferrotoroidal sublattices which together would result in a net antiferrotoroidal arrangement overall.[65] There is actually disagreement in the literature about whether the magnetic space group for YMnO_4 is $P6'_3$ (point group $6' mm'$), [182] or $P6'_3 cm'$ (point group $6'$).[183, 184] Spaldin, Fiebig, and Mostovoy do not actually cite a reference for the magnetic structure model they were using. Regardless, both possibilities would not permit either ferrotoroidal or antiferrotoroidal ordering because neither point group has the necessary $\bar{1}'$ inversion symmetry.

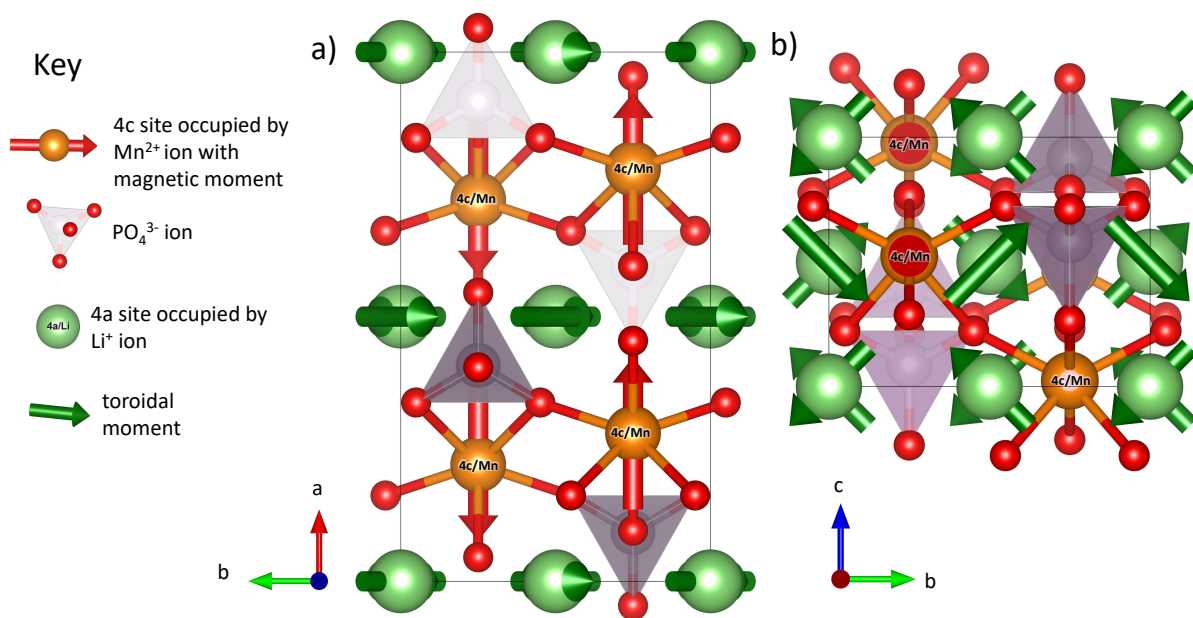


Figure 4.3: Antiferrotoroidal Structure of LiMnPO_4 , viewed along the c axis (a) and the a axis (b).

Therefore the current work is the first to suggest LiMnPO_4 as an antiferrotoroidal material. Previously our research group was interested in this material because the point group $m'm'm'$ would *not* permit a net ferrotoroidal moment. Based upon the analysis presented herein, it specifically would be antiferrotoroidal, *not* non-toroidal.

However, non-toroidal materials are also possible. It was demonstrated in §4.5 that the delithiated form of LiCoPO_4 would be non-toroidal. Its magnetic space group $Pn'm'a$ (point group $m'm'm$) would not permit the formation of individual toroidal moments at all.

Therefore, using the model presented herein, toroidal materials can be classified as ferrotoroidal, antiferrotoroidal, or non-toroidal.

As a note, there is no current model for describing a paratoroidal material, analogous to a paramagnetic material. It does not seem that such a material would be possible, since toroidal moments cannot exist independently from ordered magnetic moments.

4.9: Toroidal Structure in the Pyroxene Structure Type

The second most intensely studied candidate ferrotoroidic material is $\text{LiFeSi}_2\text{O}_6$, which has the pyroxene structure type and the chemical space group $P2_1/c$. This section will demonstrate how to construct a toroidal lattice with the pyroxene structure type, using the same method as for olivine (§4.1). This section will begin with describing the chemical and magnetic structure of $\text{LiFeSi}_2\text{O}_6$. The process for constructing the toroidal lattice will then be demonstrated for $P2_1/c'$ and $P2'_1/c$, the two magnetic structures which permit ferrotoroidal ordering in this structure type. The section will conclude by comparing the predicted toroidal moments of various silicates and germanates with analogous chemical and magnetic structures.

The three dimensional magnetic space group table for $P2'_1/c$ (14.3.88) is found on page 2619 of the Magnetic Group Tables.[178] The full magnetic space group is $P12'_1/c1$, and the point group is $2'_y/m_y$. Recall from Tab. 3.4 and 3.6 in §3.4 that this point group permits a net ferrotoroidal moment with components along the x and z axes. The coordinates of the Wyckoff positions are given in Tab. 4.12. There are eight positions with the site symmetry $\bar{1}'$ divided between four sites: $2a$, $2b$, $2c$, and $2d$.

The chemical structure of $\text{LiFeSi}_2\text{O}_6$ and various other materials with the pyroxene structure were discussed at the beginning of §2.6. Figure 4.4 depicts the magnetic structure of $\text{LiFeSi}_2\text{O}_6$. The magnetic moments are oriented mostly along the the c axis, but tilted slightly towards the a axis by about 6 degrees.[115, 123] In $\text{LiFeSi}_2\text{O}_6$, all the atoms are located on the general position $4e$. To reiterate: the $2a$, $2b$, $2c$, and $2d$ sites with $\bar{1}'$ symmetry are *not* occupied in $\text{LiFeSi}_2\text{O}_6$. Furthermore, those sites are *not* occupied in *any* pyroxene materials discussed. The primed inversion sites are labeled merely for ease of communication.

Table 4.12: Wyckoff letters in the crystallographic space groups $P2_1'/c$ and $P2_1/c'$, along with their multiplicities, site symmetries and coordinates. An index has been assigned to each coordinate for ease of communication.

Mult.	Wyck.	Sym.	Index	Coordinates
4	e	1	$e1$	x, y, z
			$e2$	$\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$
			$e3$	$\bar{x}, \bar{y}, \bar{z}$
			$e4$	$x, \bar{y} + \frac{1}{2}, z + \frac{1}{2}$
2	d	$\bar{1}'$	$d1$	$\frac{1}{2}, 0, \frac{1}{2}$
			$d2$	$\frac{1}{2}, \frac{1}{2}, 0$
2	c	$\bar{1}'$	$c1$	$0, 0, \frac{1}{2}$
			$c2$	$0, \frac{1}{2}, 0$
2	b	$\bar{1}'$	$b1$	$\frac{1}{2}, 0, 0$
			$b2$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
2	a	$\bar{1}'$	$a1$	$0, 0, 0$
			$a2$	$0, \frac{1}{2}, \frac{1}{2}$

The r vectors are defined in the same manner as the olivine structure in 4.1. For each $\mathbf{r}_\alpha^\beta$ vector, the α is the index of the magnetic atom, and the β is the index of the primed inversion site. Refer to Tab. 4.12 for the indices labels.

However, verifying the lengths of the r vectors is slightly more complicated in $P2_1/c$ than $Pnma$ because the unit cell is monoclinic. Therefore instead of Eq. 4.5, the following unit cell transformation is used, where a, b, c , and β are the unit cell parameters:

$$\begin{aligned}
 \hat{x} &= \Delta x \times a \times \sin \beta \\
 \hat{y} &= \Delta y \times b \\
 \hat{z} &= (\Delta z \times c) + (\Delta x \times a \times \cos \beta)
 \end{aligned} \tag{4.39}$$

The length of the unit vector is calculated in the same manner as in §4.1, using Eq. 4.6. An example calculation is given below for the $\mathbf{r}_{e1}^{a2}$ vector for the structure of $\text{LiFeSi}_2\text{O}_6$ depicted in Fig. 4.4.[115, 123] In the computation, $x = 0.25022$, $y = 0.64788$, and $z = 0.23528$. The unit cell

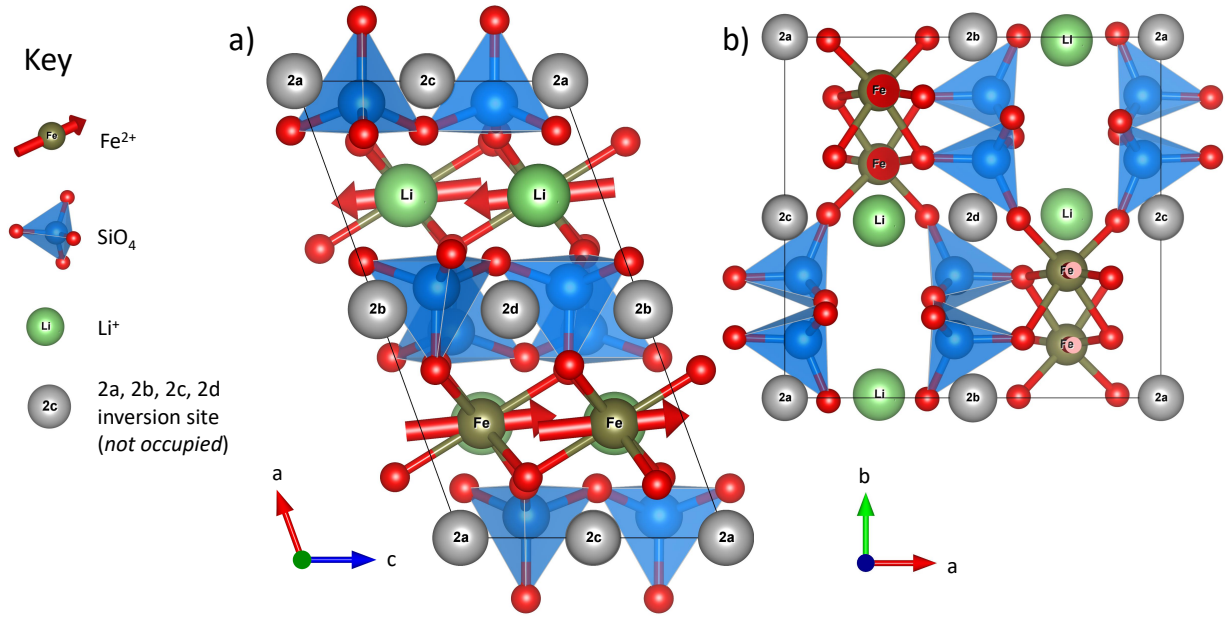


Figure 4.4: Magnetic Structure of $\text{LiFeSi}_2\text{O}_6$, viewed along the b axis (a) and the c axis (b).

parameters are: $a = 9.622\text{\AA}$, $b = 8.664\text{\AA}$, $c = 5.2555\text{\AA}$, and $\beta = 109.95^\circ$.

$$\mathbf{r}_{e1}^{a2} = \begin{pmatrix} +x \\ +(y - \frac{1}{2}) \\ -(-z + \frac{1}{2}) \end{pmatrix} = \begin{pmatrix} +0.25022 \\ +0.14788 \\ -0.26472 \end{pmatrix} \quad (4.40)$$

$$\Delta x = +0.25022 \quad \Delta y = +0.14788 \quad \Delta z = -0.26472$$

$$\hat{x} = 0.25022 \times 9.622\text{\AA} \times \sin 109.95^\circ = 2.2631\text{\AA}$$

$$\hat{y} = 0.14788 \times 8.664\text{\AA} = 1.2812\text{\AA}$$

$$\hat{z} = (-0.26472 \times 5.2555\text{\AA}) + (0.25022 \times 9.622\text{\AA} \times \cos 109.95^\circ) = -2.2127\text{\AA}$$

$$\text{length} = \sqrt{(2.2631\text{\AA})^2 + (1.2812\text{\AA})^2 + (-2.2127\text{\AA})^2} = 3.415\text{\AA}$$

The calculated length agrees with the length computed in my crystal structure viewer software.

The complete set of $\mathbf{r}_\alpha^\beta$ vectors for this structure type are listed in Tab. 4.13.

Table 4.13: Definitions of the $\mathbf{r}_\alpha^\beta$ vectors centered about the $2a$, $2b$, $2c$, and $2d$ sites for the toroidal moments in the pyroxene structure with the space group $P2_1/c$

$\mathbf{r}_{e1}^{a1} = \begin{pmatrix} +x \\ -(-y+1) \\ +z \end{pmatrix}$	$\mathbf{r}_{e3}^{a1} = \begin{pmatrix} -x \\ +(-y+1) \\ -z \end{pmatrix}$	$\mathbf{r}_{e1}^{c1} = \begin{pmatrix} +x \\ -(-y+1) \\ -(-z+\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{e3}^{c1} = \begin{pmatrix} -x \\ +(-y+1) \\ +(-z+\frac{1}{2}) \end{pmatrix}$
$\mathbf{r}_{e2}^{a1} = \begin{pmatrix} -x \\ +(y-\frac{1}{2}) \\ +(-z+\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{e4}^{a1} = \begin{pmatrix} +x \\ -(y-\frac{1}{2}) \\ -(-z+\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{e2}^{c1} = \begin{pmatrix} -x \\ +(y-\frac{1}{2}) \\ -z \end{pmatrix}$	$\mathbf{r}_{e4}^{c1} = \begin{pmatrix} +x \\ -(y-\frac{1}{2}) \\ +z \end{pmatrix}$
$\mathbf{r}_{e1}^{a2} = \begin{pmatrix} +x \\ +(y-\frac{1}{2}) \\ -(-z+\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{e3}^{a2} = \begin{pmatrix} -x \\ -(y-\frac{1}{2}) \\ +(-z+\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{e1}^{c2} = \begin{pmatrix} +x \\ +(y-\frac{1}{2}) \\ +z \end{pmatrix}$	$\mathbf{r}_{e3}^{c2} = \begin{pmatrix} -x \\ -(y-\frac{1}{2}) \\ -z \end{pmatrix}$
$\mathbf{r}_{e2}^{a2} = \begin{pmatrix} -x \\ -(-y+1) \\ -z \end{pmatrix}$	$\mathbf{r}_{e4}^{a2} = \begin{pmatrix} +x \\ +(-y+1) \\ +z \end{pmatrix}$	$\mathbf{r}_{e2}^{c2} = \begin{pmatrix} -x \\ -(-y+1) \\ +(-z+\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{e4}^{c2} = \begin{pmatrix} +x \\ +(-y+1) \\ -(-z+\frac{1}{2}) \end{pmatrix}$
$\mathbf{r}_{e1}^{b1} = \begin{pmatrix} -(-x+\frac{1}{2}) \\ -(-y+1) \\ +z \end{pmatrix}$	$\mathbf{r}_{e3}^{b1} = \begin{pmatrix} +(-x+\frac{1}{2}) \\ +(-y+1) \\ -z \end{pmatrix}$	$\mathbf{r}_{e1}^{d1} = \begin{pmatrix} -(-x+\frac{1}{2}) \\ -(-y+1) \\ -(-z+\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{e3}^{d1} = \begin{pmatrix} +(-x+\frac{1}{2}) \\ +(-y+1) \\ +(-z+\frac{1}{2}) \end{pmatrix}$
$\mathbf{r}_{e2}^{b1} = \begin{pmatrix} +(-x+\frac{1}{2}) \\ +(y-\frac{1}{2}) \\ +(-z+\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{e4}^{b1} = \begin{pmatrix} -(-x+\frac{1}{2}) \\ -(y-\frac{1}{2}) \\ -(-z+\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{e2}^{d1} = \begin{pmatrix} +(-x+\frac{1}{2}) \\ +(y-\frac{1}{2}) \\ -z \end{pmatrix}$	$\mathbf{r}_{e4}^{d1} = \begin{pmatrix} -(-x+\frac{1}{2}) \\ -(y-\frac{1}{2}) \\ +z \end{pmatrix}$
$\mathbf{r}_{e1}^{b2} = \begin{pmatrix} -(-x+\frac{1}{2}) \\ +(y-\frac{1}{2}) \\ -(-z+\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{e3}^{b2} = \begin{pmatrix} +(-x+\frac{1}{2}) \\ -(y-\frac{1}{2}) \\ +(-z+\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{e1}^{d2} = \begin{pmatrix} -(-x+\frac{1}{2}) \\ +(y-\frac{1}{2}) \\ +z \end{pmatrix}$	$\mathbf{r}_{e3}^{d2} = \begin{pmatrix} +(-x+\frac{1}{2}) \\ -(y-\frac{1}{2}) \\ -z \end{pmatrix}$
$\mathbf{r}_{e2}^{b2} = \begin{pmatrix} +(-x+\frac{1}{2}) \\ -(-y+1) \\ -z \end{pmatrix}$	$\mathbf{r}_{e4}^{b2} = \begin{pmatrix} -(-x+\frac{1}{2}) \\ +(-y+1) \\ +z \end{pmatrix}$	$\mathbf{r}_{e2}^{d2} = \begin{pmatrix} +(-x+\frac{1}{2}) \\ -(-y+1) \\ +(-z+\frac{1}{2}) \end{pmatrix}$	$\mathbf{r}_{e4}^{d2} = \begin{pmatrix} -(-x+\frac{1}{2}) \\ +(-y+1) \\ -(-z+\frac{1}{2}) \end{pmatrix}$

Table 4.14: Magnetic symmetry associated with the four irreducible representations of the parent paramagnetic space group $P2_1/c1'$. Macroscopic Properties from Tab. 3.6 in §3.4

I.R. ^a	M.S.G. ^b	M.P.G. ^c	B.V. ^d	M.O. ^e	M.P.D. ^f
Γ_1^+	$P2_1/c$	$2/m$	$G_x + F_y + G_z$	FM	$\mathbf{M}_y$
Γ_2^+	$P2_1'/c'$	$2'/m'$	$F_x + G_y + F_z$	FM	$\mathbf{M}_{xz}$
Γ_1^-	$P2_1/c'$	$2/m'$	$A_x + C_y + A_z$	AFM	$\mathbf{T}_y$
Γ_2^-	$P2_1'/c$	$2'/m$	$C_x + A_y + C_z$	AFM	$\mathbf{T}_{xz}$

^aIrreducible Representation, superscript (+) indicates gerade, superscript (-) indicates ungerade with respect to spatial inversion symmetry ($\bar{1}$); ^bMagnetic Space Group; ^cMagnetic Point Group; ^dBasis Vectors of the spin modes, which are defined as ($F = \uparrow\uparrow\uparrow\uparrow$), ($G = \uparrow\downarrow\uparrow\downarrow$), ($C = \uparrow\uparrow\downarrow\downarrow$), and ($A = \uparrow\downarrow\downarrow\uparrow$) for the four magnetic atoms. The subscripts x , y , and z define along which crystallographic direction the moments are parallel. ^eMagnetic Order; AFM = antiferromagnetic, FM = ferromagnetic ^fMacroscopic Property Direction; $\mathbf{M}$ = net magnetic moment and $\mathbf{T}$ = net toroidal moment

There are four irreducible representations for the parent paramagnetic group $P2_1/c1'$, listed in Tab. 4.14. Note the basis vectors are expressed with respect to Cartesian coordinates. This is important because the unit cell is monoclinic. As a reminder, the F -type, C -type, G -type, and A -type distinctions for the symmetry modes refer to the first, second, third, and fourth atoms sequentially. Refer to the general position of Tab. 4.12 for the order of the four iron atoms.

Notice how both *gerade* representations (Γ_1^+ and Γ_2^+) contain F -type basis vectors. Therefore these correspond to ferromagnetic configurations and cannot be ferrotoroidal. However, both ungerade representations (Γ_1^- and Γ_2^-) are antiferromagnetic. They have sites of $\bar{1}'$ inversion (Tab. 4.12). Also, their point groups permit ferrotoroidal order (Tab. 3.4). Therefore, §4.10 & 4.11 will present computations for $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$ for only these magnetic structures. They will be compared with one another in §4.12. Note that no magnetic structure for the pyroxene materials would result in an anti-ferrotoroidal arrangement.

4.10: Example defining $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$ using Γ_1^-

This section reports the expressions $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$ for $\text{LiFeSi}_2\text{O}_6$. [123] The magnetic structure is $P2_1/c'$ (point group = $2/m'$), which corresponds to Γ_1^- , according to the labeling scheme used in Tab. 4.14. The magnetic structure is indexed under the number 14.4.89 in the Magnetic Space Group Tables. [178] Its full international symbol is $P12_1/c'1$.

Tab. 4.15 lists the $\mathbf{m}^\alpha$ spin components of the basis vectors $A_x + C_y + A_z$.

Table 4.15: Definitions of the $\mathbf{m}^\alpha$ vectors for the spin modes $A_x + C_y + A_z$ of Γ_1^-

Label	Spin Mode	$\mathbf{m}_x^\alpha$
$\mathbf{m}^{e1}$	$+s_x^{e1} + s_y^{e1} + s_z^{e1}$	$+\mathbf{m}_x^{e1} + \mathbf{m}_y^{e1} + \mathbf{m}_z^{e1}$
$\mathbf{m}^{e2}$	$-s_x^{e2} + s_y^{e2} - s_z^{e2}$	$-\mathbf{m}_x^{e1} + \mathbf{m}_y^{e1} - \mathbf{m}_z^{e1}$
$\mathbf{m}^{e3}$	$-s_x^{e3} - s_y^{e3} - s_z^{e3}$	$-\mathbf{m}_x^{e1} - \mathbf{m}_y^{e1} - \mathbf{m}_z^{e1}$
$\mathbf{m}^{e4}$	$+s_x^{e4} - s_y^{e1} + s_z^{e4}$	$+\mathbf{m}_x^{e1} - \mathbf{m}_y^{e1} + \mathbf{m}_z^{e1}$

The expressions for $\mathbf{t}_\gamma$ are defined according to Eq. 4.9, using the relevant $\mathbf{r}_\alpha^\beta$ vectors from Tab. 4.13 and $\mathbf{m}^\alpha$ vectors from Tab. 4.15. The eight expressions for $\mathbf{t}_\gamma$ are given below.

$$\mathbf{t}_{a1} = \frac{1}{2} \sum_{a1} \mathbf{r}_\alpha^{a1} \times \mathbf{m}^\alpha = [\mathbf{r}_{e1}^{a1} \times \mathbf{m}^{e1}] + [\mathbf{r}_{e3}^{a1} \times \mathbf{m}^{e3}] + [\mathbf{r}_{e2}^{a1} \times \mathbf{m}^{e2}] + [\mathbf{r}_{e4}^{a1} \times \mathbf{m}^{e4}] \quad (4.41)$$

$$\mathbf{t}_{a2} = \frac{1}{2} \sum_{a2} \mathbf{r}_\alpha^{a2} \times \mathbf{m}^\alpha = [\mathbf{r}_{e1}^{a2} \times \mathbf{m}^{e1}] + [\mathbf{r}_{e3}^{a2} \times \mathbf{m}^{e3}] + [\mathbf{r}_{e2}^{a2} \times \mathbf{m}^{e2}] + [\mathbf{r}_{e4}^{a2} \times \mathbf{m}^{e4}]$$

$$\mathbf{t}_{b1} = \frac{1}{2} \sum_{b1} \mathbf{r}_\alpha^{b1} \times \mathbf{m}^\alpha = [\mathbf{r}_{e1}^{b1} \times \mathbf{m}^{e1}] + [\mathbf{r}_{e3}^{b1} \times \mathbf{m}^{e3}] + [\mathbf{r}_{e2}^{b1} \times \mathbf{m}^{e2}] + [\mathbf{r}_{e4}^{b1} \times \mathbf{m}^{e4}] \quad (4.42)$$

$$\mathbf{t}_{b2} = \frac{1}{2} \sum_{b2} \mathbf{r}_\alpha^{b2} \times \mathbf{m}^\alpha = [\mathbf{r}_{e1}^{b2} \times \mathbf{m}^{e1}] + [\mathbf{r}_{e3}^{b2} \times \mathbf{m}^{e3}] + [\mathbf{r}_{e2}^{b2} \times \mathbf{m}^{e2}] + [\mathbf{r}_{e4}^{b2} \times \mathbf{m}^{e4}]$$

$$\mathbf{t}_{c1} = \frac{1}{2} \sum_{c1} \mathbf{r}_\alpha^{c1} \times \mathbf{m}^\alpha = [\mathbf{r}_{e1}^{c1} \times \mathbf{m}^{e1}] + [\mathbf{r}_{e3}^{c1} \times \mathbf{m}^{e3}] + [\mathbf{r}_{e2}^{c1} \times \mathbf{m}^{e2}] + [\mathbf{r}_{e4}^{c1} \times \mathbf{m}^{e4}] \quad (4.43)$$

$$\mathbf{t}_{c2} = \frac{1}{2} \sum_{c2} \mathbf{r}_\alpha^{c2} \times \mathbf{m}^\alpha = [\mathbf{r}_{e1}^{c2} \times \mathbf{m}^{e1}] + [\mathbf{r}_{e3}^{c2} \times \mathbf{m}^{e3}] + [\mathbf{r}_{e2}^{c2} \times \mathbf{m}^{e2}] + [\mathbf{r}_{e4}^{c2} \times \mathbf{m}^{e4}]$$

$$\mathbf{t}_{d1} = \frac{1}{2} \sum_{d1} \mathbf{r}_{\alpha}^{d1} \times \mathbf{m}^{\alpha} = [\mathbf{r}_{e1}^{d1} \times \mathbf{m}^{e1}] + [\mathbf{r}_{e3}^{d1} \times \mathbf{m}^{e3}] + [\mathbf{r}_{e2}^{d1} \times \mathbf{m}^{e2}] + [\mathbf{r}_{e4}^{d1} \times \mathbf{m}^{e4}] \quad (4.44)$$

$$\mathbf{t}_{d2} = \frac{1}{2} \sum_{d2} \mathbf{r}_{\alpha}^{d2} \times \mathbf{m}^{\alpha} = [\mathbf{r}_{e1}^{d2} \times \mathbf{m}^{e1}] + [\mathbf{r}_{e3}^{d2} \times \mathbf{m}^{e3}] + [\mathbf{r}_{e2}^{d2} \times \mathbf{m}^{e2}] + [\mathbf{r}_{e4}^{d2} \times \mathbf{m}^{e4}]$$

Since there are x , y , and z spin mode components, Eq. 4.12 is used without modification.

To solve for $\mathbf{t}_{\gamma}$, Eq. 4.12 is substituted into Eq. 4.41, 4.42, 4.43, & 4.44. This is done in the same manner as in §4.2. The solutions are given below:

$$\mathbf{t}_{a1} = [(-1/2)\mathbf{m}_z + (-1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(2z - 1/2)\mathbf{m}_x + (-2x)\mathbf{m}_z] \hat{\mathbf{j}} + [(1/2)\mathbf{m}_x] \hat{\mathbf{k}} \quad (4.45)$$

$$\mathbf{t}_{a2} = [(1/2)\mathbf{m}_z + (1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(2z - 1/2)\mathbf{m}_x + (-2x)\mathbf{m}_z] \hat{\mathbf{j}} + [(-1/2)\mathbf{m}_x] \hat{\mathbf{k}}$$

$$\mathbf{t}_{b1} = [(-1/2)\mathbf{m}_z + (-1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(2z - 1/2)\mathbf{m}_x + (-2x + 1)\mathbf{m}_z] \hat{\mathbf{j}} + [(1/2)\mathbf{m}_x] \hat{\mathbf{k}} \quad (4.46)$$

$$\mathbf{t}_{b2} = [(1/2)\mathbf{m}_z + (1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(2z - 1/2)\mathbf{m}_x + (-2x + 1)\mathbf{m}_z] \hat{\mathbf{j}} + [(-1/2)\mathbf{m}_x] \hat{\mathbf{k}}$$

$$\mathbf{t}_{c1} = [(-1/2)\mathbf{m}_z + (1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(2z - 1/2)\mathbf{m}_x + (-2x)\mathbf{m}_z] \hat{\mathbf{j}} + [(1/2)\mathbf{m}_x] \hat{\mathbf{k}} \quad (4.47)$$

$$\mathbf{t}_{c2} = [(1/2)\mathbf{m}_z + (-1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(2z - 1/2)\mathbf{m}_x + (-2x)\mathbf{m}_z] \hat{\mathbf{j}} + [(-1/2)\mathbf{m}_x] \hat{\mathbf{k}}$$

$$\mathbf{t}_{d1} = [(-1/2)\mathbf{m}_z + (1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(2z - 1/2)\mathbf{m}_x + (-2x + 1)\mathbf{m}_z] \hat{\mathbf{j}} + [(1/2)\mathbf{m}_x] \hat{\mathbf{k}} \quad (4.48)$$

$$\mathbf{t}_{d2} = [(1/2)\mathbf{m}_z + (-1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(2z - 1/2)\mathbf{m}_x + (-2x + 1)\mathbf{m}_z] \hat{\mathbf{j}} + [(-1/2)\mathbf{m}_x] \hat{\mathbf{k}}$$

Note, the coefficients in each pair of expressions have the same magnitude, but with a different pattern of positive or negative sign.

The net toroidal moment is calculated using Eq. 4.16 from §4.2:

$$\mathbf{T}_a = \frac{[(-4x)\mathbf{m}_z + (4z - 1)\mathbf{m}_x] \hat{\mathbf{j}}}{abc \sin(\beta)}$$

$$\mathbf{T}_b = \frac{[(-4x + 2)\mathbf{m}_z + (4z - 1)\mathbf{m}_x] \hat{\mathbf{j}}}{abc \sin(\beta)}$$

$$\begin{aligned}
\mathbf{T}_c &= \frac{[(-4x)\mathbf{m}_z + (4z-1)\mathbf{m}_x]\hat{\mathbf{j}}}{abc \sin(\beta)} \\
\mathbf{T}_d &= \frac{[(-4x+2)\mathbf{m}_z + (4z-1)\mathbf{m}_x]\hat{\mathbf{j}}}{abc \sin(\beta)} \\
\mathbf{T}_{a+b+c+d} &= \frac{[4(-4x+1)\mathbf{m}_z + 4(4z-1)\mathbf{m}_x]\hat{\mathbf{j}}}{abc \sin(\beta)} \tag{4.49}
\end{aligned}$$

Unlike the olivine system, where $\mathbf{T}_a = \mathbf{T}_b$, in this system $\mathbf{T}_a = \mathbf{T}_c$ and $\mathbf{T}_b = \mathbf{T}_d$. Regardless, $\mathbf{T}_a$, $\mathbf{T}_b$, $\mathbf{T}_c$, $\mathbf{T}_d$, and $\mathbf{T}_{a+b+c+d}$ all give an expression with only a component along $\hat{\mathbf{j}}$. This corresponds to the y direction. Therefore this result is consistent with Tab. 4.14 & 3.6, which indicates that Γ_1^- would allow a toroidal moment $\mathbf{T}_y$ along the y axis.

The next section (§4.11) will report the same analysis for Γ_2^- but no others, since that is the only other representation which allows a net toroidal moment in this structure type.

4.11: Example defining $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$ using Γ_2^-

This section reports the expressions $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$ for $\text{LiCrSi}_2\text{O}_6$, $\text{LiCrGe}_2\text{O}_6$, and $\text{LiFeGe}_2\text{O}_6$. [123, 130, 131] The magnetic structure for each is $P2'_1/c$ (point group = $2'/m$), which corresponds to Γ_2^- , according to the labeling scheme used in Tab. 4.14. The magnetic structure is indexed under the number 14.3.88 in the Magnetic Space Group Tables. [178] Its full international symbol is $P12'_1/c1$.

Tab. 4.16 lists the $\mathbf{m}^\alpha$ spin components of the basis vectors $C_x + A_y + C_z$.

Table 4.16: Definitions of the $\mathbf{m}^\alpha$ vectors for the spin modes $C_x + A_y + C_z$ of Γ_2^-

Label	Spin Mode	$\mathbf{m}_x^\alpha$
$\mathbf{m}^{e1}$	$+s_x^{e1} + s_y^{e1} + s_z^{e1}$	$+\mathbf{m}_x^{e1} + \mathbf{m}_y^{e1} + \mathbf{m}_z^{e1}$
$\mathbf{m}^{e2}$	$+s_x^{e2} - s_y^{e2} + s_z^{e2}$	$+\mathbf{m}_x^{e1} - \mathbf{m}_y^{e1} + \mathbf{m}_z^{e1}$
$\mathbf{m}^{e3}$	$-s_x^{e3} - s_y^{e3} - s_z^{e3}$	$-\mathbf{m}_x^{e1} - \mathbf{m}_y^{e1} - \mathbf{m}_z^{e1}$
$\mathbf{m}^{e4}$	$-s_x^{e4} + s_y^{e1} - s_z^{e4}$	$-\mathbf{m}_x^{e1} + \mathbf{m}_y^{e1} - \mathbf{m}_z^{e1}$

Since there are x , y , and z spin mode components, Eq. 4.12 is used without modification.

The expressions for $\mathbf{t}_\gamma$ are the same as those from §4.10, Eq. 4.41, 4.42, 4.43, and & 4.44.

Substituting Eq. 4.12 into Eq. 4.41–4.44 gives the following expressions for $\mathbf{t}_\gamma$:

$$\begin{aligned}
 \mathbf{t}_{a1} &= [(2y - 3/2)\mathbf{m}_z + (-2z + 1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(+1/2)\mathbf{m}_x] \hat{\mathbf{j}} + [(2x)\mathbf{m}_y + (-2y + 3/2)\mathbf{m}_x] \hat{\mathbf{k}} \\
 \mathbf{t}_{a2} &= [(2y - 3/2)\mathbf{m}_z + (-2z + 1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(-1/2)\mathbf{m}_x] \hat{\mathbf{j}} + [(2x)\mathbf{m}_y + (-2y + 3/2)\mathbf{m}_x] \hat{\mathbf{k}} \quad (4.50) \\
 \mathbf{t}_{b1} &= [(2y - 3/2)\mathbf{m}_z + (-2z + 1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(+1/2)\mathbf{m}_x] \hat{\mathbf{j}} + [(2x - 1)\mathbf{m}_y + (-2y + 3/2)\mathbf{m}_x] \hat{\mathbf{k}} \\
 \mathbf{t}_{b2} &= [(2y - 3/2)\mathbf{m}_z + (-2z + 1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(-1/2)\mathbf{m}_x] \hat{\mathbf{j}} + [(2x - 1)\mathbf{m}_y + (-2y + 3/2)\mathbf{m}_x] \hat{\mathbf{k}} \quad (4.51)
 \end{aligned}$$

$$\begin{aligned}
 \mathbf{t}_{c1} &= [(2y - 3/2)\mathbf{m}_z + (-2z + 1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(-1/2)\mathbf{m}_x] \hat{\mathbf{j}} + [(2x)\mathbf{m}_y + (-2y + 3/2)\mathbf{m}_x] \hat{\mathbf{k}} \\
 \mathbf{t}_{c2} &= [(2y - 3/2)\mathbf{m}_z + (-2z + 1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(+1/2)\mathbf{m}_x] \hat{\mathbf{j}} + [(2x)\mathbf{m}_y + (-2y + 3/2)\mathbf{m}_x] \hat{\mathbf{k}} \quad (4.52)
 \end{aligned}$$

$$\begin{aligned}
 \mathbf{t}_{d1} &= [(2y - 3/2)\mathbf{m}_z + (-2z + 1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(-1/2)\mathbf{m}_x] \hat{\mathbf{j}} + [(2x - 1)\mathbf{m}_y + (-2y + 3/2)\mathbf{m}_x] \hat{\mathbf{k}} \\
 \mathbf{t}_{d2} &= [(2y - 3/2)\mathbf{m}_z + (-2z + 1/2)\mathbf{m}_y] \hat{\mathbf{i}} + [(+1/2)\mathbf{m}_x] \hat{\mathbf{j}} + [(2x - 1)\mathbf{m}_y + (-2y + 3/2)\mathbf{m}_x] \hat{\mathbf{k}} \quad (4.53)
 \end{aligned}$$

Again, the coefficients in each pair have the same magnitude, but have a different pattern of positive or negative sign.

The net toroidal moment is calculated using Eq. 4.16 from §4.2:

$$\mathbf{T}_a = \frac{[(4y - 3)\mathbf{m}_z + (-4z + 1)\mathbf{m}_y] \hat{\mathbf{i}} + [(4x)\mathbf{m}_y + (-4y + 3)\mathbf{m}_x] \hat{\mathbf{k}}}{abc \sin(\beta)}$$

$$\begin{aligned}
\mathbf{T}_b &= \frac{[(4y-3)\mathbf{m}_z + (-4z+1)\mathbf{m}_y]\hat{\mathbf{i}} + [(4x-2)\mathbf{m}_y + (-4y+3)\mathbf{m}_x]\hat{\mathbf{k}}}{abc \sin(\beta)} \\
\mathbf{T}_c &= \frac{[(4y-3)\mathbf{m}_z + (-4z+1)\mathbf{m}_y]\hat{\mathbf{i}} + [(4x)\mathbf{m}_y + (-4y+3)\mathbf{m}_x]\hat{\mathbf{k}}}{abc \sin(\beta)} \\
\mathbf{T}_d &= \frac{[(4y-3)\mathbf{m}_z + (-4z+1)\mathbf{m}_y]\hat{\mathbf{i}} + [(4x-2)\mathbf{m}_y + (-4y+3)\mathbf{m}_x]\hat{\mathbf{k}}}{abc \sin(\beta)} \\
\mathbf{T}_{a+b+c+d} &= \frac{[4(4y-3)\mathbf{m}_z + 4(-4z+1)\mathbf{m}_y]\hat{\mathbf{i}} + [4(4x-1)\mathbf{m}_y + 4(-4y+3)\mathbf{m}_x]\hat{\mathbf{k}}}{abc \sin(\beta)} \quad (4.54)
\end{aligned}$$

As was seen in §4.11, $\mathbf{T}_a = \mathbf{T}_c$ and $\mathbf{T}_b = \mathbf{T}_d$. In addition, $\mathbf{T}_a$, $\mathbf{T}_b$, $\mathbf{T}_c$, $\mathbf{T}_d$, and $\mathbf{T}_{a+b+c+d}$ all give an expression with the same components. In this case, it is along $\hat{\mathbf{i}}$ and $\hat{\mathbf{k}}$, which corresponds to having components along both the x and z axes. Therefore this result is also consistent with Tab. 4.14 & 3.6, which indicates that Γ_2^- would allow a toroidal moment $\mathbf{T}_{xz}$ along the x and z axes.

The next section (§4.12) is a more detailed discussion of the expressions for $\mathbf{t}_\gamma$ and $\mathbf{T}_{net}$.

4.12: Comparison of the Magnetic and Toroidal Structures in Various Antiferromagnetic Materials with the Pyroxene Structure Type

As in §4.8, the first step to calculating $\mathbf{T}_{net}$ is to obtain all the necessary computed variables from the neutron powder diffraction refinement. Since the pyroxene structure has a monoclinic unit cell, the calculation for the volume of the unit cell is given here.

The formula for the volume of the unit cell (V) for a monoclinic lattice is:

$$V = abc \sin \beta \quad (4.55)$$

where a , b , c , and β are the lattice parameters.

The formula for the propagation of error is broken into two parts. The first part (Eq. 4.56) is to

calculate the error for abc . The second (Eq. 4.57) is to calculate the error in V including the error for $\sin \beta$:

$$\frac{\Delta abc}{abc} = \sqrt{\left(\frac{\Delta a}{a}\right)^2 + \left(\frac{\Delta b}{b}\right)^2 + \left(\frac{\Delta c}{c}\right)^2} \quad (4.56)$$

$$\Delta V = \sqrt{(\sin^2 \beta) (\Delta abc)^2 + (abc)^2 (\cos^2 \beta) (\Delta \beta)^2} \quad (4.57)$$

Ref. [131] did not report the refined unit cell volume for $\text{LiCrGe}_2\text{O}_6$; and Ref. [130] did not report it for $\text{LiCrSi}_2\text{O}_6$. The example calculation below is for $\text{LiCrGe}_2\text{O}_6$. The reported unit cell parameters are: $a = 9.79037(12)$, $b = 8.71595(12)$, $c = 5.33641(7)$, and $\beta = 108.9300(7)^\circ$ which is $1.9011872(122)$ in radians.

$$abc = (9.79037 \text{ \AA})(8.71595 \text{ \AA})(5.33641 \text{ \AA})$$

$$abc = 455.3685 \text{ \AA}^3$$

$$\Delta abc = abc \times \sqrt{\left(\frac{\Delta a}{a}\right)^2 + \left(\frac{\Delta b}{b}\right)^2 + \left(\frac{\Delta c}{c}\right)^2}$$

$$\Delta abc = abc \times 0.000022624$$

$$\Delta abc = 0.010302$$

$$V = abc \sin \beta$$

$$V = (455.3685 \text{ \AA}^3) \sin(1.90118715)$$

$$V = 430.74018 \text{ \AA}^3$$

$$\Delta V = \sqrt{(\sin^2 \beta) (\Delta abc)^2 + (abc)^2 (\cos^2 \beta) (\Delta \beta)^2}$$

$$\Delta V = \sqrt{(\sin^2(1.90118715)) (0.010302)^2 + (455.3685)^2 (\cos^2(1.9011872)) (0.0000122)^2}$$

$$\Delta V = 0.011547097$$

Since a , b , and c have 6 significant figures, the volume could be rounded to 430.740. However,

the propagated error is to the hundredths decimal place. Therefore the final computed volume is 430.74(1) Å³.

On the next page is a summary table of all the relevant refinement parameters to calculate $\mathbf{T}_{net}$. It is a useful reference for the rest of this section.

Table 4.17: Summary of the magnetic symmetry and refined magnetic structure in various pyroxene analogs

Composition	B.V. ^a	M.S.G. ^b	P.G. ^c	$\mathbf{m}_x$ (μ_B)	$\mathbf{m}_y$ (μ_B)	$\mathbf{m}_z$ (μ_B)	x^d	y^e	z^f	Vol. ^g ($\text{\AA}^3$)	Ref. ^h
LiFeSi ₂ O ₆	$A_x + C_y + A_z$	$P2_1/c'$	$2/m'$	0.52(8)	n.d. ⁱ	4.83(5)	0.253(1)	0.6487(4)	0.246(2)	416.70(3)	[123]
LiFeGe ₂ O ₆	$Cx + A_y + C_z$	$P2'_1/c$	$2'/m$	4.51(2)	n.d.	1.38(5)	0.2509(2)	0.6495(2)	0.2147(2)	441.756(3)	[123]
LiCrSi ₂ O ₆	$Cx + A_y + C_z$	$P2'_1/c$	$2'/m$	2.12(4)	0.29(8)	1.15(8)	0.2515(5)	0.6582(4)	0.2348(8)	430.74(1)	[130]
LiCrGe ₂ O ₆	$Cx + A_y + C_z$	$P2'_1/c$	$2'/m$	2.41(3)	n.d.	1.24(7)	0.2513(4)	0.6591(4)	0.2121(7)	400.90(4)	[131]

^a Basis Vectors; ^b Magnetic space group; ^c Magnetic point group; ^d x = fractional coordinate at the 4 e site; ^e y = fractional coordinate at the 4 e site; ^f z = fractional coordinate at the 4 e site; ^g Refined unit cell volume; ^h References(s) for magnetic structure; ⁱ n.d. = not detected, the refined error was larger than the (very small) refined moment; ^j n.r. = not reported

The final step in the process is inputting the refined parameters from Tab. 4.17 into the appropriate expressions for $\mathbf{T}_{net}$. The first example presented here is for pyroxene materials with the Γ_1^- magnetic structure. The formula for $\mathbf{T}_{net}$ is Eq. 4.49 from §4.10, restated here with minor formatting edits for convenience:

$$\mathbf{T}_{a+b+c+d} = \frac{(4 \mathbf{m}_z)(-4x+1)\hat{\mathbf{j}} + (4 \mathbf{m}_x)(4z-1)\hat{\mathbf{j}}}{V}$$

An example calculation will be presented with the data for $\text{LiFeSi}_2\text{O}_6$. [123] The relevant refinement values are listed here, taken from Tab. 4.17: $x = 0.253(1)$, $z = 0.246(2)$, $\mathbf{m}_z = 4.83(5) \mu_B$, $\mathbf{m}_x = 0.52(8)$, and $V = 416.70(3) \text{ \AA}^3$.

$$\begin{aligned} \mathbf{T}_{a+b+c+d} &= \frac{(4 \mathbf{m}_z)(-4x+1)\hat{\mathbf{j}} + (4 \mathbf{m}_x)(4z-1)\hat{\mathbf{j}}}{V} \\ \mathbf{T}_{a+b+c+d} &= \frac{(4 \times 4.83 \mu_B)(-4 \times 0.253 + 1)\hat{\mathbf{j}} + (4 \times 0.52 \mu_B)(4 \times 0.246 - 1)\hat{\mathbf{j}}}{416.70 \text{ \AA}^3} \\ \mathbf{T}_{a+b+c+d} &= -0.000636237 \mu_B / \text{\AA}^3 \hat{\mathbf{j}} \end{aligned}$$

As in §4.8, the negative sign has no meaning in this context. Therefore the absolute value will be used for the rest of the calculations.

$$\begin{aligned} \mathbf{T}_{a+b+c+d} &= 0.636237 \mu_B / \text{nm}^3 \hat{\mathbf{j}} \\ \Delta \mathbf{T}_{net} &= \mathbf{T}_{net} \times \sqrt{\left(\frac{\Delta \mathbf{m}_x}{\mathbf{m}_x}\right)^2 + \left(\frac{\Delta \mathbf{m}_z}{\mathbf{m}_z}\right)^2 + \left(\frac{\Delta V}{V}\right)^2} \\ \Delta \mathbf{T}_{net} &= 0.000636237 \times \sqrt{\left(\frac{0.08}{0.52}\right)^2 + \left(\frac{0.05}{4.83}\right)^2 + \left(\frac{0.03}{416.70}\right)^2} \\ \Delta \mathbf{T}_{net} &= 0.00009827 \mu_B / \text{\AA}^3 \\ \Delta \mathbf{T}_{net} &= 0.09827 \mu_B / \text{nm}^3 \end{aligned}$$

The variable $\mathbf{m}_x$ has two significant figures, but the uncertainty is to the tenths place. Therefore

the final computed value is $\mathbf{T}_{net} = 0.6(1) \mu_B/\text{nm}^3 \hat{\mathbf{j}}$. This corresponds to a net toroidal moment along the y axis (*not* the b crystallographic axis).

The second and final computation for $\mathbf{T}_{net}$ is for pyroxene materials with the magnetic structure Γ_1^- . The formula for $\mathbf{T}_{net}$ is Eq. 4.54 from §4.11, restated here with minor formatting edits for convenience:

$$\mathbf{T}_{a+b+c+d} = \frac{[(4 \mathbf{m}_z)(4y - 3) + (4 \mathbf{m}_y)(-4z + 1)] \hat{\mathbf{i}} + [(4 \mathbf{m}_y)(4x - 1) + (4 \mathbf{m}_x)(-4y + 3)] \hat{\mathbf{k}}}{V}$$

An example calculation will be presented with the data for $\text{LiCrSi}_2\text{O}_6$. [130] The relevant refinement values are listed here, taken from Tab. 4.17: $x = 0.2515(5)$, $y = 0.6582(4)$, $z = 0.2348(8)$, $\mathbf{m}_x = 2.12(4) \mu_B$, $\mathbf{m}_y = 0.29(8) \mu_B$, $\mathbf{m}_z = 1.15(8) \mu_B$, and $V = 430.74(1) \text{ \AA}^3$. Eq. 4.54 will be calculated in two parts, first for the part along $\hat{\mathbf{i}}$ notated ($\mathbf{T}_{\hat{\mathbf{i}}}$), and then for the part along $\hat{\mathbf{k}}$ notated ($\mathbf{T}_{\hat{\mathbf{k}}}$).

$$\mathbf{T}_{\hat{\mathbf{i}}} = \frac{[(4 \times 1.15 \mu_B)(4 \times 0.6582 - 3) + (4 \times 0.29 \mu_B)(-4 \times 0.2348 + 1)] \hat{\mathbf{j}}}{430.74 \text{ \AA}^3}$$

$$\mathbf{T}_{\hat{\mathbf{i}}} = -0.003757701 \mu_B/\text{\AA}^3$$

$$\mathbf{T}_{\hat{\mathbf{k}}} = \frac{[(4 \times 0.29 \mu_B)(4 \times 0.2515 - 1) + (4 \times 2.12 \mu_B)(-4 \times 0.6582 + 3)] \hat{\mathbf{k}}}{430.74 \text{ \AA}^3}$$

$$\mathbf{T}_{\hat{\mathbf{k}}} = 0.007245243 \mu_B/\text{\AA}^3$$

The magnitude of two vectors can be found using the Pythagorean theorem, $c^2 = a^2 + b^2$.

$$c = \sqrt{a^2 + b^2}$$

$$\mathbf{T}_{net} = \sqrt{|\mathbf{T}_{\hat{\mathbf{i}}}|^2 + |\mathbf{T}_{\hat{\mathbf{k}}}|^2}$$

$$\mathbf{T}_{net} = \sqrt{(-0.003757701)^2 + (0.007245243)^2}$$

$$\mathbf{T}_{net} = 0.008161732 \mu_B/\text{\AA}^3$$

$$\mathbf{T}_{net} = 8.161732 \mu_B/\text{nm}^3$$

$$\Delta \mathbf{T}_{net} = \mathbf{T}_{net} \times \sqrt{\left(\frac{\Delta \mathbf{m}_x}{\mathbf{m}_x}\right)^2 + \left(\frac{\Delta \mathbf{m}_y}{\mathbf{m}_y}\right)^2 + \left(\frac{\Delta \mathbf{m}_z}{\mathbf{m}_z}\right)^2 + \left(\frac{\Delta V}{V}\right)^2}$$

$$\Delta \mathbf{T}_{net} = 0.008161732 \times \sqrt{\left(\frac{0.04}{2.12}\right)^2 + \left(\frac{0.08}{0.29}\right)^2 + \left(\frac{0.08}{1.15}\right)^2 + \left(\frac{0.01}{430.74}\right)^2}$$

$$\Delta \mathbf{T}_{net} = 0.002327 \mu_B/\text{\AA}^3$$

$$\Delta \mathbf{T}_{net} = 2.327 \mu_B/\text{nm}^3$$

The variable $\mathbf{m}_y$ has two significant figures, but the uncertainty is to the ones place. Therefore the final computed value is $\mathbf{T}_{net} = 8(2) \mu_B/\text{nm}^3$. This corresponds to a net toroidal moment along the xz plane.

A summary of the computed $\mathbf{T}_{net}$ values are presented in Tab. 4.18.

An interesting result is that $\text{LiFeSi}_2\text{O}_6$ is predicted to have the smallest net toroidal moment. Looking closely at the computations, this result came about because of the terms in the numerator of the expression. The term with $\mathbf{m}_z$ was negative, and the term with $\mathbf{m}_x$ was positive, and the sum difference between the two values was small, leading to a comparatively small value for $\mathbf{T}_{net}$. While unexpected, this expression was computed using the same methodology as all the other expression for $\mathbf{T}_{net}$ presented herein, and therefore must be considered a logically consistent result. Fig. 4.5 depicts the magnetic structure with the locations and orientations of the individual toroidal moments in $\text{LiFeSi}_2\text{O}_6$. Note that it is not in fact anti-ferrotoroidal. There is a very slight net toroidal moment allowed along the y axis. Understandably it is difficult to see in this figure. An apt term may be to call $\text{LiFeSi}_2\text{O}_6$ a “ferritoroidal” material, analogous to a “ferrimagnetic” material. Ferrimagnetic materials are permitted by symmetry to possess a net ferromagnetic moment, but the net moment is small.

Table 4.18: Summary of the toroidal order in various pyroxene analogs

Composition	T.O. ^a	$\mathbf{T}_{net}$ (μ_B/nm^3)	$\mathbf{T}_{xyz}^b$
LiFeSi ₂ O ₆	FTO	0.6(1)	$\mathbf{T}_y$
LiFeGe ₂ O ₆	FTO	17.2(6)	$\mathbf{T}_{xz}$
LiCrSi ₂ O ₆	FTO	8(2)	$\mathbf{T}_{xz}$
LiCrGe ₂ O ₆	FTO	9.8(6)	$\mathbf{T}_{xz}$

^a Toroidal Order: AFTO = antiferrotoroidal, FTO = ferrotoroidal, non = non-toroidal; ^b $\mathbf{T}_{xyz}$ = allowed toroidal moment direction(s); ^c n.c. = not computed, need more data

Another notable result is the large error in $\mathbf{T}_{net}$ for LiCrSi₂O₆. Of all the refined values, the error for the magnetic moments is always the largest in any powder neutron diffraction refinement. Since the magnetic moments had three components, there were therefore the most number of terms in the computation for the propagated error. Therefore, the computed error was the largest.

The last unexpected result was the the largest computed $\mathbf{T}_{net}$ for any material studied herein, including the pyroxene materials, is LiFeGe₂O₆ with a $\mathbf{T}_{net}$ of 17.2(6) μ_B/nm^3 . Therefore these results would suggest that any current or future researcher in ferrotoroidicity should seriously consider synthesizing and studying this material.

Before concluding this section, I wanted to mention another valid way of constructing the expressions for $\mathbf{t}_\gamma$ in the pyroxene structure type. When I originally considered this structure, I focused only on eight $\mathbf{r}_\alpha^\beta$ vectors, and assuming there would be four $\mathbf{t}_\gamma$ vectors. Their expressions are given below:

$$\begin{aligned}
 \mathbf{t}_{b1} &= \frac{1}{2} \sum_{b1} \mathbf{r}_\alpha^{b1} \times \mathbf{m}^\alpha = [\mathbf{r}_{e2}^{b1} \times \mathbf{m}^{e2}] + [\mathbf{r}_{e4}^{b1} \times \mathbf{m}^{e4}] \\
 \mathbf{t}_{b2} &= \frac{1}{2} \sum_{b2} \mathbf{r}_\alpha^{b2} \times \mathbf{m}^\alpha = [\mathbf{r}_{e1}^{b2} \times \mathbf{m}^{e1}] + [\mathbf{r}_{e3}^{b2} \times \mathbf{m}^{e3}] + \\
 \mathbf{t}_{c1} &= \frac{1}{2} \sum_{c1} \mathbf{r}_\alpha^{c1} \times \mathbf{m}^\alpha = [\mathbf{r}_{e2}^{c1} \times \mathbf{m}^{e2}] + [\mathbf{r}_{e4}^{c1} \times \mathbf{m}^{e4}]
 \end{aligned} \tag{4.58}$$

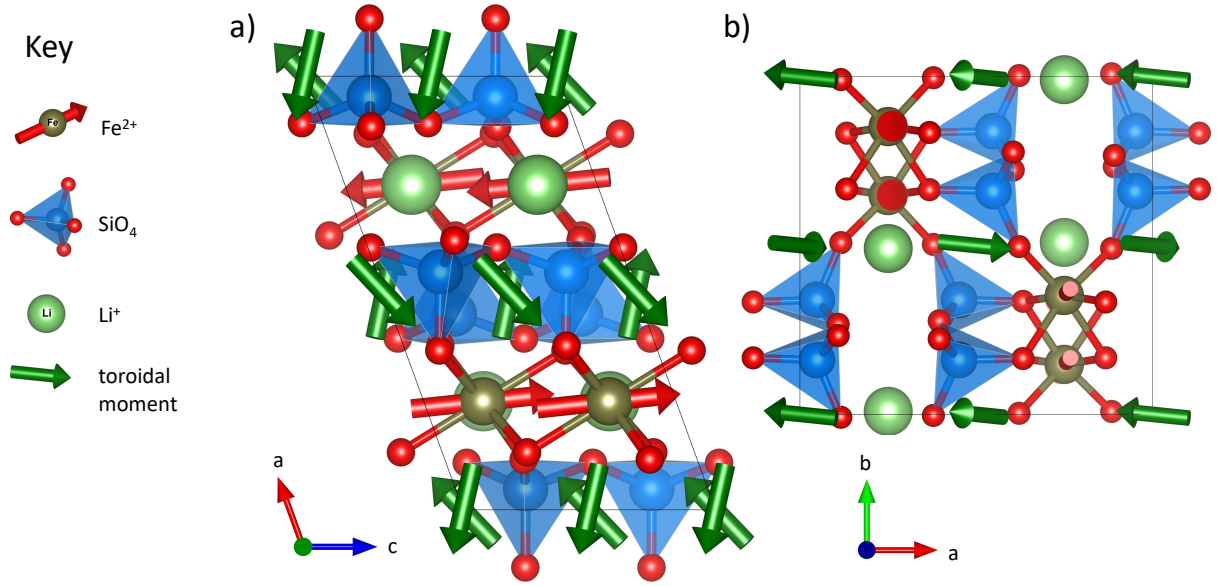


Figure 4.5: Ferrotoroidal Structure of $\text{LiFeSi}_2\text{O}_6$, viewed along the b axis (a) and the c axis (b).

$$\mathbf{t}_{c2} = \frac{1}{2} \sum_{c2} \mathbf{r}_{\alpha}^{c2} \times \mathbf{m}^{\alpha} = [\mathbf{r}_{e1}^{c2} \times \mathbf{m}^{e1}] + [\mathbf{r}_{e3}^{c2} \times \mathbf{m}^{e3}] +$$

I chose this subset because those vectors seemed to be pointed along the dominant super-super-exchange paths in the system. At the time, I was pondering what physical property could exist which would give rise to physical toroidal moments within a system. Since super-exchange and super-super-exchange is so vital to the formation of antiferromagnetic structures, I was attempting to find any connection between exchange paths and toroidal moments. Coincidentally, this subset of $\mathbf{r}_{\alpha}^{\beta}$ vectors gave the same general result, allowing a toroidal moment only along the y direction, or the xz plane (depending upon the magnetic structure). The reason for this is the four vectors chosen in each class (b and c) have the same magnitudes. This is due to particularities in the pyroxene structure and symmetry. Similar sets of four can also be found in the a and c sites. As long as pairs of vectors related by inversion are selected, and sets of pairs are chosen with the same magnitudes, the process is the same. Therefore select $\mathbf{t}_\gamma$ vectors can be created to only consider $\mathbf{r}_{\alpha}^{\beta}$ vectors of interest for some physical reason. I ultimately decided to leave

such decisions to qualified theoretical physicists and mathematicians to pursue. Once there is more experimental evidence for the formation of toroidal moments, such an investigation can be undertaken. In the meantime, I only aim to demonstrate the process, function, and versatility of this method.

4.13: General Summary and Discussion of the Methodology

Let us circle back now to the original guiding questions for a ferrotoroidal model:

- Which variables contribute to the value of a toroidal moment, and the net toroidization in a material?
- How can the structure be chemically tuned (*i.e.* altered) to maximize the net toroidization?

According to Eq. 2.12 from §2.2, $\mathbf{t} \propto \mathbf{r} \times \mathbf{m}$ and $\mathbf{T} \propto 1/V$. This implies that increasing $\mathbf{r}$, $\mathbf{m}$, or both would increase the magnitude of the individual toroidal moments. Likewise, increasing V would decrease $\mathbf{T}_{net}$.

However, this is an over-simplification. First of all, even if the individual toroidal moments ($\mathbf{t}$) are quite large, if they are in an anti-ferrotoroidal configuration, $\mathbf{T}_{net} = 0$. In addition, $\mathbf{T}_{net}$ would increase as the number of pairs of magnetic moments per unit cell increases. That is best described by expressions tailored to each structure type, as was demonstrated in this chapter for olivine and pyroxene. Also, $\mathbf{t}$ would be maximized when the vectors of $\mathbf{r}$ and $\mathbf{m}$ are perpendicular to one another, which is already expressed by having them be a cross product of one another when calculating $\mathbf{t}$.

The most complex issue is the treatment of r . If a “ring of spins” is understood as a circle, then r is a distance. However, distance vectors are treated differently in crystallography than

simple geometry, due to the three-dimensional periodicity of a lattice. Locations within a unit cell are described in terms of fractional coordinates. Likewise, vectors describing the translation from one point to another point are also described in terms of fractional coordinates. One can easily find the distance between two points using the lattice constants of the unit cell. This is routinely done when determining bond distances, for example. However, as explained throughout this document a much more consistent definition for a “ring of spins” is pairs of r vectors related by inversion.

In addition, it does not even make sense that as r increases, t would increase. If r is half the distance between two magnetic moments, it would not make sense that a phenomena caused by the interaction between two magnetic moments would be *larger* if the magnetic moments were *further away* from one another.

Furthermore, the distances between the magnetic moments is already taken into account when dividing by the unit cell volume. In addition, the volume of the unit cell will always be a much larger numerical value than small differences in bond distances, angles between magnetic moments, or magnetic moment magnitudes. Therefore the volume term will always dominate in the $\mathbf{T}_{net}$ expression. All of this is to say that it is most useful to treat r in terms of fractional coordinates when modeling toroidal structure, not as a bond distance.

However, this has implications for the units of toroidization. If r is in terms of fractional coordinates, it is unitless. Therefore the final units for $\mathbf{T}_{net}$ should be μ_B/nm^3 , not μ_B/nm^2 . This is in contrast to the units $\mu_B/\text{\AA}^2$ Ederer and Spaldin used.[63, 64] Note, the choice of nm or $\text{\AA}$ is inconsequential and only impacts the scientific notation of the numerical value. I personally find it easiest when comparing values to avoid scientific notation by changing the unit prefix.

In summary: Any alteration to $\mathbf{r}$ would only be reasonably possible by changing the

structure type (and therefore chemical system).

To select a suitable structure type:

- The magnetic point group of the magnetic space group must be a ferrotoroidal point group.
- When choosing between structure types, choose the one with more magnetic ions per unit cell volume.
- When choosing between structure types, choose the one where the angle between $\mathbf{r}$ and $\mathbf{m}$ is closer to 90 degrees. When they are perpendicular, the length of the $\mathbf{r}$ vector will be minimized.

To maximize $\mathbf{T}_{net}$ in structurally analogous materials through chemical manipulation:

- Chemically substitute both magnetic and non-magnetic ions which would minimize the unit cell volume (i.e. decrease V).
- Choose magnetic ions with a larger effective magnetic moment (i.e. maximize $\mathbf{m}$).

It is my sincere hope that these methods and insights are useful guidelines, and lead to fruitful scientific endeavors verifying the existence of ferrotoroidicity.

Chapter 5: Magnetism and Magnetic Structure of LiCoPO_4 and LiMnPO_4

This chapter is the contents of Gnewuch 2020, reorganized and rephrased.

Gnewuch, S.; Rodriguez, E. E. Distinguishing the Intrinsic Antiferromagnetism in Polycrystalline LiCoPO_4 and LiMnPO_4 Olivines. *Inorg Chem* **2020**, 59, 5883-5895.

While the previous chapters on toroidal theory logically built upon one another, none of the work in this chapter directly contributes to the understanding or development of toroidal theory. Rather, this chapter presents my published work on the synthesis, and magnetization and neutron powder diffraction studies of select olivine materials.

While my synthesis work does not have any direct impact on the development of ferrotoroidal theory, in order to test any hypothesis you need quality specimens for experimentation. Therefore the purpose of the work in this chapter was to support the development of efficient and robust methods for the preparation of quality powder (polycrystalline) and single crystalline olivine materials. The second objective was to perform a detailed neutron powder diffraction refinement of the magnetic structure of LiCoPO_4 and LiMnPO_4 . At the time, the published papers on them were from the 1960's, and magnetic diffraction and refinement has improved substantially since then.

I also knew that my method of creating toroidal models was going to be based upon the data one would obtain from neutron powder diffraction refinement. That is because it can be

very challenging to grow large, quality single crystals of inorganic solid state materials. As a general rule, powders are much easier to synthesize. Therefore preliminary magnetic structure determination is almost universally performed on powder data. That is why the ferrotoroidal model I developed uses the information obtained from neutron powder diffraction patterns. In this way, optimal materials could be targeted for single crystal growth. In addition, once single crystals are grown, detailed physical properties experiments can also be performed with aligned crystals, since my ferrotoroidal model would indicate in which crystallographic direction(s) the toroidal moments would lie.

The beginning of this chapter (§5.1) discusses the crystal chemistry of olivine materials in detail. This is followed by detailed discussions of the solid state (§5.3) and hydrothermal (§5.4) methodologies I used for preparing quality LiCoPO_4 and LiMnPO_4 samples. I then compared the magnetic susceptibility data of samples prepared by both methods (§5.7), in order to assess which would produce better quality samples. Finally, I present the magnetic symmetry analysis based upon the neutron powder diffraction experiments, given the magnetic structures used in the olivine-related sections of Chp. 4.

5.1: Olivine Structure Type

Throughout this dissertation I have referred to the “olivine” and “pyroxene” structure types, and briefly introduced them in §2.1 and §2.6, respectively. However, the term “olivine” corresponds to a wide variety of different chemical compositions.

Olivine materials are a subtype of the AB_2O_4 complex oxides, which includes chrysoberyl, spinel, and phenacite.[185] Olivines take the general form $B_2(AO_4)$ where the AO_4 unit is a

tetrahedral oxyanion. The oxyanions do not share any edges or vertices. Rather, the terminal oxygen atoms form highly distorted octahedra around the $4a$ and $4c$ sites. I have thus far only discussed orthophosphates, but olivines include orthosilicates as well. Both orthosilicates and orthophosphates have the chemical space group type $Pnma$, and the cations are located on the $4a$ and $4c$ sites.

The orthosilicate ion has a 4^- charge, and so both anions must be divalent, or one monovalent and one trivalent. Examples of divalent orthosilicates include $(Mg, M)_2SiO_4$ ($M = Co, Fe, Mn, Ni, Zn, Mg$).[\[186, 187, 188\]](#) They can form end members such as forsterite (Mg_2SiO_4), fayalite (Fe_2SiO_4), and tephroite (Mn_2SiO_4). They also form solid solutions between the $4a$ and $4c$ sites, since the divalent cations have a similar charge and radii. Examples with mono- and trivalent cations are $LiScSiO_4$ and $LiInSiO_4$.[\[188\]](#) Due to the differences in charge and radii, the lithium ion lies on the $4a$ site.

Since the phosphate ion has a 3^- charge, the orthophosphate olivines have one monovalent and one divalent cation. Again, due to differences in the charges and radii, the lithium ion is located on the $4a$ site in the $LiMPO_4$ ($M = Co, Fe, Mn, Ni$) series. They also form solid solutions, but with different divalent ions on the $4c$ site. A common example is triphylite, the iron-rich member of the $LiFe_xMn_{1-x}PO_4$ solid solution.[\[189\]](#) Lithiophyllite is the manganese-rich member. However, in practice the more general term “olivine” is used to describe these materials in the chemical literature. The ease with which the lithium ions can move through the structure make them well-known cathode materials.[\[190\]](#) The partially delithiated form of the iron-rich member is ferrisicklerite and the manganese-rich member is sicklerite; the fully delithiated form of the iron-rich member is heterosite and the manganese-rich member is purpurite.[\[8\]](#)

Olivine orthophosphate with sodium ions are also known, particularly $NaMPO_4$ ($M = Fe,$

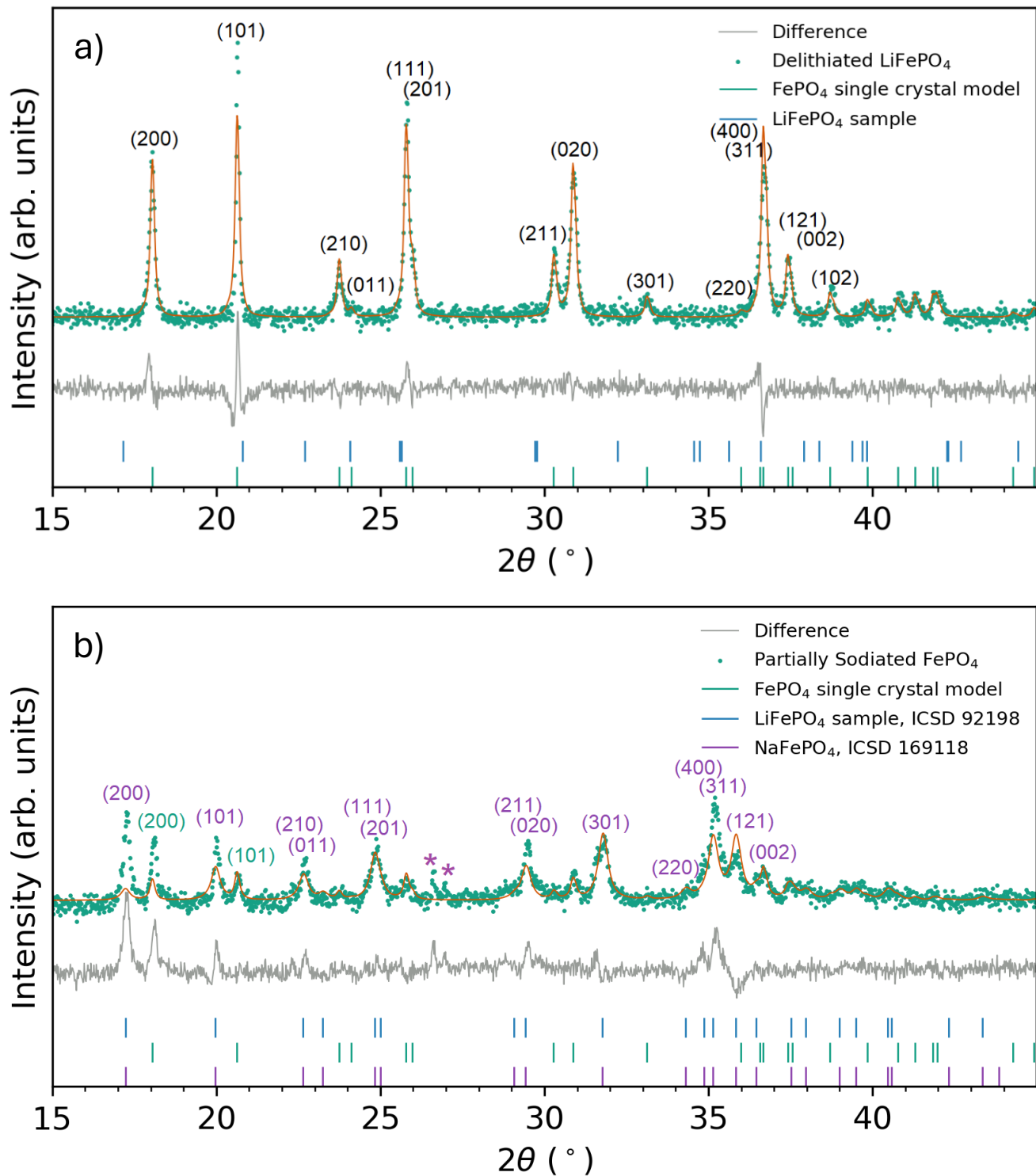


Figure 5.1: a) Delithiated LiFePO_4 sample to be used for the sodiation attempt. b) Partially sodiated FePO_4 sample. Data taken in the Fall 2017 semester. (Unpublished)

Mn, Ni, Co).[2, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200] However, due to the size of the sodium ion, the sodium ion lies on the 4c site and the transition metal ion on the 4a site. This polymorph is called maricite. Unfortunately maricite is electrochemically inactive, and so there have been efforts to form olivine sodium transition metal orthophosphates, but this is challenging. It involves sodiating a delithiated form of LiMPO_4 . [2, 193, 199]

Noah Bender and I attempted forming triphylite NaFePO_4 from delithiated LiFePO_4 . We used a mild peracetic acid solution method as the oxidant, to avoid using PF_4 which hydrolyzes HF . [4, 5] The sodiation was attempted using sodium iodide in acetonitrile. [2, 201, 202] Unfortunately, the chemical treatment process greatly reduced the crystallinity of the product (see Fig. 5.1). The (200) and (101) reflections are still visible from the delithiated LiFePO_4 sample, and there are two weak reflections around $27^\circ 2\theta$ which do not fit with either model. The two sets of peaks indicated we only achieve partial sodiation. Note, the LiFePO_4 and NaFePO_4 models are very similar and the software TOPAS refined the lattice parameters making them essentially the same. Sometime in early 2018 we learned that we were only partially delithiating the samples. Indeed, it is difficult to detect lithium ions using X-ray diffraction since lithium only has three electrons, which complicated our initial analysis of the delithiated samples. Moving forward, we were concerned about the poor crystallinity, particularly because our ultimate goal was to grow large single crystals. When Tim Diethrich took the lead on the project after Noah graduated, he focused only on the chemical delithiation process.

From this point forward, I will only present data on my LiCoPO_4 and LiMnPO_4 samples, and will only present data which is published. If I included in this document every synthesis I did, and every powder pattern I took, this document would be excessively long.

5.2: Experimental: General Goals of Synthesis Methodology

As explained in the beginning of this chapter, my ultimate goal was to grow large single crystals. This greatly impacted my synthetic approach. There are a large number of solid state and hydrothermal processes used for producing lithium transition metal orthophosphate olivine materials. However, the conditions for most are optimized for cathode materials research.[[1](#), [203](#), [204](#)] For example, nanometer-sized particles are optimal for lithium-ion diffusion. In addition, coating the particles with amorphous carbon increases the conductivity. Neither of these are desirable for crystallographic studies, nor for single crystal growth. The small particle sizes increase Scherrer broadening. Amorphous material increases the background and is an undesirable contaminant in the flux growth process. They also make identifying synthetic impurities more challenging.

Therefore the general objectives were to prepare materials with good crystallinity and were phase-pure.

There are two techniques I used in the preparation of powder polycrystalline materials: hydrothermal synthesis, and solid state synthesis.

The premise behind hydrothermal synthesis is that at increased pressures, the solubility of metal salts increases. Traditionally hydrothermal synthesis is done in costly reactors that simulate the high temperatures and pressures found in geologic conditions. But hydrothermal synthesis can also be performed at temperatures below 250°C in Teflon-lined acid digestion vessels. If the crystal growth conditions are optimized, quality crystalline materials can be formed much faster and at lower temperatures than solid state ceramic techniques. Metal salt precursors are chosen based upon their solubility, and the synthesis temperature and cooling rate is chosen to

optimize the crystallization of the product. Additives are chosen to control the pH and therefore the oxidation state of the transition metal ions. In addition, if the metal salts are prone to oxidation from the atmosphere, the water used for the reaction can be degassed, and the headspace for the reaction vessel can be purged with inert gas.

Solid state ceramic synthesis uses high temperatures, grinding, and repeated heating treatments to produce highly crystalline materials. The oxidation state of the transition metal ions are heavily impacted by the experimental atmosphere, and so reactions often are run under vacuum, oxidizing gases, reducing gases, or inert gases to control the synthesis. This is important for the LiMnPO_4 and LiFePO_4 synthesis, but not required for synthesis of LiNiPO_4 and LiCoPO_4 . The nickel and cobalt analogs readily form using NiO (Co_3O_4) under ambient atmosphere.^[205] Thoroughly grinding the products before and intermittently during heating treatments can improve the homogeneity of the product and reduce reaction times. Pressing the heated powders into pellets after regrinding for additional heating treatments can also improve the homogeneity and crystallinity of the final product. Techniques include ball milling or grinding by hand with an agate mortar and pestle. It is also helpful to perform the milling or grinding with a volatile solvent, forming a paste which is easier to handle. Different crystallographic phases form at different temperatures, and therefore the heating profile is another important factor in solid state synthesis. The ramp rate, dwell time, and cooling rate are all optimized to achieve the desired crystalline phase.

Throughout the rest of this chapter “hydrothermal $\text{LiCoPO}_4/\text{LiMnPO}_4$ ” refers to materials synthesized via the hydrothermal method described in §5.4. Likewise, “solid state $\text{LiCoPO}_4/\text{LiMnPO}_4$ ” refers to materials synthesized via the solid state method described in §5.3.

5.3: Experimental: Hydrothermal Synthesis Methodology

The syntheses for LiCoPO_4 and LiMnPO_4 were performed identically, except the precursor salt was cobalt(II) sulfate heptahydrate (Alfa Aesar) for the cobalt analog, and manganese(II) sulfate monohydrate (Alfa Aesar) for the manganese analog.

The reagents were reagent-grade and used as-received without further purification. The water was deionized in-house through reverse osmosis. Based upon the work of numerous authors, citric acid and ammonium hydroxide were used to control the pH between 6.5-8.[206, 207, 208, 209] As the reaction occurs, the pH decreases due to the precipitation of the phosphate in the form of the olivine product so that upon filtering the final product at the end the pH is around 4-5. Citric acid is an ideal weak acid because of its chelating ability, both controlling the pH and acting as a mild reducing agent to prevent oxidation of the transition metal. To minimize the presence of oxygen, the water was degassed by bubbling with argon gas for 30 minutes prior to use. The headspace of the reaction vessel was also purged by bubbling the contents with argon gas vigorously for 60 seconds before sealing. The heating conditions were based upon two studies by Manzi and coworkers.[208, 210] Although the temperature of 220°C was also chosen because that is the maximum temperature rating for the 45 mL Parr acid digestion vessels I used. The phosphate precursor chosen is ammonium phosphate because of its good solubility and it is an added source of ammonium to control the pH.

Amount of reagents used: The precursor solids were measured out based upon a calculation of 0.01 mol of phosphate concentration, and a ratio of 1 mol transition metal cation: 1 mol phosphate ion: 1.5 mol lithium ion: 0.04 mol citrate. The lithium is in excess to ensure full occupancy, particularly because lithium hydroxide is hygroscopic. Mathematically, this computes

to: 1.8740 g cobalt(II) sulfate heptahydrate (1.7506 g of manganese (II) sulfate monohydrate), 0.6294 g of lithium hydroxide monohydrate, 1.1503 g of ammonium phosphate monobasic, and 0.0768 g of citric acid.

To prepare the precursor solutions, ammonium phosphate monobasic (Fisher Scientific), citric acid (Sigma-Aldrich), and the transition metal sulfate mentioned in the first paragraph were dissolved in a few milliliters of degassed water inside a 50 mL vacuum flask. The flask was lightly sealed with parafilm with a hole punched in it with argon gas flowing over the solution. In a separate 50 mL beaker, the lithium hydroxide (Alfa Aesar) was dissolved in a few milliliters of degassed water. The metal salt is dissolved separately from the lithium hydroxide to avoid the formation of metal hydroxides, which easily oxidize in aqueous solution. A separate solution of 10-fold dilute ammonium hydroxide (BDH) is also prepared. I would re-use the solution for up to one month. The lithium hydroxide solution was then added to the vacuum flask with vigorous swirling. Immediately this forms a thick paste. Then 2-3 mL of ammonium hydroxide was added dropwise to adjust the pH to the desired range. Then additional water was added to obtain a final total volume of 23.0 mL. If a greater volume was added, during the heating process the vessel would over-pressurize and be extremely difficult to open after cooling.

The pH of the mixture was tested with a pH probe, which was kept submerged in water and rinsed promptly afterwards to remove the paste from the delicate probe surface. After the pH measurement was taken, the entire contents of the 50 mL beaker was poured quickly into a 45 mL Teflon acid digestion vessel sleeve, and argon was bubbled through the mixture for at least 60 seconds. Then the sleeve was quickly sealed inside the outer stainless steel vessel. The vessel was then placed in a glassware drying convection oven preheated to 220°C and set to turn off after 10 hr. If I put the vessels into the oven before noon, the oven would be cooled to room temperature

by the following morning at 8 AM. The product was then filtered by gravity filtration, washed with water, and allowed to dry under ambient conditions overnight. This yields about half a gram of product. The LiCoPO_4 is bright purple, and the LiMnPO_4 is a tan color.

5.4: Experimental: Solid State Synthesis Methodology

The reagents and heating profile for the synthesis of LiMnPO_4 was based upon the work by Baker and coauthors.[205] Stoichiometric proportions were prepared at a 4 g scale, a suitable size for the 25 mL alumina crucible used for the heat treatments. Mathematically, this computes to: 1.8091 g manganese, oxide, 3.3675 g ammonium dihydrogen phosphate, and 0.9421 g of lithium carbonate. The manganese(II) oxide (Alfa Aesar), ammonium dihydrogen phosphate (Fisher Scientific), and lithium carbonate (Honeywell) were ground in ethanol with an agate mortar and pestle, forming a homogeneous paste. The excess ethanol was allowed to evaporate for 20-40 minutes, and then the damp powder was transferred to the alumina crucible. The crucible was then transferred to a tube furnace under argon flow gas. The furnace was set to ramp to 800°C at a rate of 300°C/hr , dwell for 12-14 hr, and then turn off and naturally cool to room temperature. The product was reground, pelletized, and the heating treatment was repeated. The final product was light tan in color.

The reagents and heating profile for the synthesis of LiCoPO_4 were based upon the work by Kellerman and coauthors.[211] Stoichiometric proportions were prepared at a 5 g scale. Mathematically, this computes to: 1.1484 g lithium carbonate, 3.5757 g ammonium dihydrogen phosphate, and 2.4951 g of cobalt(II,III) oxide. The cobalt(II,III) oxide (Alfa Aesar), ammonium dihydrogen phosphate (Fisher Scientific), and lithium carbonate (Honeywell) were ground in a

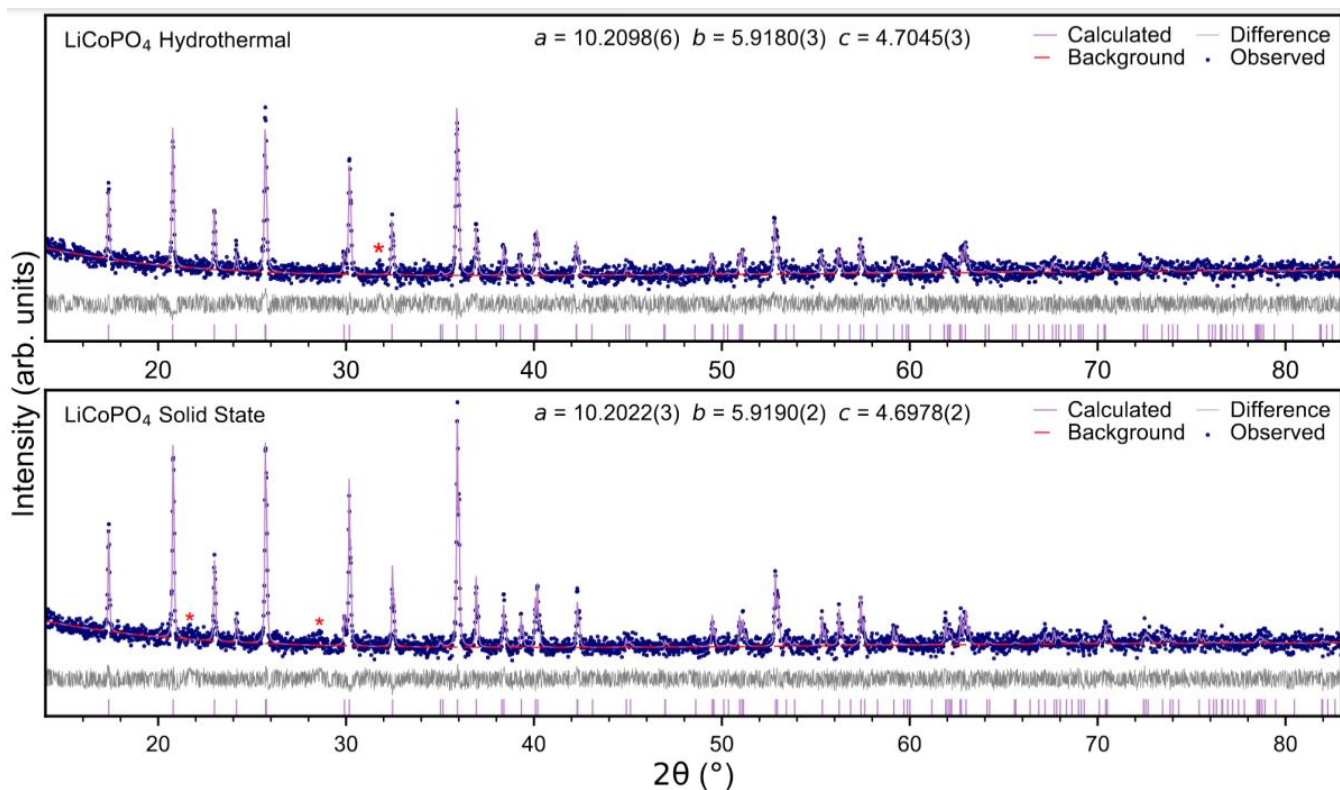


Figure 5.2: Preliminary refinements from X-ray powder diffraction data of hydrothermal and solid state LiCoPO_4 . Reproduced from Fig. S1 of Gnewuch & Rodriguez (2020).

similar manner to the LiMnPO_4 . The damp powder was transferred to an alumina crucible and placed inside a box furnace inside a fume hood. The ventilation of the fume hood is to address the ethanol fumes during the beginning of the heating process. It also helps keep the laboratory cool. The sample was placed in the oven preheated to 375°C . It was allowed to heat for 2 hr, then set to naturally cool to room temperature. The powder was then reground, pelletized, and heated for a second time at 800°C for 12 hr. The final product was a bright purple color.

5.5: Experimental: Preliminary Phase Identification with Laboratory Powder X-ray Diffraction

Preliminary phase identification was determined using preliminary structural refinements of laboratory powder X-ray diffraction data. The data were collected on a Bruker D8 Advance diffractometer with a LynxEye detector with Cu K α radiation ($\lambda_{\alpha 1} = 1.54059 \text{ \AA}$, $\lambda_{\alpha 2} = 1.54443 \text{ \AA}$). The experiments were performed under ambient conditions. The preliminary structural refinements were performed using the software TOPAS 5.[212] The initial model for LiCoPO₄ was from Kubel;[213] the initial model for LiMnPO₄ was from Urusova *et al.*[214] The preliminary refinements are presented in Fig. 5.2 & 5.3. All the reflections were indexed to the space group type *Pnma*. The calculated and measured intensities are in good agreement with one another.

As a note, the hydrothermal samples are a much finer powder than the solid state samples. Therefore, great care was taken to avoid packing the hydrothermal samples in the sample holder. Otherwise, it lead to strong preferred orientation along the *b* axis. The fineness of the powder also in general made the peaks from the hydrothermal samples slightly broader and less intense than the solid state samples. The particle size was not directly measured. These are qualitative observations.

It is also worth noting that no colored impurities were not observed for any of the hydrothermal or solid state samples used in this work. This is to be expected for the hydrothermal samples, since the pH was well-controlled. This is also not unexpected for the LiCoPO₄ since it readily reduces to Co²⁺ from Co^{2.5+} in the starting Co₃O₄ reagent. However, this is particularly important to note for the solid state LiMnPO₄ sample.

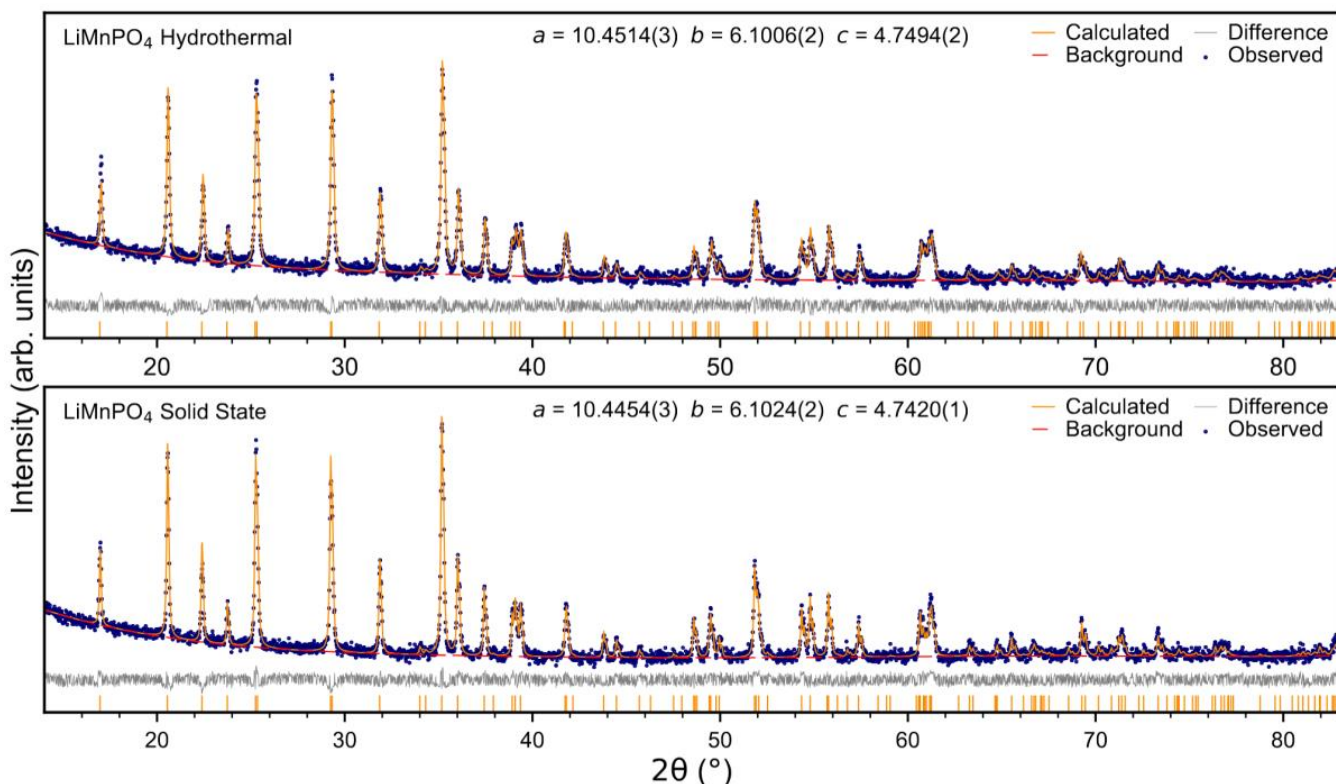


Figure 5.3: Preliminary refinements from X-ray powder diffraction data of hydrothermal and solid state LiMnPO_4 . Reproduced from Fig. S1 of Gnewuch & Rodriguez (2020).

In Tim Diethrich's 2022 paper,^[164] he explained that with the small tube furnace with a quartz tube, we often observed red or black impurities, particularly towards the end of the tube closest to the inlet for the flow gas. In that paper, he was preparing samples composed of varying manganese and iron ratios. When preparing the LiMnPO_4 sample in this study, I used the Carbolite 1500 furnace with an alumina tube, which is a much larger furnace and better insulated. It was a homogeneous light tan color, the best I ever prepared. Understandably, that was a popular furnace in our research group and I could not use it regularly for lithium phosphate synthesis, which is why we switched to using the smaller tube furnaces.

It is also important to note that low levels of impurities ($<1\%$) are not visible with laboratory powder X-ray diffraction.

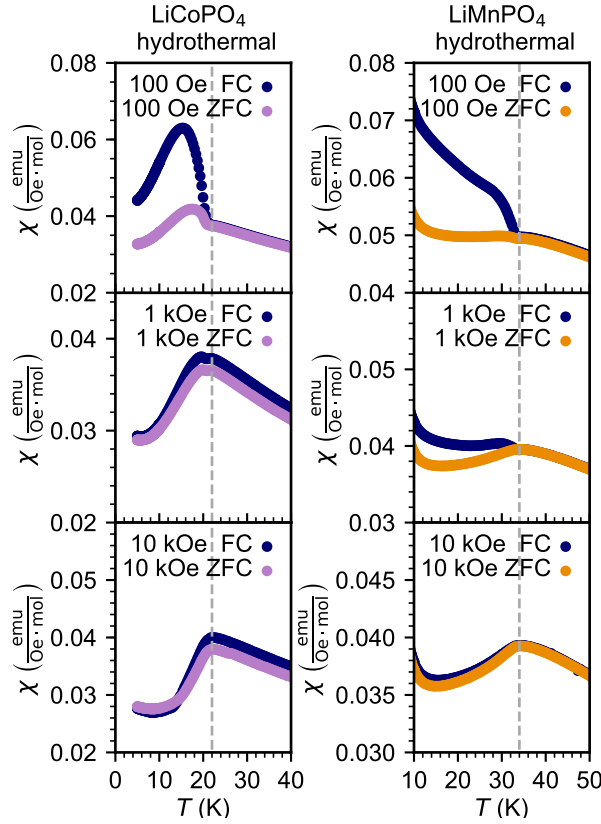


Figure 5.4: Temperature-dependent magnetic susceptibility of hydrothermal LiCoPO_4 and LiMnPO_4 at 100 Oe, 1 kOe, and 10 kOe. The dotted line indicates the Néel temperature presented in Table 5.1. It has been added to aid comparison of the measurements at different fields. Reproduced from Fig. 2 of Gnewuch & Rodriguez (2020).[175]

5.6: Magnetic Susceptibility Measurements

The objective of the magnetic susceptibility studies was to probe for any magnetic impurities. To do this, the experiments were performed under a variety of field and temperature conditions. All experiments were performed on a commercial SQUID magnetic property measurement system (7 T, MPMS, Quantum Design). Each sample was loaded into a gel capsule with sufficient cotton so that the approximately (measured) 100 mg sample would not shake during measurement. The gel capsule was then suspended in a plastic straw, and aligned in the instrument.

Field-cooled and zero field-cooled measurements were performed in direct current mode.

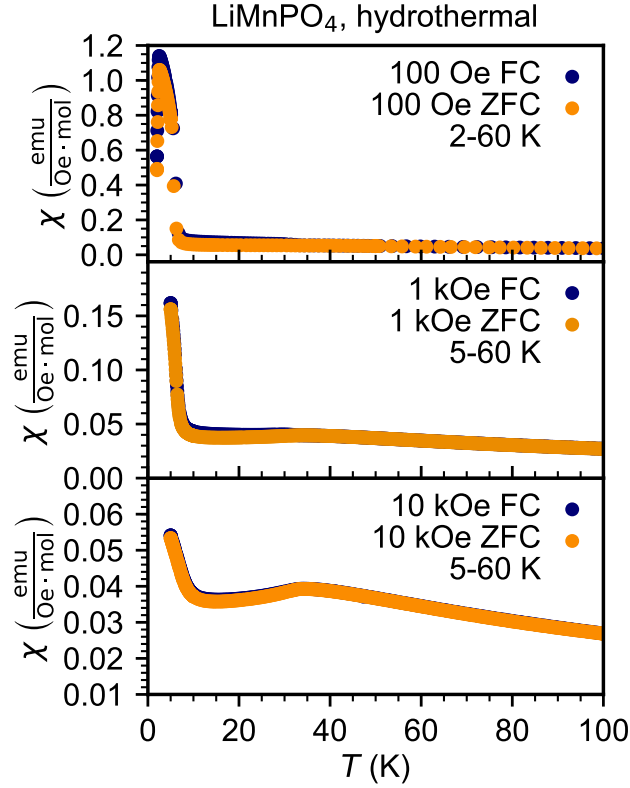


Figure 5.5: Temperature-dependent magnetic susceptibility of hydrothermal LiMnPO_4 from base temperature to 100 K. Reproduced from Fig. S2 of Gnewuch & Rodriguez (2020).[175]

The temperatures were swept from 300 K to base temperature (2-5 K), with different applied fields: 100 Oe, 1 kOe, and 10 kOe. The base temperature which could be achieved depended upon how well the Helium cryostat was working at the time.

Fig. 5.4 is the temperature-dependent magnetization measurements for the hydrothermal LiCoPO_4 and LiMnPO_4 samples, show in the region around the Néel temperature. The characteristic cusp indicating the transition from paramagnetic to antiferromagnetic behavior is observed in each of the zero field-cooled measurements. Both the field-cooled and zero field-cooled measurements diverge dramatically below the transition temperature for the measurements taken at 100 Oe, particularly for the hydrothermal LiMnPO_4 . Fig. 5.5 is another view of the measurements, in a larger temperature range. In Fig. 5.4 the temperature range was truncated to 5 K for the 100 Oe

sample for clarity. If the plot is scaled to allow the whole view of the data set below 50 K, the strong positive signal below 10 K obscures the cusp of the susceptibility, and the divergence in the field-cooled and zero-field cooled curves.

The Néel temperature is indicated with a grey dotted line in Fig. 5.4, and was determined using the 10 kOe measurement. For both samples, the cusp was most clearly defined at that applied field. In addition, the divergence of the field-cooled and zero field-cooled curves was suppressed at this field. The Néel temperature is reported in Tab. 5.1. The Néel temperature agrees well, (within ± 2 K) for the hydrothermal samples at all applied fields. It is important to note that at 100 Oe applied field, the LiCoP₄ transition temperature appear a few degrees lower than at 10 kOe.

Fig. 5.4 is the temperature-dependent magnetization measurements for the solid state LiCoPO₄ and LiMnPO₄ samples, also show in the region around the Néel temperature. Again, it is observed that the field-cooled and zero field-cooled measurements diverge below the transition temperature, but only for the LiMnPO₄ solid state sample. Interestingly, there is good agreement between the field-cooled and zero field-cooled measurements for the LiCoPO₄.

The Néel temperature is depicted with a dotted grey line in Fig. 5.6. Again, it was determined using the measurement at 10 kOe. This is particularly important to note for LiMnPO₄, because at the lowest measured field, 100 Oe, the transition temperature shifts to a slightly higher temperature.

All four samples (solid state and hydrothermal) exhibited a linear paramagnetic signal in the high-temperature region (150 - 300 K), suitable for analysis with the Curie-Weiss equation:

$$\chi = \chi_0 + \frac{C}{T - \theta_{CW}} \quad (5.1)$$

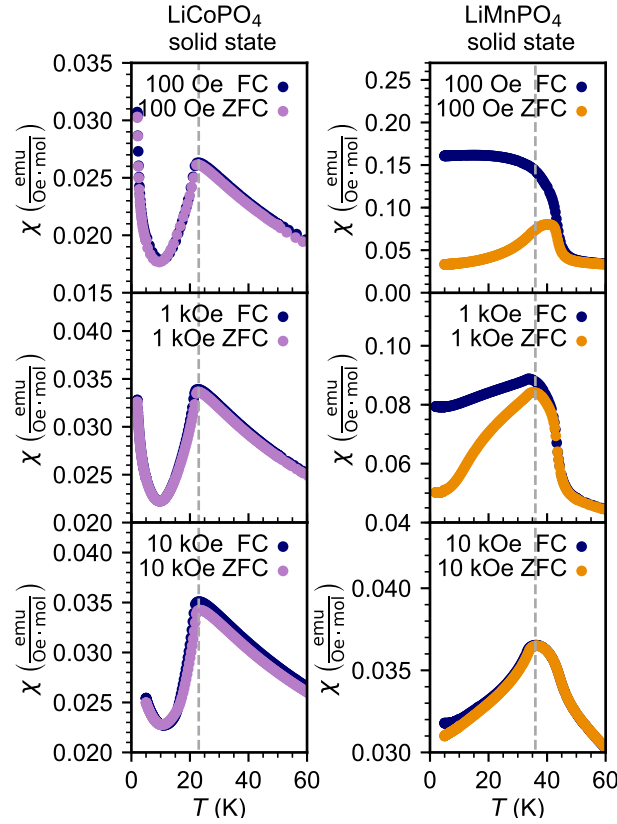


Figure 5.6: Temperature-dependent magnetic susceptibility of solid state LiCoPO_4 and LiMnPO_4 at 100 Oe, 1 kOe, and 10 kOe. The dotted line indicates the Néel temperature presented in Table 5.1. It has been added to aid comparison of the measurements at different fields. Reproduced from Fig. 2 of Gnewuch & Rodriguez (2020).[175]

where θ_{CW} is the Curie-Weiss temperature and C is the Curie constant. The variable χ_0 are the temperature-independent contributions to the signal, such as from the sample holder. These were negligibly small. Fig. 5.7 shows the fitted data, and Tab. 5.1 summarizes the fitting parameters.

The slope for hydrothermal LiCoPO_4 measurements were very similar at each applied field. However, for the hydrothermal LiMnPO_4 sample, the slope for the 100 Oe sample is significantly lower than the other two measurements at higher fields. Likewise, for the solid state LiCoPO_4 sample, the slope for the 100 Oe sample is significantly higher than the other two measurements. Lastly, for the solid state LiMnPO_4 , the slope is very slightly lower for the 100 Oe and 1 kOe measurements than for the 10 kOe measurement. All of these results are unsurprising, since it

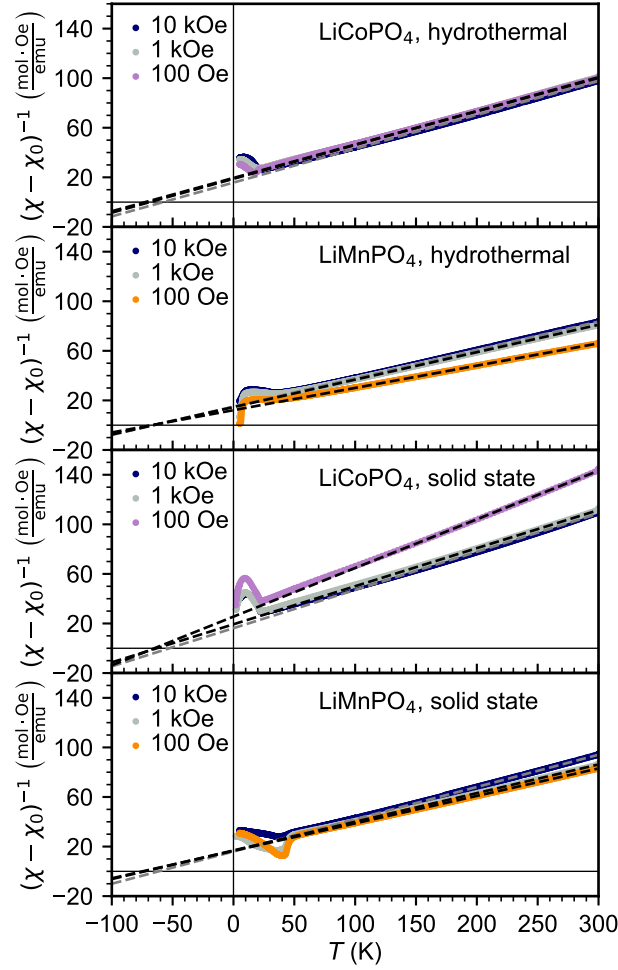


Figure 5.7: Inverse susceptibility of solid state and hydrothermal LiCoPO_4 and LiMnPO_4 fitted with the linear best fit lines fitted according to the Curie-Weiss Law. Reproduced from Fig. 3 of Gnewuch & Rodriguez (2020).[175]

was clear from observing the raw data in Fig. 5.4 & 5.6 that the measurements were strongly impacted by the strength of the applied field.

Because of these variability in the data at different applied fields, only the data measured at 10 kOe is included in Tab. 5.1. The table also includes the calculated frustration parameter, $|\theta_{\text{CW}}|/T_N$, which is used to compare the magnetic frustration between different antiferromagnetic systems. The effective magnetic moment $\mu_{\text{eff}} = \sqrt{8C}$ is also included.

Table 5.1: Summary of the Curie-Weiss fitting parameters for LiCoPO₄ and LiMnPO₄ from data obtained with a 10 kOe applied field.

	LiCoPO ₄		LiMnPO ₄	
	Hyd. ^a	S.S. ^b	Hyd.	SS.
T_N (K) ^c	22(2)	24(2)	34(2)	36(2)
θ_{CW} (K)	-58(2)	-53(3)	-66(0)	-62(1)
C ($\frac{\text{emu}\cdot\text{K}}{\text{mol}\cdot\text{Oe}}$)	3.66(4)	3.24(7)	4.37(1)	3.84(4)
μ_{eff} (μ_B)	5.4(1)	5.1(1)	5.91(2)	5.54(6)
$ \theta_{CW} /T_N$	2.6(3)	2.2(3)	1.9(1)	1.7(1)

^aSample prepared via a hydrothermal method; ^bSample prepared via a solid state method; ^cAn error of ± 2 K was estimated based upon the number of data points measured around the transition temperature.

Reproduced from Tab. 1 of Gnewuch & Rodriguez (2020).[175]

The Curie-Weiss parameters in Tab. 5.1 are in good agreement with other reported literature values. For all the samples, the Curie-Weiss temperature was negative, which is characteristic for antiferromagnetic samples. Unfortunately single crystal measurements reported by other researchers indicate there is strong single-ion anisotropy in the system.[48, 96, 215] Therefore detailed analysis of the exchange based solely upon the Curie-Weiss parameter is unreliable.

The Néel temperature of 22(2) K for hydrothermal LiCoPO₄ and 24(2) K for solid state LiCoPO₄ is in good agreement with the other reported values, which range between 22-23 K.[48, 53, 96, 186, 215, 216] The effective moment from polycrystalline magnetic susceptibility measurements have been measured as low as 4.77 μ_B ,[216] and as high as 5.7(1) μ_B . [53] Our measured values were in-between: 5.4(1) μ_B for the hydrothermal sample and 5.1(1) μ_B for the solid state sample. The theoretical value for the the effective moment with unquenched orbital angular momentum is 5.2 μ_B (see Tab. 5.8). The effective moment will be discussed again in §5.8.

The Néel temperature and effective moment for the LiMnPO₄ samples was in good agreement with literature as well. The Néel temperature 34(2) K for hydrothermal LiMnPO₄ and 36(2) for

solid state LiMnPO_4 is in good agreement with the 34-35 K range of temperatures reported in other literature.[40, 88, 217, 218, 219] The theoretical effective moment is $5.9 \mu_B$. Our measured value for the hydrothermal sample was the same value, $5.91(2) \mu_B$. It was slightly lower for the solid state sample, $5.54(6) \mu_B$. Other reported values from the literature ranged from $5.82(2) \mu_B$ to $6.1(1) \mu_B$. [40, 217]

Field-dependent measurements were performed on the aforementioned SQUID-MPMS from ± 7 T at various temperatures above and below the Néel temperature for each sample. These data are presented in Fig. 5.8 The samples were the same used for the temperature-dependent experiments described previously. The purpose of the field-dependent measurements was to search for any hysteresis, which would suggest a small ferromagnetic signal.

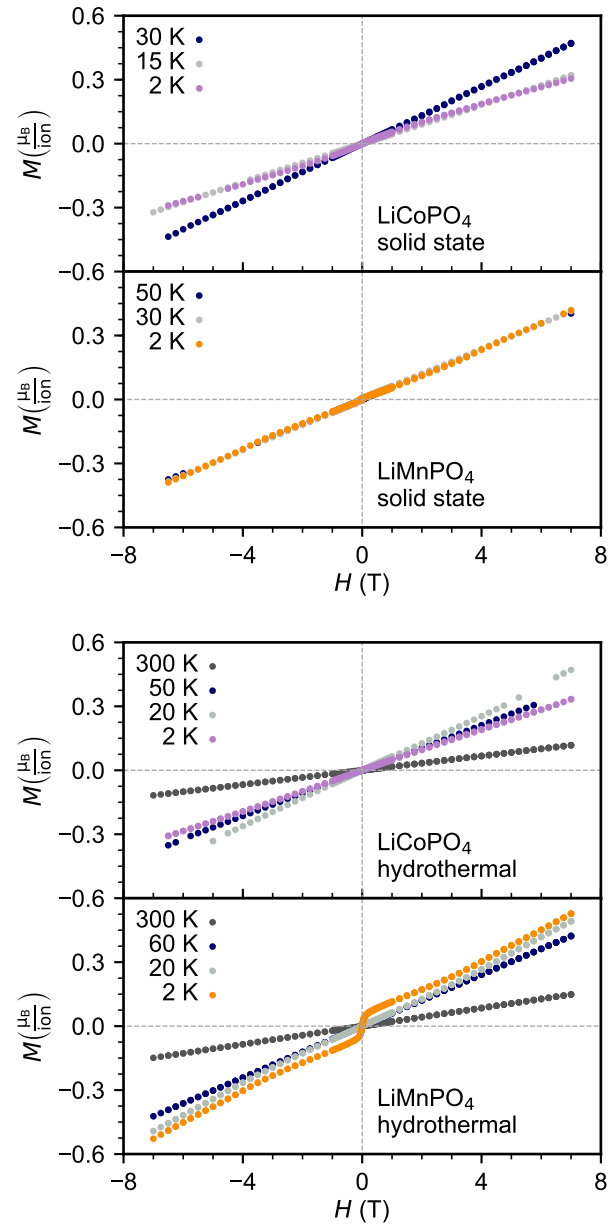


Figure 5.8: Field-dependent magnetic susceptibility of solid state and hydrothermal LiCoPO_4 and LiMnPO_4 at various temperatures above and below the Néel temperature. Reproduced from Fig. 4 of Gnewuch & Rodriguez (2020).[175]

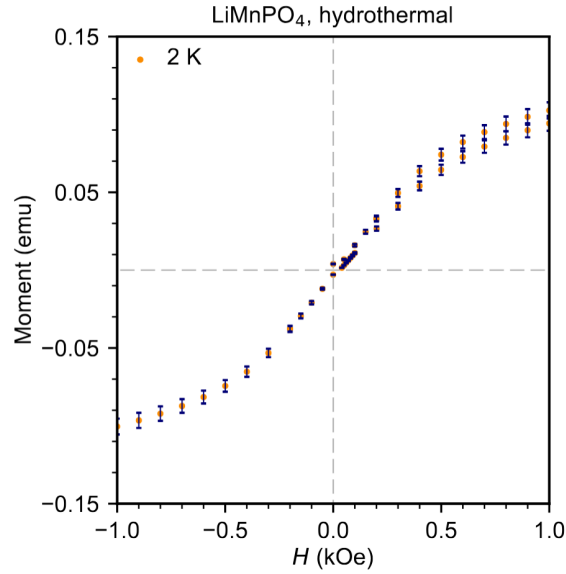


Figure 5.9: Field-dependent magnetic susceptibility of hydrothermal LiMnPO_4 at 2 K from -1 kOe to 1 kOe. Reproduced from Fig. S3 of Gnewuch & Rodriguez (2020).[175]

Indeed, ferromagnetic remanence is observed clearly in the LiMnPO_4 hydrothermal sample at 2K. At all the other temperatures, the field-dependent magnetization is linear. Recall that in the temperature range from 2-5 K, there is a strong signal in the hydrothermal LiMnPO_4 temperature-dependent susceptibility. (See Fig. 5.5). Fig. 5.9 is the 2 K field-dependent data plotted in the region between ± 1 kOe. It is difficult to determine a coercive field from this data, but a good estimate would be on the order 100 Oe. Therefore this strongly suggests the signal is from an unidentified ferro- or ferri-magnetic impurity.

The other samples at all other fields appear linear, with the exception of the 2 K temperature measurements. There is a subtle curvature in the 2 K measurements for solid state LiCoPO_4 , solid state LiMnPO_4 , and hydrothermal LiCoPO_4 . The data for LiCoPO_4 and LiMnPO_4 are shown larger in Fig. 5.10. A slight remanence is observable in the region below ± 250 Oe, but the data is insufficient to estimate a coercive field.

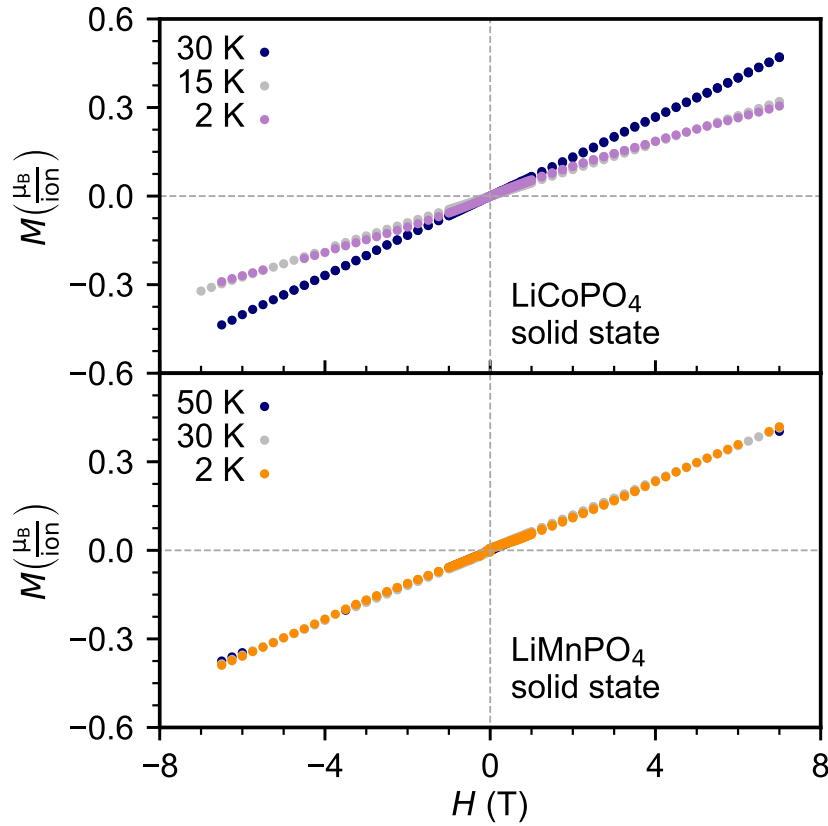


Figure 5.10: Field-dependent magnetic susceptibility of (*top*) solid state LiCoPO_4 at 2 K, 15 K and 30 K and (*bottom*) solid state LiMnPO_4 at 2 K, 30 K, and 50 K. Reproduced from Fig. S4 & S5 of Gnewuch & Rodriguez (2020).[\[175\]](#)

5.7: Neutron Powder Diffraction Experiments of Solid State Samples

The solid state samples were used for the neutron diffraction experiments because the synthesis yielded about three grams of sample. The experiments were performed on the constant-wavelength diffractometer BT-1 located at the NIST Center for Neutron Research (NCNR). The samples were loaded into Vanadium sample cans under Helium atmosphere. A 2.7 g portion of LiMnPO_4 was used, and a 4.5 g portion of LiCoP_4 was used. The monochromator chosen was Ge(311) which produces a beam of neutron with the wavelength $2.079 \text{ \AA}$, to maximize the resolution at low-angles. The experiment was performed with $60'$ collimation to maximize the

neutron flux. Measurements were taken at 10 K (below the transition temperature) and above the transition temperature (50 K for LiMnPO₄ and 30 K for LiCoPO₄). To better probe the onset of the magnetic order, a single high-intensity magnetic reflection was chosen for each sample. Then, over a dozen temperature measurements were taken around and below the transition temperature. For LiCoPO₄ the (012) magnetic reflection at 56.9° 2θ was measured at 13 temperatures from 32.2 K cooling down to 4.6 K. For LiMnPO₄ the (010) reflection at 19.6° 2θ was measured at 17 temperatures from 50.0 K cooling down to 10.0 K. These reflections were chosen because they were prominent, and had only magnetic contributions to the reflection. All measurements taken in the experiment were normalized to monitor counts.

Indexing and refinement was performed using the software GSAS-II.[168] The starting model for LiCoPO₄ was reported by Kubel.[213] The starting model for LiMnPO₄ was reported by Urusova and colleagues.[214]

Fig. 5.11 shows the raw data for LiCoPO₄ at 10 K and 30 K overlain to better emphasize the reflections which appeared at low angles attributable to long-range magnetic ordering. Any reflections present in the measurement above the transition temperature which cannot be indexed to the lithium transition metal orthophosphate model must be assumed to be an impurity phase. For LiCoPO₄, a few weak reflections were observed at: 4.40 Å⁻¹, 3.10 Å⁻¹, 2.80 Å⁻¹, 2.02 Å⁻¹, and 1.53 Å⁻¹. With so few reflections, all attempts at indexing and thus identifying the unknown impurity were unsuccessful.

The 30 K pattern was indexed to the space group type *Pnma*, and was in good agreement with Kubel's model. The 10 K pattern was indexed to the magnetic space group type *Pnma'*. The powder patterns and refinements are included in Fig. 5.13 and the refined structures are reported in Tab. 5.2. A summary of the refinement crystallographic parameters are included in Tab. 5.4.

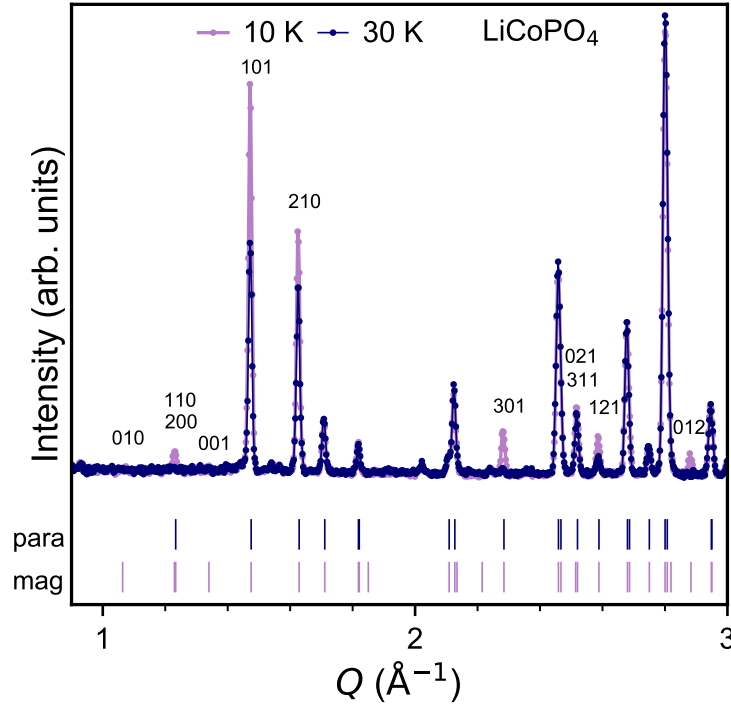


Figure 5.11: Indexed neutron powder diffraction patterns for LiCoPO_4 data taken at 10 K. The pattern taken at 30 K is overlaid to distinguish the intensity of the reflections in the 10 K pattern attributable to magnetic ordering. The tick marks for the paramagnetic (high-temperature) phase are labeled "para." Those for the magnetically ordered (10 K) phase are labeled "mag." Reproduced from Fig. 5 of Gnewuch & Rodriguez (2020).

A full discussion of the indexing process for the magnetic structure is included in §5.8.

Fig. 5.12 shows the raw data for LiMnPO_4 at 10 K and 50 K overlain to better see the magnetic reflections. There were a few reflections present in the 50 K pattern which are assumed to be an impurity and were unable to be indexed: $4.41 \text{ \AA}^{-1}$, $2.82 \text{ \AA}^{-1}$, $2.46 \text{ \AA}^{-1}$, and $1.54 \text{ \AA}^{-1}$. While the reflection at $4.41 \text{ \AA}^{-1}$ is easily noticeable, the other reflections are barely above the level of the background. Therefore all attempts at indexing and identifying the impurity were unsuccessful.

The 50 K pattern was indexed to the space group type $Pnma$, and was in good agreement with Urusova's model. The 10 K pattern was indexed to the magnetic space group type $Pn'm'a'$.

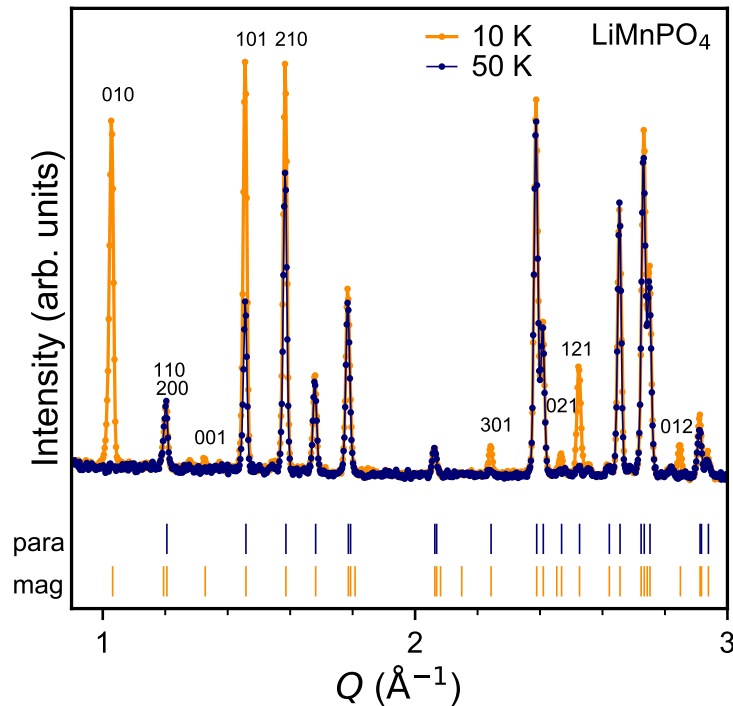


Figure 5.12: Indexed neutron powder diffraction patterns for LiMnPO_4 data taken at 10 K. The pattern taken at 50 K is overlaid to distinguish the intensity of the reflections in the 10 K pattern attributable to magnetic ordering. The tick marks for the paramagnetic (high-temperature) phase are labeled "para." Those for the magnetically ordered (10 K) phase are labeled "mag." Reproduced from Fig. 5 of Gnewuch & Rodriguez (2020).

The powder patterns and refinements are included in Fig. 5.13, and the refined structures are reported in Tab. 5.3. A summary of the refinement crystallographic parameters are included in Tab. 5.4. The next section (§5.8) is a full discussion of the indexing and refinement process for the magnetic structure.

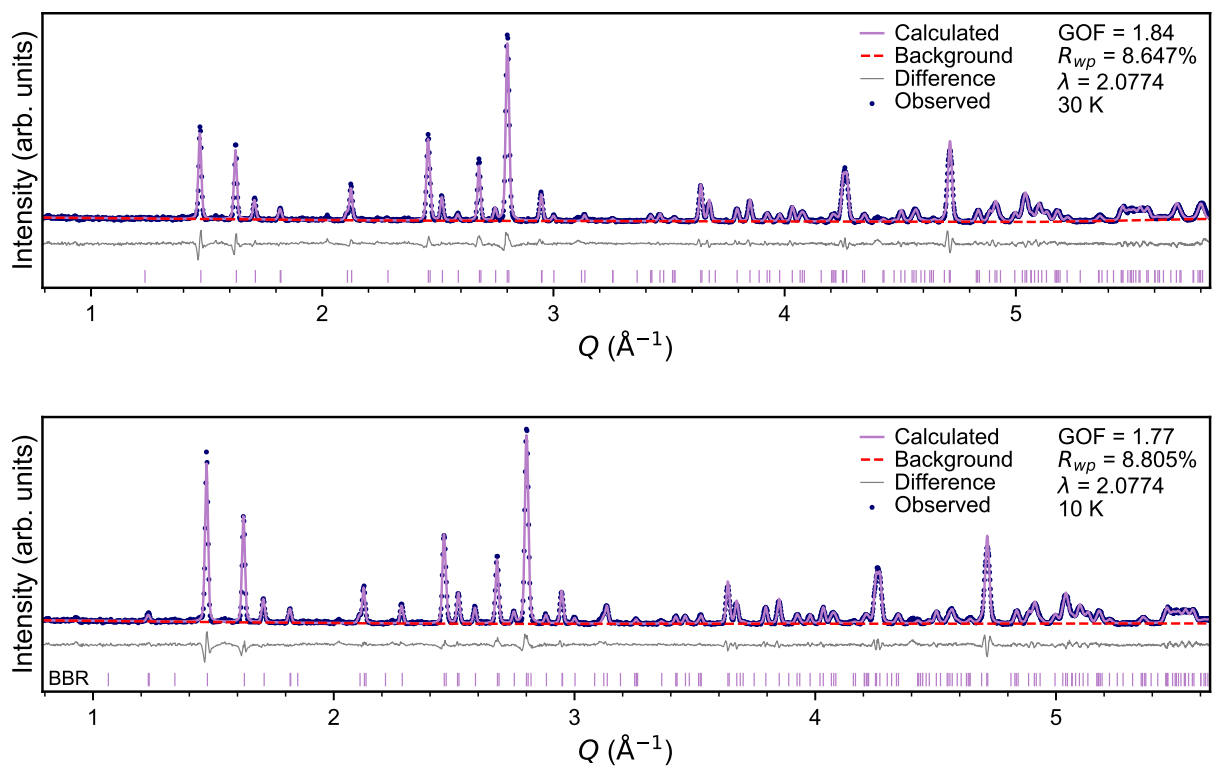


Figure 5.13: Refinements of the nuclear and magnetic structures with neutron powder diffraction data of LiCoPO_4 above and below the ordering temperature. Reproduced from Fig. 7 of Gnewuch & Rodriguez (2020).[\[175\]](#)

Table 5.2: Refined structural models for LiCoPO₄ above and below the ordering temperature.

30 K LiCoPO ₄									
Label ^a	Type ^b	Wyk. ^c	Mult. ^d	Sym. ^e	x	y	z	Frac. ^f	U _{iso}
Li	Li ⁺	a	4	$\bar{1}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1	0.012(3)
Co	Co ²⁺	c	4	m	0.2776(9)	$\frac{1}{4}$	0.975(2)	1	0.005(2)
P	P	c	4	m	0.0930(4)	$\frac{1}{4}$	0.4178(9)	1	0.005(1)
O1	O ²⁻	c	4	m	0.0972(4)	$\frac{1}{4}$	0.7416(9)	1	0.0053(9)
O2	O ²⁻	c	4	m	0.4547(3)	$\frac{1}{4}$	0.2065(9)	1	0.0044(1)
O3	O ²⁻	d	8	1	0.1663(3)	0.0430(4)	0.2836(6)	1	0.0015(7)
10 K LiCoPO ₄									
Label	Type	Wyk.	Mult.	Sym.	x	y	z	Frac.	U _{iso}
Li	Li ⁺	a	4	$\bar{1}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1	0.007(3)
Co	Co ²⁺	c	4	m	0.2758(7)	$\frac{1}{4}$	0.983(2)	1	0.000(2)
P	P	c	4	m	0.0942(4)	$\frac{1}{4}$	0.4173(8)	1	0.005(1)
O1	O ²⁻	c	4	m	0.0965(4)	$\frac{1}{4}$	0.746(1)	1	0.0056(7)
O2	O ²⁻	c	4	m	0.4554(3)	$\frac{1}{4}$	0.2056(9)	1	0.002(1)
O3	O ²⁻	d	8	1	0.1664(3)	0.0438(4)	0.2801(6)	1	0.0023(6)

^a Atom Label; ^b Atom Type; ^c Site Wyckoff Letter; ^d Site Multiplicity; ^e Site Symmetry; ^f Fractional Occupancy, which was not refined
Reproduced from Tab. S2 of Gnewuch & Rodriguez (2020).[175]

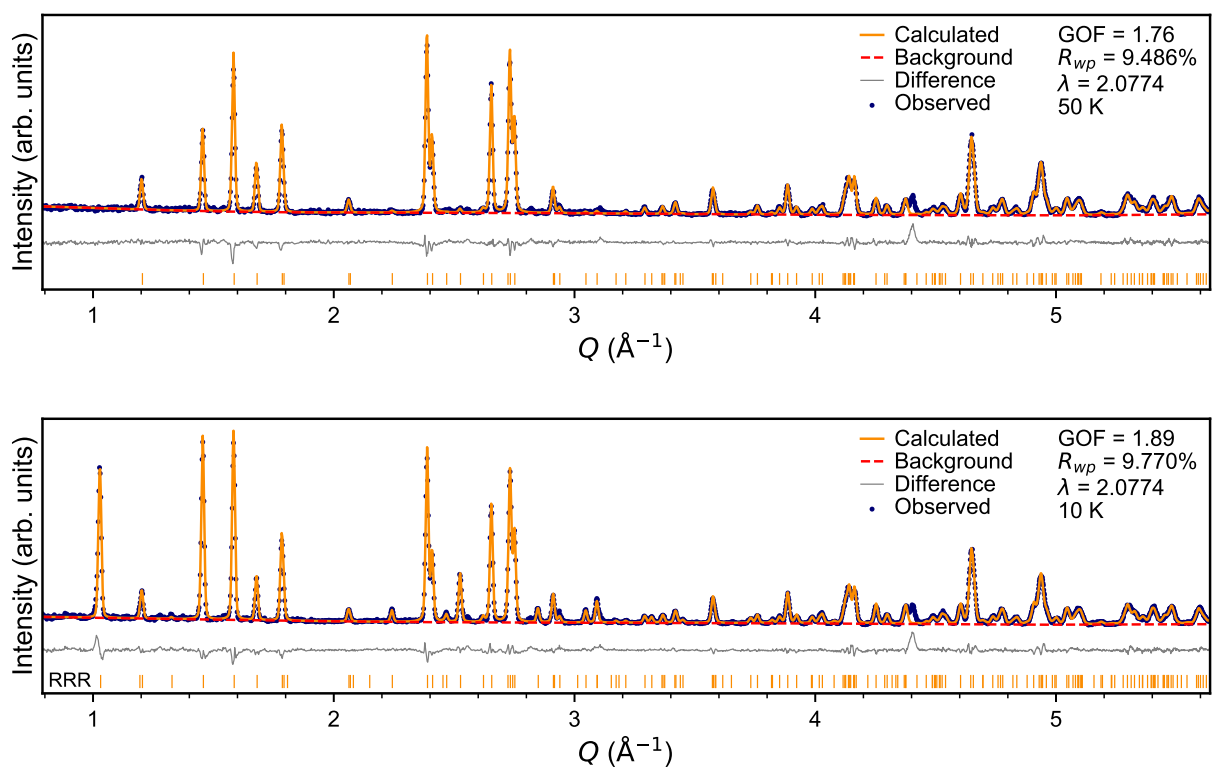


Figure 5.14: Refinements of the nuclear and magnetic structures with neutron powder diffraction data of LiMnPO_4 above and below the ordering temperature. Reproduced from Fig. 8 of Gnewuch & Rodriguez (2020).[175]

Table 5.3: Refined structural models for LiMnPO_4 above and below the ordering temperature.

50 K LiMnPO_4									
Label ^a	Type ^b	Wyk. ^c	Mult. ^d	Sym. ^e	x	y	z	Frac. ^f	U _{iso}
Li	Li^+	a	4	$\bar{1}$	0	0	0	1	0.019(4)
Co	Mn^{2+}	c	4	m	0.2798(6)	$\frac{1}{4}$	0.973(2)	1	0.009(2)
P	P	c	4	m	0.0921(4)	$\frac{1}{4}$	0.409(1)	1	0.003(1)
O1	O^{2-}	c	4	m	0.0957(4)	$\frac{1}{4}$	0.7337(9)	1	0.0082(9)
O2	O^{2-}	c	4	m	0.4539(3)	$\frac{1}{4}$	0.214(1)	1	0.007(1)
O3	O^{2-}	d	8	1	0.1617(3)	0.0493(4)	0.2776(7)	1	0.0096(7)
10 K LiMnPO_4									
Label	Type	Wyk.	Mult.	Sym.	x	y	z	Frac.	U _{iso}
Li	Li^+	a	4	$\bar{1}$	0	0	0	1	0.015(4)
Co	Mn^{2+}	c	4	m	0.2795(6)	$\frac{1}{4}$	0.976(1)	1	0.004(2)
P	P	c	4	m	0.0920(5)	$\frac{1}{4}$	0.413(1)	1	0.000(1)
O1	O^{2-}	c	4	m	0.0957(4)	$\frac{1}{4}$	0.734(1)	1	0.009(1)
O2	O^{2-}	c	4	m	0.4545(3)	$\frac{1}{4}$	0.212(1)	1	0.005(1)
O3	O^{2-}	d	8	1	0.1622(3)	0.0495(4)	0.2765(8)	1	0.0080(7)

^aAtom Label; ^bAtom Type; ^cSite Wyckoff Letter; ^dSite Multiplicity; ^eSite Symmetry; ^fFractional Occupancy, which was not refined
Reproduced from Tab. S2 of Gnewuch & Rodriguez (2020).[175]

Table 5.4: Crystallographic parameters of LiCoPO_4 and LiMnPO_4 determined from Rietveld refinement of neutron powder diffraction data.

LiMnPO_4	50 K	10 K
S.G.	<i>Pnma</i>	<i>Pnma</i>
a (Å)	10.4270(3)	10.4264(3)
b (Å)	6.0915(2)	6.0909(2)
c (Å)	4.7309(1)	4.7310(1)
V (Å ³)	300.49(1)	300.45(1)
R_p	6.546%	6.547%
R_{wp}	9.486%	9.770%
G.O.F.	1.762	1.888
LiCoPO_4	30 K	10 K
S.G.	<i>Pnma</i>	<i>Pnma</i>
a (Å)	10.1888(3)	10.1877(3)
b (Å)	5.9074(2)	5.9073(2)
c (Å)	4.6891(1)	4.6891(1)
V (Å ³)	282.23(1)	282.20(1)
R_p	6.688%	6.814%
R_{wp}	8.647%	8.805%
G.O.F.	1.841	1.773

Reproduced from Tab. 2 of Gnewuch & Rodriguez (2020).[175]

The final data presented in this section are the integrated intensity of the (012) reflection for LiCoPO_4 (Fig. 5.15) and (010) reflection for LiMnPO_4 (Fig. 5.16) at a number of temperatures above and below the transition. The significance of this experiment is it enables analysis of the magnetic phase transition.

When a system undergoes a transition from a paramagnetic state to an ordered magnetic state (in this case an antiferromagnetic state), the transition can be modeled using an order parameter. In other words, the “ordering can be parameterized.” For magnetic ordering, the order parameter is the magnetization of the magnetic sublattice M . The integrated intensity of the magnetic reflection is dependent upon the temperature so that it can be said that $M(T) \propto$

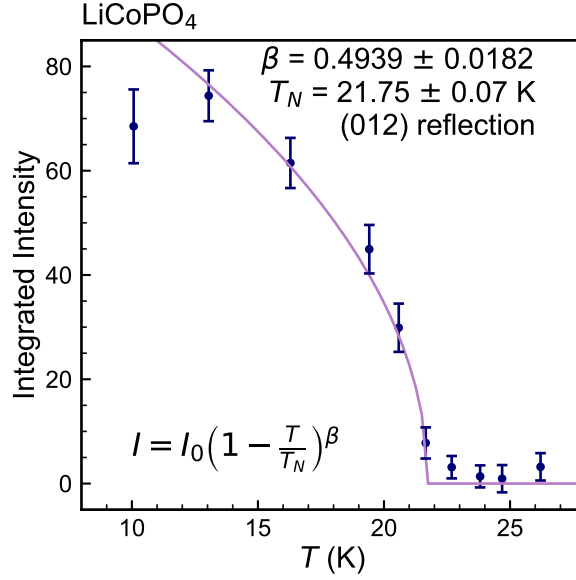


Figure 5.15: Temperature dependence of the integrated intensity of the (012) reflection of LiCoPO₄. The data set is fit to a power law (Eq. 5.3). Reproduced from Fig. 6 of Gnewuch & Rodriguez (2020).[175]

$\sqrt{I(T)}$. [47, 82, 93] This can be substituted into a power law:

$$\frac{M(T)}{M(0)} = A \left(1 - \frac{T}{T_N}\right)^\beta \quad (5.2)$$

where β is the critical exponent of the order parameter. Since magnetization is not begin directly measured, but rather integrated intensity, the form of the power law used to analyze the data is:

$$I = I_0 \left(1 - \frac{T}{T_N}\right)^{2\beta}. \quad (5.3)$$

Note, for LiCoPO₄ the following low-temperature data was excluded to better model the data at the transition: 5 K and 10 K. Likewise, for LiMnPO₄ the following low-temperature and high-temperature data was excluded: 10 K, 15 K, 20 K, and 50 K.

The fitted parameters for LiCoPO₄ from Fig. 5.15 are $T_N = 21.71(7)$ and $\beta = 0.21(4)$. This

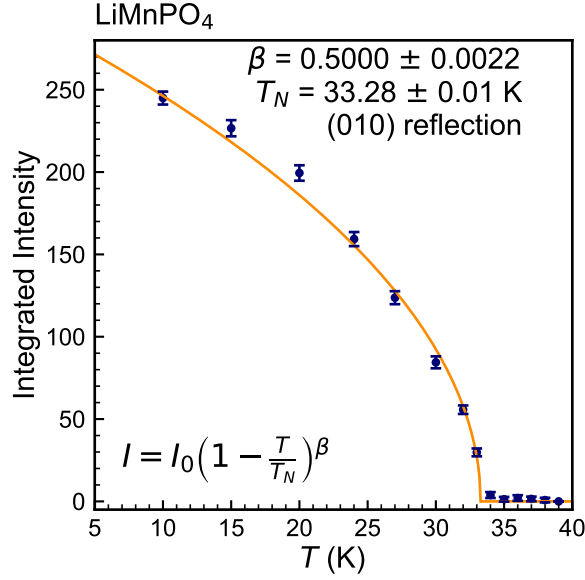


Figure 5.16: Temperature dependence of the integrated intensity of the (010) reflection of LiMnPO₄. The data set is fit to a power law (Eq. 5.3). Reproduced from Fig. 6 of Gnewuch & Rodriguez (2020).[175]

is in good agreement with a similar experiment performed on a single crystal of LiCoPO₄ by Vaknin and his colleagues.[48] They measured the (200) and (010) reflections, and also assigned 21 K to the transition temperature. Their measured order parameter is in close agreement with ours ($\beta \approx 0.218$). The value is intermediate between that expected for a 2D or a 3D Ising system, and suggests intermediate behavior. A more recent experiment on a single crystal of LiCoPO₄ was performed by Fogh and her colleagues, and they obtained a result closer to a 3D Ising system.[7]. They measured the (100) and (301) reflections and obtained $T_N = 21.55(2)$ K and $\beta = 0.34(1)$. At a much higher field (10 T), they obtained a similar critical parameter ($\beta = 0.30(1)$), but the transition temperature was depressed down to 17.51(2) K.

The fitted parameters for LiMnPO₄ from Fig. 5.16 are $T_N = 33.7(2)$ and $\beta = 0.31(3)$. Similar measurements have been performed on single crystal LiMnPO₄ as well. Li,[83] Toft-Petersen,[93] and their coauthors performed a number of experiments on LiMnPO₄. They found

the temperature dependence of the (010) reflection gave a transition temperature and critical parameter of $T_N = 33.9(1)$ and $\beta = 0.126(17)$,^[83] and $T_N = 33.40(1)$ and $\beta = 0.150(3)$,^[93], respectively. While their transition temperatures were similar to those from the powder sample in this work, their order parameters are closer to that for a 2D Ising system. (The ideal order parameter for a 2D Ising system is $\beta = 0.125$, and for a 3D Ising system is $\beta = 0.326$).^[220] However, the error for our calculated β is larger than theirs due to the smaller number of data points available..

5.8: Magnetic Symmetry Analysis

As was mentioned in §5.7, the 10 K patterns for both LiCoPO_4 and LiMnPO_4 were indexed and refined using the software GSAS-II. Since both 10 K patterns had a number of magnetic peaks, representational analysis was performed to determine the magnetic structure.

The predicted magnetic reflections for the indexing process were determined using *k*-SUBGROUPSMAG, which is integrated into the GSAS-II software. All reflections were reconciled using the propagation vector $k = 0,0,0$. This indicates the structure is commensurate.

In both LiCoPO_4 and LiMnPO_4 the magnetic ion is located on the 4*c* Wyckoff position. This information must be inputted into the software program to correctly calculate the site symmetry.

Since the magnetic susceptibility measurements exhibited a smooth cusp during the transition from the paramagnetic to antiferromagnetic state, we assume this is a continuous Landau-type phase transition. Therefore, the ordering process will occur according to a single order parameter according to one of the maximal subgroups for the paramagnetic space group. For both samples, the paramagnetic space group is $Pnma1'$, which decomposes into eight maximal subgroups. The

Table 5.5: Character table for the irreducible representations of $Pnma1'$ from k -SUBGROUPSMAG[161].

Γ^a	$1'$	$2'_z$	$2'_y$	$2'_x$	$\bar{1}'$	m'_z	m'_y	m'_x
Γ_1^+	-1	-1	-1	-1	-1	-1	-1	-1
Γ_2^+	-1	-1	1	1	-1	-1	1	1
Γ_3^+	-1	1	1	-1	-1	1	1	-1
Γ_4^+	-1	1	-1	1	-1	1	-1	1
Γ_1^-	-1	-1	-1	-1	1	1	1	1
Γ_2^-	-1	-1	1	1	1	1	-1	-1
Γ_3^-	-1	1	1	-1	1	-1	-1	1
Γ_4^-	-1	1	-1	1	1	-1	1	-1

^aIrreducible Representation; For the symmetry elements without the time inversion operator (e.g. $1'$), the character table is the same, except the signs of all the characters are changed from positive to negative and vice versa. Reproduced from Tab. S1 of Gnewuch & Rodriguez (2020).[175]

Character Table for each of these subgroup representations is presented in Tab. 5.5

The symmetry analysis is performed by k -SUBGROUPSMAG on the Bilbao Crystallographic Server and the results are automatically downloaded into the GSAS-II interface. The symmetry mode decomposition gives the following:

$$\Gamma_{M^{2+}}(4c) = 1\Gamma_1^+ \oplus 2\Gamma_1^- \oplus 2\Gamma_2^+ \oplus 1\Gamma_2^- \oplus 2\Gamma_3^+ \oplus 1\Gamma_3^- \oplus 1\Gamma_4^+ \oplus 2\Gamma_4^- \quad (5.4)$$

This expression states that for the symmetry at the $4c$ position, there are eight one-dimensional irreducible coset representations (IRs). In this case, four of those representations occur two times, and four one time. This gives a total of twelve basis vectors (also called symmetry modes). The notation used above is an adaptation of the notation for symmetry modes used by Stokes and Campbell *et al.* in k -SUBGROUPSMAG [221] The (+) symbol denotes *gerade* with respect to spatial inversion, and the (-) denotes *ungerade*. The number one (1) in parentheses in superscript indicates the order (or dimension) of the representation. Since they are all one-dimensional in this case, the (1) will be omitted for the remainder of this chapter.

The corresponding magnetic space group for each irreducible representation is listed in

Table 5.6: Magnetic symmetry associated with the eight irreducible representations of the parent paramagnetic space group $Pnma1'$.

I.R. ^a	M.S.G. ^b	M.P.G. ^c	B.V.C. ^d	M.O. ^e
Γ_1^+	$Pnma$	mmm	A_y	AFM
Γ_2^+	$Pn'm'a$	$m'm'm$	$A_x + F_z$	FM
Γ_3^+	$Pnm'a'$	$mm'm'$	$F_x + A_z$	FM
Γ_4^+	$Pn'ma'$	$m'mm'$	F_y	FM
Γ_1^-	$Pn'm'a'$	$m'm'm'$	$C_x + G_z$	AFM
Γ_2^-	$Pnma'$	mmm'	C_y	AFM
Γ_3^-	$Pn'ma$	$m'mm$	G_y	AFM
Γ_4^-	$Pnm'a$	$mm'm$	$G_x + C_z$	AFM

^aIrreducible Representation, superscript (+) indicates gerade, superscript (-) indicates ungerade with respect to spatial inversion symmetry; ^bMagnetic Space Group; ^cMagnetic Point Group;

^dBasis Vector Components of the spin modes, which are defined as ($F = \uparrow\uparrow\uparrow\uparrow$), ($G = \uparrow\downarrow\uparrow\downarrow$), ($C = \uparrow\uparrow\downarrow\downarrow$), and ($A = \uparrow\downarrow\downarrow\uparrow$) for the four magnetic atoms. The subscripts a , b , and c define along which crystallographic direction the moments are parallel. ^eMagnetic Order

Reproduced from Tab. 3 of Gnewuch & Rodriguez (2020).[175]

Tab. 5.6. The table also indicates the magnetic point group associated with the magnetic space group, the basic vector components associated with that representation, and the magnetic ordering (ferromagnetic or antiferromagnetic). The basis vectors are expressed in Tab. 5.6 using the conventions of Bertaut, where if all four atoms are ferromagnetic, the configuration is labeled F ($\uparrow\uparrow\uparrow\uparrow$). The additional configuration possibilities are labeled A ($\uparrow\downarrow\downarrow\uparrow$), C ($\uparrow\uparrow\downarrow\downarrow$), and G ($\uparrow\downarrow\uparrow\downarrow$). The first through fourth atoms are defined as follows: 1($x, (1/4), z$), 2($-x + 1/2, (3/4), z + (1/2)$), 3($-x, (3/4), z + (1/2)$), and 4($x + (1/2), (1/4), -z + (1/2)$).

At this point, GSAS-II computes the expected reflections for each given magnetic structure, and displays the results of the indexing. Favorable candidates can then be chosen and saved for later use in the refinement process. Since the Weiss temperature was negative for all of the samples, only the antiferromagnetic configurations are considered. The observed reflections also narrow down the possibilities. For example, for LiMnPO_4 there is a strong (010) reflection, but this reflection is absent in LiCoPO_4 . Since magnetic scattering only occurs perpendicular to the

Table 5.7: Magnetic model and parameters deduced from Rietveld refinement of neutron powder diffraction patterns taken at 10 K.

	LiCoPO ₄	LiMnPO ₄
I.R.	Γ_2^-	Γ_1^-
M.S.G.	$Pnma'$	$Pn'm'a'$
M.P.G.	mmm'	$m'm'm'$
B.V.Com.	C_y	$C_x + G_z$
Obs. B.V.Com. ^a	C_y	C_x
All. M.M.Com. ^b	M_y	M_x, M_z
Obs. M.M.Com. ^c	M_y	M_x
Ref. M.M.Com. ^d	3.28(4)	4.28(3)

^aObserved Basis Vector Components; ^bAllowed Magnetic Moment Components; ^cObserved Magnetic Moment Components; ^dRefined Magnetic Moment Magnitudes
Reproduced from Tab. 5 of Gnewuch & Rodriguez (2020).[175]

magnetic moments, for LiMnPO₄ the spins cannot be aligned along the b axis. This narrows down the choices to either Γ_1^- , or Γ_4^- . The opposite is true of LiCoPO₄, and therefore the two remaining possibilities are Γ_2^- and Γ_3^- .

The next step in the process is to refine the data to the structural and magnetic model, and assess which gives the best fit to the data. For LiMnPO₄ the best fit was obtained with Γ_1^- , which corresponds to the magnetic space group $P'n'm'a'$. While the magnetic moment is allowed along both the x and z axes, the error in the refined magnetic moment along z was larger than the very small refined value. Therefore the magnetic component along z was set to zero and the model refined without this component. The observed spin configuration was therefore C_x . For LiCoPO₄ the best fit was obtained with Γ_2^- , which corresponds to the magnetic space group $Pnma'$. The refined magnetic moments are listed in Tab. 5.7. These magnetic structures are in good agreement with the structures originally determined by Santoro and Newnham and their colleagues in the 1960s.[53, 87, 88]

Using the notation described by Gallego and his colleagues,[222] the symmetry-breaking Landau transition for LiCoPO₄ would be formally notated:

$$Pnma1' \rightarrow Pnma'(\mathbf{a}, \mathbf{b}, \mathbf{c}; 0, 0, 0). \quad (5.5)$$

For LiMnPO_4 the transition is described as:

$$Pnma1' \rightarrow Pn'm'a'(\mathbf{a}, \mathbf{b}, \mathbf{c}; 0, 0, 0). \quad (5.6)$$

The information to the right in parentheses indicates there is neither a change in the crystallographic basis nor the origin during the magnetic phase transition. This type information is crucial for Gallego and his colleagues at the Bilbao Crystallographic Server, as they are creating a database of magnetic structures. In order to properly convert a structure solved using irreducible representations to one using magnetic space groups, this information must be explicitly provided.

For LiCoPO_4 , the refined atomic moment was $gS = 3.28(4)\mu_B$ (10 K) per magnetic ion. While Santoro and Newnham reported the structure in 1966, they unfortunately did not report a refined atomic moment. However, there are two published studies on refinements of single crystal LiCoPO_4 . The first reported a moment of $4.2 \mu_B$ (10 K),[\[48\]](#) and the second $3.54(5) \mu_B$ (2 K).[\[7\]](#) A different group of authors performed high-magnetic field studies on LiMnPO_4 and reported to saturated magnetic moment to be only $3.6 \mu_B/\text{ion}$. Therefore the $4.2 \mu_B$ measurement is not possible. In addition, Ref. [48](#) relied upon the (200) and the very weak (010) reflection in their determination of the net magnetic moment. In Ref. [7](#) they used 130 commensurate magnetic reflections and 241 nuclear Bragg reflections to normalize the intensities. This therefore gave a more reasonable result of $3.54(5) \mu_B$. Since our experiment was performed using polycrystalline sample, we also used hundreds of reflections: 156 commensurate magnetic reflections and 124 nuclear Bragg reflections. The normalization process ensures the scale factor is determined correctly during the refinement. Therefore our results confirm those of Ref. [48](#) that there is partially unquenched orbital angular momentum for the Co^{2+} ion. See Tab. [5.8](#) for a comparison of the theoretical magnetic moment values.[\[223\]](#)

Table 5.8: Theoretical magnetic moment values for LiCoPO₄ and LiMnPO₄.[\[223\]](#)

	LiCoPO ₄	LiMnPO ₄
El. config. ^a	$d^7: t_{2g}^5 e_g^2$	$d^5: t_{2g}^3 e_g^2$
	$S = 3/2$	$S = 5/2$
	$L = 3$	$L = 0$
Term sym. ^b	⁴ F	⁶ S
$\mu_{L+S} (\mu_B)^c$	5.2	5.9
$\mu_S (\mu_B)^d$	3.9	5.9
$m (\mu_B)^e$	3	5

^aElectronic configuration; ^bFree ion ground term symbol; ^c $\mu_{L+S} = \sqrt{4S(S+1) + L(L+1)}$; ^d $\mu_S = 2\sqrt{S(S+1)}$; ^e $m = gS$; Reproduced from Tab. 4 of Gnewuch & Rodriguez (2020).[\[175\]](#)

For LiMnPO₄ the refined magnetic moment of $gS = 4.28(3)\mu_B$ (10 K) is significantly lower than Santoro and Newnham's originally reported $5.2 \mu_B$ (6 K). A recent neutron powder diffraction study of LiMnPO₄ was reported,[\[214\]](#) with data for LiMnPO₄ obtained at six temperatures from 2-37 K. They did not include any discussion of representational analysis, magnetic space groups, nor the type of antiferromagnetic ordering observed. They did report the structure had the magnetic moment aligned along the a axis and reported a refined moment of $4.0 \mu_B$ (3.5 K). Like with the LiCoPO₄ samples, our refinement using polycrystalline sample normalized the intensities from 163 commensurate magnetic reflections and 130 nuclear Bragg reflections.

Toft-Petersen, Vaknin, and their colleagues also performed field-dependent magnetic structure studies on single crystal LiMnPO₄, at 2 K under a 4.5 T applied field.[\[93\]](#) They were able to detect a field-induced ferromagnetic component along the a axis. The magnetic moment they observed was then $3.95(9) \mu_B$ (2K), closer to ours.

5.9: General Discussion of the Magnetic Susceptibility for LiMnPO₄

In general, the results demonstrate that different synthetic methods result in different features in the $\chi(T)$ curves for LiMnPO₄, particularly the shift in the cusp of the transition temperature

as well as the FC/ZFC bifurcation. Therefore the experimental conditions for the magnetization measurements as well as the synthesis procedure will be discussed in this section.

We are not the only group to observe FC/ZFC bifurcation in polycrystalline samples around 42-43 K at low applied fields (100 - 200 Oe range).[211, 217, 224] Arčon *et al.* used a sol-gel method followed by high temperature annealing. Kellerman *et al.* used high-temperature sintering. Both observed prominent hysteresis. Arčon *et al.* reported a coercive field of 1 kOe and Kellerman *et al.* a much smaller 200 Oe field. In our samples, we observe a very weak hysteresis in the solid state sample, for which a coercive field cannot be assigned. Since the hysteresis varies between samples prepared by different methods, this strongly suggests the weak ferromagnetic signal is due to manganese oxide impurities.

Indeed, the most likely impurity is Hausmannite (Mn_3O_4). Manganese oxides are invariably present in divalent manganese oxide samples prepared at high temperatures, even if they are prepared under inert atmosphere.[225] At 42 K, Hausmannite transitions to an incommensurate sinusoidal structure until 33 K, where it then displays commensurate ferrimagnetic order down to base temperature.[81, 226, 227, 228] The weak ferrimagnetic signal is observed as a FC/ZFC bifurcation in the magnetic susceptibility, but only visible at low applied fields (≤ 200 Oe) and if the particle size is large (≥ 15 nm).[229, 230, 231, 232] In addition, Hausmannite is black in color. In our own research, we observed that greyish impurities would form on manganese-containing samples if care was not taken to prevent oxidation. The samples used in this work did not have any visible impurities, but low-levels of impurity are still possible. Since both Arčon and Kellerman used high-temperature synthetic techniques as well, it would be unsurprising they also had Hausmannite impurity in their samples. Therefore the “cusp” at 42 K is not due to intrinsic magnetism in the LiMnPO_4 , but rather is from the Hausmannite impurity.

It is also important to emphasize the bifurcation is dependent upon the strength of the applied magnetic field, and is suppressed at high fields. Kellerman and colleagues performed additional measurements at fields up to 5 T and observed the bifurcation is suppressed above 0.8 Tesla. This is consistent with our results, where the bifurcation is suppressed in the 10 kOe (1 T) measurements. Likewise, Yamada and colleagues reported bifurcation in their samples prepared below 500°C, but not in the samples prepared at 700°C.[218] However, the temperature-dependent magnetic susceptibility measurements Yamada reported were performed at 1 kOe. This high field likely suppressed the bifurcation in the higher quality samples. The samples also likely had a larger crystallite size, since the purpose of high-temperature sintering is to improve the crystallinity and increase the particle size.

In our samples, there appears to be a shift in the transition temperature from 42 K at low applied fields to 35 K at high applied fields. However, given the evidence for Hausmannite impurities, one must conclude the Hausmannite signal is dominating at low applied fields but is suppressed at high fields, so that the intrinsic antiferromagnetic signal is more pronounced, and the cusp appears at 35 K. Indeed, reports on single crystals confirm unanimously the Néel temperature for LiMnPO_4 is 34-35 K.[40, 83, 88, 219] Likewise, the neutron diffraction experiments in this work and elsewhere indicate 34 K is the true Néel temperature.

Our measurements on hydrothermal sample did not exhibit any sign of hysteresis, which is unsurprising because Hausmannite would not have formed under the low-temperature hydrothermal conditions used in the synthesis. There is no signal at 42 K, and the antiferromagnetic cusp occurs around 34 K, as expected. the prominent upturn at low temperatures is likely due to the paramagnetic signal dominating over the antiferromagnetic signal as the experiment approaches base temperature.

5.10: General Discussion of the Magnetic Susceptibility for LiCoPO₄

The Néel temperature for LiCoPO₄ is much clearer. All reports assign it as 21-23 K.[48, 53, 55, 96, 97, 186, 215, 216] This is consistent with our measurements as well.

However, in the hydrothermal samples, the antiferromagnetic cusp appears to shift about two degrees higher with increasing applied field. We are not the first to observe this. Kharchenko and his colleagues performed a detailed study of the temperature dependence on the magnetic susceptibility of single crystal LiCoPO₄. [56] They observed the magnitude of the susceptibility was highly field dependent, measuring with applied fields as low as 50 Oe and as high as 5 T. They also observed slight hysteresis below the Néel temperature.[55] They attributed this to a weak ferromagnetic ground state.

We did not observe FC/ZFC bifurcation in the solid state sample. The solid state sample exhibited conventional antiferromagnetic behavior. This is unsurprising because the Co²⁺ ion is stable under the synthetic conditions and less susceptible to oxidation than LiMnPO₄.

We did observe FC/ZFC bifurcation in the hydrothermal samples. The bifurcation could be due either to an antiferromagnetic impurity around 20 K, or could be due to the particle size of the samples. Particle size has also been demonstrated to affect the bifurcation in Co₃O₄. [233, 234, 235] In addition, particle size can affect the observed transition temperature. As with LiMnPO₄, the bifurcation was suppressed at high magnetic field.

Our hydrothermal synthesis was performed at low temperature and for only 10 hr of direct heating time. While the finest particles were removed during washing and filtration, the particles of powder were still noticeably finer than the powder prepared by solid state ceramic sintering. This is supported by the XRD data, because the reflections for the hydrothermal samples are

slightly broader and are less intense than for the samples prepared with solid state methods.

5.11: General Discussion of the Magnetic Structure

For LiMnPO_4 , the refined magnetic structure is in good agreement with previous reports.[87, 88, 93, 214] A depiction of the magnetic structure is included in Fig. 5.11. However, Newnham and Santoro's first report from powder neutron diffraction reported a refined moment of $5.2 \mu_B$. [87] Ours is much lower, at $4.28(3) \mu_B$. As discussed in §5.9, the effective moment determined from Curie-Weiss analysis is in good agreement with theory. The moment $5.1(1) \mu_B$ is in good agreement with a high-spin d^5 metal ion. Since all the d-orbitals are half-filled, they form strong covalent bonds with the surrounding oxygen atoms of the phosphate, which form a highly distorted octahedral center. The covalency reduces the total moment size, because it alters the localized spin density around the metal ion site. This in turn alters the form factor for the ion. This strong bond covalency is also manifested in the transition temperature. The LiMnPO_4 analog has the highest Néel temperature in the LiMPO_4 ($M = \text{Mn, Co, Fe, Ni}$) series. This is due to the increased exchanged interactions between the ions, due to this strong covalency.

LiCoPO_4 , the refined magnetic structure is consistent with previous reports. Fig. 5.11 depicts the magnetic structure. The refined magnetic moment of $3.28(4) \mu_B$ is higher than expected due to unquenched orbital angular momentum. This was also observed in the effective moment measurements from Curie-Weiss analysis.

Recall from §5.8, we did not observe any intensity for the (010) reflection for LiCoPO_4 . This was in fact a deciding factor in determining the magnetic space group was $Pnma'$. However, Vaknin *et al.* did observe a very weak signal for this reflection in single crystal diffraction

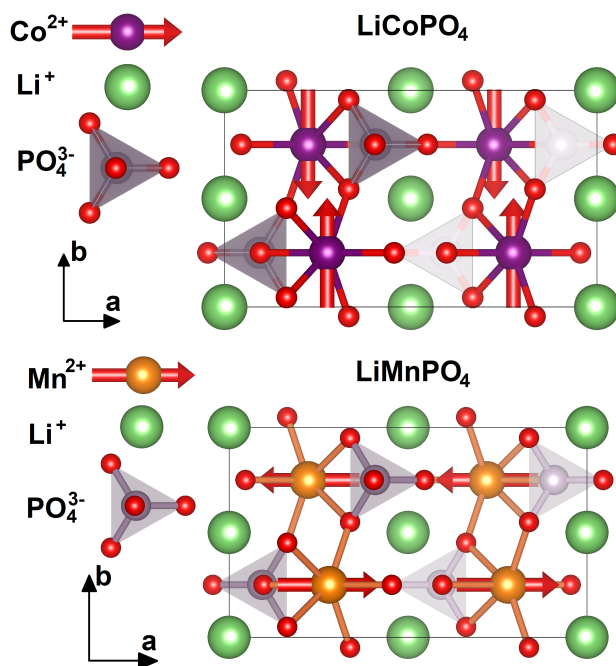


Figure 5.17: Magnetic structure model of LiCoPO_4 and LiMnPO_4 able to be resolved from powder neutron powder diffraction. The figure was created using the modeling software *VESTA* 3.[179] Reproduced from Fig. 9 of Gnewuch & Rodriguez (2020).[175]

studies.[48] Based upon this, they concluded they were a spin rotation off the b axis by 4.6° . This would then lower the point symmetry to $2'_x/m_x$. In support of this theory, they cited Kharchenko's evidence for weak ferromagnetism, in which they proposed the true point group was $2'$ or m' . [55] Vaknin and his colleagues suggested the weak ferromagnetic component would then lower the symmetry from $2'_x/m'$ to $2'_x$. Second Harmonic Generation studies on a LiCoPO_4 crystal provided further evidence the true point group is $2'_x$. [59, 138]

Fore recently Fogh, Vaknin, Toft-Petersen, and their colleagues performed meticulous neutron diffraction studies on a LiCoPO_4 single crystal and were unable to observe the (010) reflection.[7] Instead, they observed a weak (100) reflection. This would result in an A_z component with a canting angle of $7(1)^\circ$. The canting would reduce the point group to $2_z/m'_z$, and the weak ferromagnetism would further reduce the point symmetry to m'_z .

Since this report was with powder sample, we observed neither the (010) nor (100) reflections. Indeed, even Fogh mentioned she and her colleagues were unable to observe any evidence of magnetic structure besides mmm' until they used an instrument with a lower background.[7] We therefore only provide confirmation that the structure is primarily described by the magnetic space group $Pnma'$ with the magnetic point group mmm' .

5.12: Conclusions

We synthesized LiCoPO_4 and LiMnPO_4 using both hydrothermal and solid state methods. The magnetic susceptibility differs significantly based upon the synthetic conditions used. LiMnPO_4 produced by ceramic sintering results in low levels of Hausmannite impurities, which dominates the signal at low applied magnetic fields. In addition, there is noticeably FC/ZFC bifurcation in the solid state LiMnPO_4 and both hydrothermal samples. The bifurcation could either be due to an unidentified impurity, or particle size effects. The bifurcation is suppressed at high applied magnetic fields. The Curie-Weiss analysis at high fields was reasonable, suggesting using high fields ≥ 10 kOe is a helpful experimental condition.

We also performed neutron powder diffraction on the two samples prepared by solid state methods. The order parameter for LiMnPO_4 suggested 3D Ising behavior for the system, whereas the order parameter for LiCoPO_4 was in-between 2D and 3D Ising behavior. Powder diffraction is unable to observe low-intensity reflections, indicative of canting or spin rotation. The magnetic models confirm the magnetic structure for both is C-type, with the spins aligned primarily along the x axis for LiMnPO_4 , and primarily along the y axis for LiCoPO_4 . The refined moment of $3.28(4) \mu_B$ for LiCoPO_4 is characteristic of an orbital contribution to the total magnetic moment.

The refined moment of $4.28(3) \mu_{\text{B}}$ is due to the strong covalency between the Mn^{2+} ion and the surrounding oxygen atoms.

Chapter 6: Conclusions and Future Directions

“To conclude this brief excursion into the magic land of symmetry...”

Edgar Ascher

Int. J. Magnetism **1974**, 5, 287-295.

I end this document with a tribute to Ascher’s seminal paper which originally inspired this subfield of ferrotoroidicity. His work began with a love of symmetry and it only seems right that progress could only be made on toroidal structure theory with equal passion for the intricacies of the symmetry in candidate structures.

For too long candidate ferrotoroidal materials have been determined by point symmetry alone. However, if a three-dimensional motif, such as a ring of spins, would create toroidal moments, then there must be an understanding of how a three-dimensional structure can fulfill these symmetry requirements.

To that end, I propose that a ring of spins is not possible in every antiferromagnetic material with the appropriate point group of the space group. Rather, it is imperative to examine the unit cell and identify sites of $\bar{1}$ ’ symmetry between the magnetic moment sites where toroidal moment could occur. The orientation of the magnetic moments would then determine the orientation of the toroidal moments, since the toroidal moments must be perpendicular to the “ring of spins” by definition.

Certainly, there would be interest in using some method to search a database of magnetic structures to identify additional ferrotoroidal candidates. In addition to narrowing the search by magnetic point group, it is also necessary to narrow the search to magnetic space group. The magnetic space group must have sites of $\bar{1}'$. As a reminder, these occur wherever there is an even numbered rotation axis perpendicular to a mirror plane and one and only one of those symmetry elements are primed.

A new class of magnetic materials has recently been defined called alter magnets.[236, 237, 238] They are a type of colinear ferromagnets and antiferromagnets which exhibit an additional colinear order. Since most of the toroidal candidates identified in this work exhibit colinear antiferromagnetism, it would be interesting to explore the connection between toroidal materials and altermagnets.

Another area which has not been explored is the connection between toroidal moments and the lithiation/delithiation intercalation process in the LiMPO_4 ($M = \text{Fe, Co, Mn, Ni}$) series of olivine materials. These are well-known cathode materials, particularly LiFePO_4 which is favored due to its low toxicity. Do the toroidal moments facilitate this intercalation process?

As for how toroidal moments occur from magnetic moments, that is for the work of qualified theoretical physicists. There are several unanswered questions which must first be resolved before future detailed diffraction experiments can be performed to probe for toroidal structure:

- How would a neutron (which has a magnetic spin) interact with a toroidal moment?
- Would it scatter? In which direction?
- Would it have a “scattering cross-section?”
- Can a scattering event even occur where there is no atom, but only a moment (a toroidal

moment) to interact with the neutron?

Indeed, toroidal moments have not yet even been proven to exist. However, any experiments probing for a novel property need one or more samples to test. Therefore it is my sincere hope that the ferrotoroidal model presented herein is a valuable resource for any individual hoping to undertake that endeavor.

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