ULTRASONIC STUDIES OF THE JAHN-TELLER EFFECT IN A MODEL SYSTEM

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The Jahn-Teller effect occurs when degenerate atomic levels lower their energy by distorting and therefore lowering the symmetry of the system. This effect occurs in a range of molecular and crystalline systems, but here we focus on one in particular, the crystal series $\text{Tm}_x Y_{1-x} \text{VO}_4$. The x = 1 member of this series was studied extensively in the 1970's and 1980's as a paradigmatic example of the cooperative version of the Jahn-Teller effect. In this material, Jahn-Tellersusceptible energy levels on the Tm^{3+} ions interact with each other to drive a phase transition at T = 2.15 K. On the dilute end of the series, for $x \ll 1$, Tm^3 + ions replace yttrium at such a low density that they are unable to interact with each other and therefore act as though they are isolated.

In this thesis, we examine both the cooperative and isolated Jahn-Teller effect as well as the regions in between where neither paradigm is completely true. We first use ultrasound-driven transitions between localized 4f levels to study the microscopic environment of isolated Jahn-Teller ions. We then present ultrasonic measurements of the speed of sound across this material series and show how we can use this data to extract an effective interaction distance between Jahn-Teller ions. Finally, we examine the formation of Jahn-Teller strains at both the isolated and the cooperative ends of the series.

BIOGRAPHICAL SKETCH

Patrick Hollister was born in 1993 in Vallejo, California. As a child he enjoyed learning about space and watching science documentaries. He started to become interested in studying math and physics in middle school and high school when he realized that he really liked solving math and physics problems. He graduated from Benicia High School in 2011 and then went to study physics at the University of Pennsylvania. At UPenn, he learned more about physics and realized that he wanted to continue studying it in graduate school. He was thrilled when he learned about his admission to Cornell, and in the summer of 2015 he flew to Ithaca to start graduate school.

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CHAPTER 1 INTRODUCTION

1.1 Outline of Thesis

In this thesis, we present our work from the last several years on a class of materials that undergo the Jahn-Teller effect. This is an effect that has been studied for decades [3] and plays an important role in many physical and chemical systems [4] [5]. In this effect, degenerate energy levels are unstable to changes in the structure of the crystal. Under certain circumstance, this effect can even drive a cooperative transition where the entire lattice deforms [6]. This thesis will be an examination of several aspects of this effect in a model material series: $Tm_x Y_{1-x} VO_4$. In this chapter, we will attempt to situate where this thesis fits in the context of modern research in condensed matter and provide motivation for our work. We will also provide a more thorough introduction to the Jahn-Teller effect. Chapter 2 will examine some of the theoretical concepts required to understand to the Jahn-Teller effect in more depth. Chapter 3 will discuss the experiment methodologies used to make our measurements. Chapter 4 will discuss our first study in which we use a technique known as ultrasonic paramagnetic resonance to examine internal distributions of strain in the x = 0.01and x = 0.03 samples. The second study, seen in chapter 5, focuses on extracting the range of interaction between these Jahn-Teller states. In chapter 6, we examine effects of static Jahn-Teller strains on the speed of sound in the dilute and cooperative Jahn-Teller systems.

1.2 Nematicity in the Iron Superconductors

The materials motivating this thesis are the cuprates [7] [8] and in particular the iron superconductors [9] [1]. The iron superconductors are a class of high T_c superconductors that were discovered in 2008 [10] and that triggered a landslide of research investigating the driving mechanisms behind the multiple phases seen in their phase diagrams. One very well studied member of this series, which we will discuss more, is Ba(Fe_xCo_{1-x})₂As₂. The low-temperature phase diagram of this material is shown in Figure 1.1 [1].

In this temperature vs doping phase diagram, we see what happens as we either electron dope or hole dope the system. Initially at 0 doping, and as the temperature is lowered, there is a simultaneous transition into an antiferromagnetic and nematic state. Upon electron doping of this system (via Co for example), these transitions are split with the nematic transition now occurring at a higher temperature. In addition, the electron doping suppresses these two transitions so at some critical doping, the transition temperature goes to 0 K. As these two transitions are suppressed, superconductivity emerges and reaches it's highest T_c near the doping where the magnetism and nematicity are completely suppressed. Complicating the matter even more is that these materials are multi-band conductors [11] and that adding dopants also results in the introduction of disorder into the materials. All this physics in close proximity, which makes determining cause and effect an incredibly difficult problem. As a result, developing an understanding of this phase diagram is still an active area of research. Our research interests involve developing a better understanding of one of these phases, nematicity, and its relation with the other physics in this diagram, such as disorder or superconductivity [12].

But first, what is nematicity? Nematicity is an idea that originally comes from the world of liquid crystals and describes a transition that breaks the continuous rotational symmetry of the system while maintaining the continuous translation symmetry [13] [14]. A similar idea exists in solids, with electron nematicity referring to a phase in which the high energy electronic degrees of freedom drive a phase transition that lowers the rotational symmetry of the lattice while maintaining the long-range lattice translational symmetry [15]. This is what is meant by nematicity in the phase diagram in Figure 1.1.

We'll be taking an alternate approach to understanding the interactions of nematicity and other physics. Instead of examining nematicity in the context of the complicated phase diagrams of the iron superconductors, we will examine it in a simple, model system. The idea is to then slowly introduce complexity into the materials and see how this affects the behavior of the nematic phase. We are currently at the beginning of this long-term study with several other groups [16] [17] [18] and are starting by studying the effect of disorder on nematicity. The cooperative Jahn-Teller effect, which can drive ferroquadrupolar order, is one manifestation of electron nematicity [19] and is the focus of our research.

1.3 Introduction to the Jahn-Teller Effect and Quadrupolar Physics

As mentioned before, the Jahn-Teller effect describes when degenerate energy levels are unstable to changes in the structure of the crystal. In this section, we will build up a simple cartoon to help develop some intuition for this effect. Before we get started, however, we should first mention an important exception:



Figure 1.1: **Phase diagram for the iron-based superconductors**. A typical example of the phase diagram for the iron-based superconductors upon either electron or hole doping. Superconductivity emerges upon suppression of nematicity and magnetism on sides of the diagram. On the electron side, doping splits these two transitions. The insets show the behavior of the nematic and magnetic order parameters at different dopings on the diagram. Reproduced from [1]

Kramers' doublets. A Kramer's doublet is a state with half-integer spin that is doubly degenerate due to time-reversal symmetry and cannot be split by electric fields and therefore deformations of the lattice [20]. Only fields that break timereversal symmetry, such as a magnetic field, can split these levels. The rest of our discussion on the Jahn-Teller effect will therefore ignore Kramer's doublets.

Now let's investigate a simple example of the Jahn-Teller effect to build intuition for the rest of this thesis. Imagine taking two atomic *d*-orbitals (d_{xz} and d_{yz}) and placing them in the center of square unit cell as Figure 1.2. These objects, as depicted, represent the charge distribution of these orbitals. The lowest order multipole moment of each orbital, if we include an atomic nucleus at the center,



Figure 1.2: **Cartoon of the Jahn-Teller effect.** This image shows a cartoon of the single ion Jahn-Teller effect. Two *d*-orbitals, each with their own quadrupole moment, are placed in a square environment. The net quadrupole moment here is $\langle Q \rangle = 0$. These quadrupoles have the same energy because they see the identical environment due to the symmetry of the square. This configuration is unstable to deformations of the square. Stretching the square in one direction or the other lowers the energy of one orbital compared to the other and the electrons end up living in one of these states. This breaks the symmetry of the system as and induces a quadrupole moment.

is an electric quadrupole moment. These objects don't have a monopole moment because there's no net charge on the atoms since the electric and nuclear charges cancel out. Due to the symmetry of the orbitals, there's also no electric dipole moment. The lowest order non-zero moment is therefore a quadrupole moment associated with each object. When the electrons in the atom sit in both the d_{xz} and d_{yz} as in the original square environment in Figure 1.2, the average quadrupole $\langle Q \rangle$ is zero. In addition, two states have the same energy due to the symmetry of the square.

First, imagine stretching this square along one direction. This changes the environment of one of the *d*-orbitals compared to the other, which lowers the energy of one of the *d*-orbitals. For example, in our cartoon, stretching the cell along the x-direction lowers the energy of the d_{xz} orbital, while stretching along the *y*-direction lowers the energy of the d_{yz} orbital. The electron will fall into the lower energy state (depends on the stretching direction) and will lower the energy of the system. In addition, this will result in the formation of a net average quadrupole moment since these moments no longer cancel out.

We now place these d_{xz} and d_{yz} orbitals into a square lattice such as in Figure 1.3. In the single ion case, the distortion from the Jahn-Teller emerges gradually as the temperature is lowered and the electrons fall into the lower energy state. However, in a lattice with many of these Jahn-Teller states in close proximity, this emergence of a Jahn-Teller distortion does not happen gradually as in the isolated case. At high temperatures, the orbitals/distortions act independently and can fight against each other suppressing local distortions. However, below a certain temperature they may undergo a cooperative transition where all of the orbitals and distortions start to act together. Then as the temperature

is lowered, the distortion of the cell increases cooperatively across the whole lattice. We can now see how the Jahn-Teller effect maps onto nematicity. Here we have a phase transition that breaks the rotational symmetry by choosing one orbital and distorting along that orbital's direction while approximately maintaining the lattice translation symmetry.

In our studies, we will be looking at perturbations from the ideal cases of the purely isolated Jahn-Teller effect and the purely cooperative Jahn-Teller effect. For example, at the cooperative end we can remove the Jahn-Teller orbitals from sites such as in Figure 1.4. This will add disorder into the system by destroying the periodicity of the lattice, as well as creating distortions that can extend throughout the lattice. We can then examine how these effects suppress the cooperative transition and also effect fluctuations above the transition temperature. On the isolated end, such as in Figure 1.5, we will examine what happens as we add more Jahn-Teller active sites to a lattice and they start communicating with each other. Hopefully this will also give us more insight into the cooperative end of the Jahn-Teller effect as well. We will examine these effects in in a model Jahn-Teller material which will be described in the next section.

1.3.1 Nematicity in TmVO₄

The Jahn-Teller/nematic system we choose is $\text{Tm}_x Y_{1-x} \text{VO}_4$, a well-studied material from the 70's and 80's that was considered a paradigm of the cooperative Jahn-Teller Effect [6] [21]. We approach this material from both ends of the Tm substitution series. At one end, we have TmVO_4 where the Tm ions behave cooperatively and participate in a cooperative Jahn-Teller phase transition (ne-



Figure 1.3: **Jahn-Teller effect on a lattice.** This image shows a cartoon of the Jahn-Teller effect in a lattice. In panel a), two quadrupoles with the same energy sit at the center of each unit cell. This configuration is unstable to deformations of the lattice. This results in the lattice stretching in one direction, which lowers the overall energy of the system and induces a non-zero quadrupole moment.

matic) at $T_c = 2.15$ K [22]. This transition can be suppressed with a magnetic field of approximately 0.5 T along the c-axis of crystal [16]. On the other end we have YVO₄ with Tm ions replacing Y sites resulting in essentially isolated Jahn-Teller ions in an otherwise inert lattice. On the cooperative end, the goal is to examine how disorder suppresses the cooperative Jahn-Teller transition and attempt to understand its role on the properties of nematicity. On the isolated end, we attempt to study what happens as isolated ions start to interact each other. The goal of these studies is to gain an understanding of this sort of



Figure 1.4: **Perturbations from the cooperative Jahn-Teller effect.** This image shows one of the regions of the Jahn-Teller effect we will examine. In our studies, we will see what happens when we add disorder to the cooperative Jahn-Teller effect by removing quadrupoles from the lattice.

orbital-driven nematicity and disorder in an environment where "nothing else" is happening.

In this thesis, we primarily use pulse echo ultrasound to characterize the physics of the Jahn-Teller effect. Ultrasound is a powerful technique that sends high frequency sound into a material to probe the behavior of the elastic constants as a function of an external tuning parameter. The elastic constants directly probe the sensitivity of the lattice to distortions and can give us exceptionally detailed information about the strains present in a crystal. Since the Jahn-Teller effect results in distortions of the lattice, ultrasound is particularly



Figure 1.5: **Perturbations from the isolated Jahn-Teller effect.** This image shows another region of the Jahn-Teller effect that we will examine. Our studies will investigate what happens as we add more quadrupoles to the lattice and they begin to communicate with each other.

sensitive to extracting information about what is happening from this effect. In the rest of this thesis, we will discuss what information ultrasound can give us about the Jahn-Teller effect in $\text{Tm}_x Y_{1-x} \text{VO}_4$. Although ultrasound has been measured in TmVO_4 before [23] [24] [25] [26], these measurements have tended to be in the pure TmVO_4 sample. In our studies, while we have measurements in the pure sample, we will typically examine samples with substantial fractions of yttrium present. We will begin with a more detailed theoretical discussion of this effect and then an intro to how to perform ultrasound experiments. The next three chapters will present our major findings from ultrasound and we will end with a conclusion summarizing our results.

CHAPTER 2 THEORY

In this chapter, we will describe the theoretical background necessary to understand the results presented in later chapters. We wil start with a brief discussion of group theory and representation theory, which is a powerful framework in which to understand the effects of symmetry on the physics. The idea of a representation is very common in our work, and it will be worth time developing intuition about this idea. After this introduction, we will examine the different energy scales present in $Tm_xY_{1-x}VO_4$. This discussion will start at the largest energy scale and move to lower energy scales, eventually showing how the physics in which we are interested emerges.

2.1 Intro to Group Theory

This section will be a simplified discussion of the key elements of representation theory that are necessary to understand the physics in TmVO₄. Our discussion will also enable us to understand character tables. We will begin with an introduction of the basic ideas of group theory and then move quickly into representation theory. This general discussion will follow the book by Dresselhause titled *Applications of Group Theory to the Solid State* [27]. More detailed explanations and proofs can be found in the full text.

A group is a collection of objects *A* belonging to a set G ($A \in G$) with a binary operation * that takes two objects and maps them to another and which obeys the following axioms:

- A * B is another element of the set $(A * B \in G)$.
- There exists an identity element such that A * E = E
- For every element A, there exists an element A^{-1} such that $A * A^{-1} = E$
- Associativity (A * B) * C = A * (B * C)

A group where all its elements commute (A * B = B * A) is known as Abelian while one where not all elements commute is known as non-Abelian.

One of the most important ideas of group theory is that of an homomorphism. This is a function f that takes an element of one group G to another group G' while preserving the group operations.

$$f(A * B) = f(A) * f(B)$$
 (2.1)

This concept allows us to take more difficult to work with objects (symmetry operations) and map them onto more concrete ones while preserving the basic rules of that group. For example, we can map the group of symmetry operators onto square matrices. The group properties will be the same but we will gain the additional utility of linear algebra theory.

The final basic group property that will be used is the idea of a class. A class *C* is a set of objects that are related to each other by a similarity transformation which is defined as the multiplication $R^{-1}XR = Y$ where R is defined for all elements of the group. Notice that if the group is Abelian, that each class only has one element.

The ideas presented so far are quite abstract but they will become more concrete with the introduction of the canonical example of the symmetry operations on an equilateral triangle. Figure 2.1 shows such an equilateral triangle



Figure 2.1: **Symmetry operations on an equilateral triangle.** This figure shows the operations on an equilateral triangle which interchange the vertices but preserve the overall shape and orientation of the triangle. These are the identity operation, two rotations, and reflections across three mirror planes.

	1	R_+	<i>R</i> ₊	m_1	m_2	m_3
1	1	R_+	<i>R</i> ₊	m_1	m_2	m_3
R_+	<i>R</i> ₊	R_{-}	1	m_3	m_1	m_2
R_{-}	<i>R</i> _	1	R_+	m_2	m_3	m_1
m_1	m_1	m_2	m_3	1	<i>R</i> ₊	R_{-}
m_2	m_2	m_3	m_1	<i>R</i> _	1	R_+
<i>m</i> ₃	m_3	m_1	m_2	R_+	<i>R</i> _	1

Table 2.1: **Multiplication table for symmetry operations on a triangle.** The element 1 is the identity element, the element R_{\pm} are rotations around the center of the triangle by $\pm 120^{\circ}$, and the m_i are reflections across the three mirror planes.

centered at the origin with each of its vertices labeled 1, 2, or 3. There are 6 possible symmetry operations which interchange the vertices while keeping the triangle looking the same. They are the identity operation, two rotations (120° and -120°), and three reflections across the mirror planes m_1 , m_2 , and m_3 . The effect of the different operations on the vertices is that the identity leaves the points unchanged, rotations permute all three points, while the mirror planes switch two of the points. The multiplication table shows the rules for combining multiple operations in a row where the order of the multiplication is row label first times column label such that *row* * *column* = *product*. Our convention will be that the symmetry operator on the right will be the one applied to the triangle first. Then the next symmetry operator is applied to the resultant state.

The first thing to prove is that these symmetry operations form a group. As can be seen in the multiplication table, multiplying any combination of symmetry elements results in another symmetry element meaning that the symmetry operators are closed. The identity element exists and is just the operation with no corners moving. Each element has an inverse as well. The identity element is its own inverse, the mirror operations are there own inverses as well. Finally the rotation in the opposite direction is the inverse of a rotation element. These elements also obey associativity, which can be seen by using the multiplication table.

Now that we have shown that these symmetry operations form a group, we can examine some of the group properties in a more concrete setting starting with the idea of a class. If we find the conjugates for all the group elements we find that the identity element always transforms to itself, the rotations transform to each other, and the reflections transform into each other. We find that there are three classes formed by the identity, rotations, and reflections. Each class contain all the symmetry operations that are alike and which can be transformed into each other via changes in the "coordinates."

The other group property that becomes clearer with this example is the idea of a homomorphism. The first example of a homomorphism was actually shown by Table 2.1. The symmetry operations themselves are geometric operations that physically transform the points on the triangle. We mapped these operations to the different symbols in Table 2.1 so that the group multiplication is preserved (a homomorphism). This simplifies thinking about these symmetry operations since now if we want to combine multiple symmetry operations we don't have to think about physically transforming the triangle in our heads. Instead we can just look at the multiplication table. Another example of a homomorphism which will lead directly into the idea of representations can be seen by the mapping: $1, R_+, R_- \rightarrow 1$ and $m_1, m_2, m_3 \rightarrow -1$. This mapping is not one-to-one but it preserves the group multiplications and is still a homomorphism. It turns out this mapping is our first example of a representation.

Representations

We will now introduce the idea of a representation of a group and some of their important/relevant properties. A representation is a homomorphism from one group to a group of square matrices. This means that in a particular representation, each matrix represents a different group element (or symmetry operation). The dimensionality of the matrices in different representations can range in any value and the mapping does not have to be one-to one. For example, the symmetry operations of the triangle can be mapped to the factor group which is just the group of 1 and -1 as seen before. This group is not a one-to-mapping but still is a representation.

Although a representation can be any dimension, not all representations are "fundamental" (irreducible). If every matrix in a representation, through some similarity transformation $A^{-1}RA$, can be brought into a block diagonal form then this representation is known as reducible. If it can't be brought into that form it is irreducible. If the matrix is brought into block diagonal form, each block is a different irreducible representation. Each block is now independent of each other in that the matrix. For example, the different blocks do not mix together during a matrix multiplication. We can think of this reducible representation as being decomposed into a combination of different irreducible representations.

One of the reasons representation theory is so useful in the study of quantum mechanics comes from the orthogonality relations of irreducible representations. The following equation shows the orthonormality relation for irreducible representations.

$$\sum D_{\mu\nu}^{l_1}(R) D_{\mu'\nu'}^{l_2}(R^{-1}) = \frac{h}{l_1} \delta_{\Gamma_1 \Gamma_2} \delta_{\mu\mu'} \delta_{\nu\nu'}$$
(2.2)

The $D_{\mu\nu}^{l_i}(R)$ are the matrix representations of the the symmetry operations *R*. The μ and ν are the indices of the matrix, the Γ_i represent the particular representation, *h* is the number of symmetry elements, and l_i is the dimension of the representation. This sort of orthonormality relation is immediately evocative of such sums over basis vectors in quantum mechanics and linear algebra that with which we are quite familiar.

We will now try to build some intuition for representations by re-examining the case of the symmetry operations on an equilateral triangle. Recall that there are six symmetry operations on an equilateral triangle and three distinct types of operations (classes). A theorem from representation theory states that the number of irreducible representations is equal to the number of classes in a point group. Therefore we expect to find three distinct irreducible representations. The first representation is the easiest to understand, it's the mapping of all the symmetry operations onto a 1x1 matrices with value 1 and is known as the identity representation. The second operation is the factor group as described before $1, R_+, R_- \rightarrow 1$ and $m_1, m_2, m_3 \rightarrow -1$. So far these representations are only one dimensional, but irreducible representations can also have more than one dimension. The final representation, which we will not derived, is given by:

$$1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, R_{+} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, R_{-} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, m_{1} = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, m_{2} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, m_{3} = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$
(2.3)

In representation theory in solid state physics, the actual matrix representations are not used nearly as frequently as the characters of the groups. A character is simply the trace of a matrix or the sum of the diagonal elements of a matrix. Many of the useful theorems of representation theory can be written in terms of traces. In addition, the trace for all symmetry elements in the same class are identical, which again simplifies the math. In fact, when looking up information about point groups, the characters are given instead of the actual representations due to their simplicity. Now, if we take the trace of all the representations of the symmetry elements of equilateral triangle, we find the character table given by Table 2.2. This character table is the same as we would find in any reference for point groups. In fact, this is the character table for the $C_{3\nu}$ point group. We now have the knowledge to read character tables and to understand what is meant by irreducible representations throughout the rest of this thesis.

	1	2R	3m
Γ_1	1	1	1
Γ_2	1	1	-1
Γ ₃	2	-1	0

Table 2.2: **Character table for symmetry operations on a triangle.** Each row shows the characters for a different irreducible representation. The first row is the identity representation, the second is the factor group representation, and the final is the 2x2 matrix representation just given. The columns correspond to the different classes with the number of symmetry operations in each class given as well.

2.2 Intro to TmVO₄

In this section, we'll examine in detail the physics of $\text{Tm}_x Y_{1-x} \text{VO}_4$. In particular, we'll explain how the Jahn-Teller effect emerges from the Hamiltonian describing the behavior of the 4*f* electrons on the Tm ions. These 4*f* electrons are the primary drivers of much of the observed low temperature physics in these materials, and there are a range of energy scales associated with them. Starting from largest to smallest these are the Coulomb energy (H_{Cou}), the spin-orbit coupling (H_{SO}), and the crystal fields (H_{CEF}). The Jahn-Teller effect and much of the physics we study emerges at the crystal field energy scale and will be discussed after we discuss the crystal field splittings.

For now we'll focus on these three energy scales and how they affect the physics of the 4f electrons. The Hamiltonian describing the splitting of the 4f electrons on Tm is summarized by Equation 2.4:

$$H = H_{Cou} + H_{SO} + H_{CEF} \tag{2.4}$$

2.2.1 Coulomb Energy (*H*_{Cou})

The largest energy scales in Tm are due to the Coulomb attraction between the electrons and the nucleus. The inner most electrons are the most tightly bound to the nucleus and have by far the largest energy scale in the atom. For example the binding energy of the K electrons (n = 1) is 59.379 keV [28]. Since the energies required to liberate these electrons are so large, inner electrons typically don't contribute to the physics or chemistry. Instead, the valence electrons, which are much less tightly bound, tend drive much of the observed differences between different chemicals and solids. The neutral atom has an electron configuration given by [Xe]4 f^{13} 6s². Tm typically gives up 3 electrons when bonding resulting in the ion Tm³⁺ whose electron configuration is characterized by 12 valence 4f electrons: [Xe]4 f^{12} . For some context of scale, the first ionization 4 energies from smallest to largest are 6.184 eV , 12.065 eV, 23.66 eV and finally 42.41 eV [29] which is the ionization energy for the Tm³⁺ species. These are the largest energy scales for the valence 4f electrons in the problem.

2.2.2 Spin-Orbit Energy (H_{SO})

The next largest energy scale in Tm is due to spin-orbit coupling. Spin-orbit coupling is a relativistic effect that emerges directly from the Dirac equation but can be included by hand into the Schrodinger equation. This effect is a magnetic coupling between the spin and the orbital angular momentum of an electron. This equation takes the form:

$$H_{SO} \propto \vec{L} \cdot \vec{S} \propto J^2 - L^2 - S^2 \tag{2.5}$$

In this equation, \vec{L} represents the orbital angular momentum, \vec{S} the spin angular momentum of the electron, and \vec{J} the total angular momentum. When actually determining the energy splitting from this term, it's found that the energy goes as the 4th power of the atomic number. This means that rare earth materials such as Tm tend to have a very large spin orbit energies. Now that an additional term is added to the Hamiltonian, the atomic quantum numbers (l, m, s, s_z) no longer form a set of good quantum numbers that describe energy levels. Instead the good quantum numbers are now (j, j_z, l, s) [30]. The originally degenerate ground state is now split into a new set of levels which can be characterized by these new quantum numbers. The energy diagram given by Figure 2.2 shows the first few measured spin-orbit levels in $Tm_xY_{1-x}VO_4$ [31]. The ground state is the state ${}^{3}H_{6}$, which corresponds to the 13 j_{z} states with j = 6, s = 1 (3-fold spin degeneracy), and l = 5. The first excited state of ${}^{3}F_{4}$ occurs at an energy approximately 0.7 eV (8300 K) above the ground state, which is much larger than the temperatures at which we work. For our applications we can ignore the excited spin-orbit levels and just focus on the behavior of the ground state.

2.2.3 Crystal Field Energy (*H*_{CEF})

The next energy scale to consider is due to crystal electric fields. As previously mentioned, crystal fields arise from the static Coulomb interaction from nearby atoms. In materials with a large atomic number, the crystal field energy scales are typically much smaller than the spin-orbit energy scales and our material is no exception. The crystal field energies are small perturbations on the much larger spin-orbit splittings that act to split the previously degenerate levels. For
example, the effect of placing a multipolar moment such as our J = 6 (³H₆) level into a crystal field environment is to split the 13 once-degenerate j_z levels. The precise Hamiltonian and splitting depend on the exact microscopic environment of the Tm³⁺ ion though we can learn a great deal just from knowledge of the point group symmetry.

The overall electric potential energy acting between each particle can be described by the classic Coulomb equation:

$$V = \frac{q_1 q_2}{|r - r_0|} \tag{2.6}$$

Since the crystal field is made up of purely electrostatic terms, it can be expanded in terms of spherical harmonics, Y_{lm} . At this stage, this is a classical energy. For the quantum Hamiltonian, we must write this in terms of operators. The quantum crystal field Hamiltonian is typically written in terms of the operators associated with the real space versions of the spherical harmonics: the Stevens operators O_k^q [32]. These operators are written in terms of angular momentum operators. Their eigenfunctions are the real space spherical harmonics while their eigenvalues are the associated multipolar moments [33]. The crystal electric field can then be written as:

$$H_{CEF} = \sum_{q,k} B_k^q O_k^q$$

In this equation the B_k^q are the coefficients describing the splittings of the crystal field levels, and the O_k^q are the Stevens operators. The superscript q is the total angular momentum with q = 0 associated with the monopole moment, q = 1 the dipole moments, and q = 2 the quadrupole moments. The subscript k describes which component of a particular multipole moment we are examining. For example, for q = 2, there are 5 k-values, which describe all possible

quadrupole moments. Though this is the generic form of the crystal field Hamiltonian, many of the terms in this sum will actually be zero due to symmetry. The terms that are nonzero must respect the symmetry of the environment which depends on the point group of the site of interest. In the case of the material series $Tm_xY_{1-x}VO_4$, the overall crystal symmetry is D_{4h} while the site symmetry of Tm is D_{2d} . Therefore, if we wish to determine the splitting of the ³ H_6 ground state, we would use the form of the Hamiltonian for the Tm site at the D_{2d} site.

One of the strengths of group theory becomes apparent in this situation. While we need the exact form of the Hamiltonian expansion with all it's coefficients in order to get the correct crystal field splittings, often determining these coefficients from first principles is difficult. However, representation theory and symmetry properties can tell us the number of levels which it splits into, the degeneracy of these levels, and the irreducible representation associated with these levels.

In free space, the J = 6 state is an 13-dimensional irreducible representation of the full rotation group. The energy levels associated with this representation are degenerate. However, when placed in a crystalline environment this is no longer true. The symmetry of this multipole's environment is now reduced, and this representation is no longer irreducible. This representation can now be decomposed into the irreducible representations of the point group of its new environment (D_{2d} in this case). The once degenerate energy levels will now split according to this decomposition. After performing this decomposition we find:

$$\Gamma_{J=6} = 2A_1 + A_2 + 2B_1 + 2B_2 + 3E \tag{2.7}$$

The J = 6 multipole is now written in terms of the irreducible representations of the D_{2d} point group which tells us how the energy levels split. For example, from this decomposition we know that there are 7 singly degenerate levels and their associated irreducible representations and 3 sets of doubly degenerate levels (*E*) required by symmetry. However, to get the energy differences requires either measurement or a detailed microscopic calculation. The measured/numerical values of the crystal field splittings are given in Figure 2.2 [31]. The ground state is a doubly degenerate state with symmetry *E* while the next state is approximately 75 K higher and is associated with the irreducible representation *A*₁. This isolated ground state drives much of the physics at lower temperatures. Our measurements our primarily taken below 15 K, and at this temperature only about 0.7% of the electrons lie in the excited state. This confirms that below these temperatures it's safe to ignore the excited states and focus only on the isolated doublet. The approximate wavefunction of this ground state is given by $|\pm \rangle = 0.92|\pm 5 \rangle +0.37|\pm 1 \rangle +0.12|\mp 3 \rangle$ [34] where the eigenstates are written in the $|j_z\rangle$ basis. The coefficients are determined from the knowledge of the energy levels splittings from Knoll [35].

By restricting the Hamiltonian to these two states at low temperatures, we can rewrite the Hamiltonian in terms of pseudospin S = 1/2 operators which simplifies the analysis. In the next few subsections we'll show how to write the relevant operators in the pseudo-spin basis.

2.2.4 Jahn-Teller Effect

Up to now, we have examined how the ground state in TmVO_4 emerges from the atomic coulomb potential, spin-orbit coupling, and the electrostatic interaction of the ions with the lattice. However, we haven't yet examined how the



Figure 2.2: Energy-level splittings in TmVO_4 . A diagram of the splittings at different energy scales in TmVO_4 . The first energy scale, the Coulomb energy, is split by the spin-orbit coupling. This ground state has total angular momentum J = 6 and is 13-fold degenerate. The crystal field further splits this level into additional levels determined by the environment of the Tm^{3+} ions. The ground state is a doubly degenerate non-Kramer's doublet, which drives much of the physics studied in this thesis.

Tm ions interact with each other or with external fields. These new terms in the Hamiltonian are the terms that are driving the low-temperature physics in this material and in particular will be driving the Jahn-Teller effect. The Hamiltonian describing these interactions is given schematically by the following equation [36]:

$$H_{in} = H_z + H_Q + H_{Q-Q} + H_{el} + H_{Dipole}$$
(2.8)

The first term, H_z , represents the Zeeman coupling of the the magnetic dipole with an external magnetic field. The next term, H_Q , is the coupling of a uniform

strain with quadrupolar moments. The term H_{Q-Q} represents the quadrupolequadrupole coupling via all phonons except k = 0 acoustic phonons. The next term, H_{el} , is the elastic energy of the lattice. Finally, H_{Dipole} is the interaction energy between magnetic dipoles. However, this term is small in TmVO₄ and will not play a major role in the physics of the Jahn-Teller effect in this material. We will now discuss these terms in more detail describing their form in the J = 6spin-orbit basis first and then describing how to write these in their simplified pseudospin basis.

Zeeman Coupling (*H_z*)

The first term describes how an external magnetic field couples to the J = 6 spinorbit levels. In anticipation of our experiments, we'll consider only a magnetic field along the c-axis. This results in a term in the Hamiltonian of the form:

$$H_z = -\frac{1}{2}g_c\mu_B B_c J_z \tag{2.9}$$

In this equation g_c is the magnetic *g*-factor, μ_B is the Bohr magneton, B_c is the magnetic field along the c-axis, and J_z is the z-component of the angular momentum operator. This Zeeman term commutes with the spin-orbit Hamiltonian and is diagonal in the eigenbasis of the spin-orbit operator. The values of the diagonal are then

$$H_{z,ii} = -g_c \mu_B B_c j_{z,i} \tag{2.10}$$

where for an object with J = 6 angular momentum, $j_{z,i}$ range from -6 to 6. Now we can try to write this matrix in the restricted basis of the ground state by calculating the matrix elements:

$$S_z = \langle \pm | J_z | \pm \rangle \tag{2.11}$$

Calculating this matrix in this basis gives:

$$S^{z} = -\frac{1}{2}g_{c}\mu_{B}B\begin{pmatrix} 1 & 0\\ 0 & -1 \end{pmatrix}$$
 (2.12)

where $g_c = 10.2$ for the crystal field ground state doublet [34].

There are few interesting magnetic properties of this ground state which are worth mentioning. The first is that only the magnetic field component along the c-axis contributes to magnetic energy to first order. As a result, we can ignore the Zeeman coupling along the *x* and *y* directions. In general, the *g*-factor is a tensor that relates the coupling of magnetic field in one direction to the dipole in any direction. However, for an isolated non-Kramers doublet such as in TmVO₄ at low temperatures, there's a theorem showing that the g-factor is only nonzero along one direction [37]. The other important observation is that in zero magnetic field this doubly degenerate ground state has zero dipole moment. This can be seen by calculating the expectation value of the dipole moment for these two states using the density matrix formalism:

$$\langle S^{z} \rangle_{gr} = Tr(\rho S^{z}) \tag{2.13}$$

Here ρ is the density matrix of these two states and is given by:

$$\rho = |+><+|+|-><-| \tag{2.14}$$

Plugging in this equation for ρ into the definition of the trace we find the expectation value takes the form:

$$\langle S^{z} \rangle_{gr} = Tr(\rho S^{z}) = \langle +|+\rangle \langle +|S^{z}|+\rangle + \langle -|-\rangle \langle -|S^{z}|-\rangle = 0$$
 (2.15)

It turns out that the dipole moment of the ground state is 0 in no external magnetic field. However, the application of a magnetic field is able to induce a dipole moment.

Elastic Energy (H_{el})

Since deformations of the lattice are an integral part of the Jahn-Teller effect as well as our ultrasound measurement technique, we must include the elastic energy when describing the physics of the ground state. In this model, we approximate the elastic energy as being harmonic which means that elastic energy will be expanded in terms of the strain to a maximum power of 2. The energy can be written in terms of irreducible strains and for a crystal with D_{4h} point group symmetry, the elastic energy takes the form [38]

$$H_{el} = \frac{1}{2} \left(\frac{c_{11} + c_{12}}{2} (\epsilon_{xx} + \epsilon_{yy})^2 + c_{33} \epsilon_{zz}^2 + 2c_{13} (\epsilon_{xx} + \epsilon_{yy}) \epsilon_{zz} + \frac{c_{11} - c_{12}}{2} (\epsilon_{xx} - \epsilon_{yy})^2 + 4c_{44} (\epsilon_{xz}^2 + \epsilon_{yz}^2) + 4c_{66} \epsilon_{xy}^2 \right) \mathbf{1}$$

$$(2.16)$$

$$H_{el} = \frac{1}{2} (c_{A_{1g,1}} \epsilon_{A_{1g,1}}^2 + c_{A_{1g,2}} \epsilon_{A_{1g,2}}^2 + 2c_{A_{1g,3}} \epsilon_{A_{1g,1}} \epsilon_{A_{1g,2}} + c_{B_{1g}} \epsilon_{B_{1g}}^2 + c_{B_{2g}} \epsilon_{B_{2g}}^2 + c_{E_g} |\epsilon_{E_g}|^2) \mathbf{1} \quad (2.17)$$

In the first equation, we write down the full elastic energy. The next equation shows each strain and elastic constant mapped onto the irreducible representation of the point group. This term doesn't couple to the electronic states at this point, and as a result, the energy levels are represented by the identity matrix, **1**. The dimension of the identity matrix depends on the dimension of the states which we are examining. For the whole J = 6 state, the identity matrix will be 13x13 in the J_z basis while for the restricted pseudospin space of the ground state this matrix is only 2x2.

Another simplification for this problem is that we'll only be interested in strains that can split the degenerate ground state since these are the strains that will result in a Jahn-Teller effect. In the next subsection we'll see that only the B_{1g} and B_{2g} strains will contribute to the Jahn-Teller effect, so we only need to include terms of this symmetry. As a result, the relevant elastic component of

the Hamiltonian reduces to:

$$H_{el} = \frac{1}{2} (c_{B_{1g}} \epsilon_{B_{1g}}^2 + c_{B_{2g}} \epsilon_{B_{2g}}^2) \mathbf{1} = \frac{1}{2} \left(\frac{c_{11} - c_{12}}{2} \epsilon_{B_{1g}}^2 + c_{66} \epsilon_{B_{2g}}^2 \right) \mathbf{1}$$
(2.18)

Strain-Quadrupole Coupling (*H*_Q)

The quadrupole moments located on the 4f electrons are able to interact with the strains in the system. This interaction is the foundation of the Jahn-Teller effect, which is the main focus of this thesis. In this section, we'll focus mostly on constructing the Hamiltonian and leave a more detailed discussion of the physics to later. The most general magneto-elastic Hamiltonian takes the form:

$$H_{Q} = -\left(B^{A_{1g,1}}\epsilon_{A_{1g,1}} + B^{A_{1g,2}}\epsilon_{A_{1g,2}}\right)O_{2}^{0} - B^{B_{1g}}\epsilon_{B_{1g}}O_{2}^{2} - B^{B_{2g}}\epsilon_{B_{2g}}P_{xy} - B^{E_{g}}\left(\epsilon_{E_{g,1}}P_{zx} + \epsilon_{E_{g,2}}P_{yz}\right)$$
(2.19)

In this equation, the terms $O_{2'}^0$, $O_{2'}^2$, P_{xy} , P_{zx} , and P_{yz} are the operators corresponding to the different quadrupole moments. Each of these quadrupole moments is coupled to the corresponding conjugate strains which are shown in Equation 2.16 and Equation 2.17. As a note the strains $\epsilon_{E_{g,1}}$ and $\epsilon_{E_{g,2}}$ correspond to the strains ϵ_{zx} and ϵ_{yx} respectively. Finally their *B* values are the coupling strengths for this strain-quadrupole coupling.

Now we'll examine which terms are actually important to the Jahn-Teller effect. The first term is the coupling between the A_{1g} strain and quadrupole moment with A_{1g} symmetry. This term will not split the ground state, instead shifting both equally. As a result, this term can be ignored since it will just cause a constant offset. The last term in this sum represents the coupling between the

 E_g strain and the corresponding quadrupole moments. The matrix elements in the restricted pseudo spin basis are zero for this term and this term won't contribute [6].

The terms that survive are the ones that couple the B_{1g} strain $\epsilon_{B_{1g}} = \frac{1}{\sqrt{2}} (\epsilon_{xx} - \epsilon_{xy})$ and the quadrupole $O_2^2 = J_x^2 - J_y^2$ and the B_{2g} strain, $\epsilon_{B_{2g}}$, and $P_{xy} = \frac{1}{2} (J_x J_y + J_y J_x)$. We now want to write these quadrupole operators in the restricted basis of the ground state. This can be done by computing the matrix elements:

$$O_{2,ground}^{2} = \langle \pm | O_{2}^{2} | \pm \rangle = \langle \pm | J_{x}^{2} - J_{y}^{2} | \pm \rangle \propto \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \propto S^{x}$$
(2.20)

$$P_{xy,ground} = <\pm |P_{xy}| \pm > = <\pm |\frac{1}{2} \left(J_x J_y + J_y J_x \right)| \pm > \begin{pmatrix} 0 & -i \\ & \\ i & 0 \end{pmatrix} \propto S^y$$
(2.21)

Then rewriting this Hamiltonian in terms of pseudospins we find:

$$H_Q = -B'^{B_{1g}} \epsilon_{B_{1g}} S^x - B'^{B_{2g}} \epsilon_{B_{2g}} S^y$$
(2.22)

Here we write the coupling coefficients as *B*′ to account for a possible change in prefactors from the conversion to the pseudospin basis.

Quadrupole-Quadrupole Coupling (H_{Q-Q})

The final term in the Hamiltonian describes the coupling between nearby quadrupoles. This term appears very similar to the uniform strain-quadrupolar coupling term just described. As before, there are 5 possible quadrupole moments but only two of these moments will be relevant for the Jahn-Teller effect in our E_g ground state. These will be the O_2^2 and P_{xy} quadrupoles. The most general term is a sum over all pairs of quadrupoles, but following the discussion by

Morin and Rouchy [39], we will write this term in the mean-field approximation:

$$H_{Q-Q} = -K^{\gamma} \langle O_2^2 \rangle O_2^2 - K^{\delta} \langle P_{xy} \rangle P_{xy}$$
(2.23)

Here, the *K* values are the coupling strengths between the quadrupole moments and the average quadrupolar fields. Rewriting this in terms of the pseudo-spin operators we find the following equation:

$$H_{Q-Q} = -K^{\gamma} \langle S^x \rangle S^x - K^{\delta} \langle S^y \rangle S^y$$
(2.24)

As before, the addition of the prime to the coupling coefficients *K*' accounts for the possible change in the coupling coefficient upon writing these Hamiltonians in the pseudospin basis.

Finally, there will also be a term that is a correction from the mean-field theory approximation [39]:

$$H_{\langle Q \rangle} = \frac{1}{2} K^{\prime \gamma} \langle S^x \rangle^2 + \frac{1}{2} K^{\prime \delta} \langle S^y \rangle^2$$
(2.25)

This term should be a constant and will be ignored throughout the rest of this thesis.

2.3 The Jahn-Teller Effect

In the previous section, we discussed the Hamiltonian that describes the Jahn-Teller effect in TmVO₄. In this section, we'll discuss some of the qualitative features that can emerge from this Jahn-Teller Hamiltonian to build more intuition for this effect. We'll do this by looking at a simplified version of the Hamiltonian from the previous section that only includes a one-dimensional distortion instead of the full two-dimensional distortion. As an additional simplification, we'll ignore the effect of interactions between quadrupoles and only examine the Jahn-Teller effect for an isolated atom. Finally, if we also allow for the inclusion of the magnetic field energy, this Hamiltonian takes the form:

$$H = \frac{1}{2}c\epsilon^2 - \frac{1}{2}g_c\mu_B BS^z - V_s\epsilon S^x$$
(2.26)

In this equation for this section, we write the Jahn-Teller coupling energy as V_s to be consistent with Gehring and Gehring [6]. If we wish to know what the energy levels look like vs strain, we must diagonalize this 2x2 Hamiltonian. This gives the equation:

$$E_{\pm} = \frac{1}{2}c\epsilon^2 + \sqrt{\left(\frac{1}{2}g_c\mu_B B\right)^2 + (V_s\epsilon)^2}$$
(2.27)

Figure 2.3 shows the Jahn-Teller energy levels from Equation 2.27 for different values of the magnetic field strength and Jahn-Teller coupling strengths. In panel a), we plot the energy vs strain in the case where the magnetic field and the Jahn-Teller coupling is 0. Without any coupling, the energy takes the form of a standard elastic energy. At this stage, these energy levels are doubly degenerate. If we allow for a Jahn-Teller coupling ($V_s \neq 0$), as in panel b), the degeneracy is broken. The minima of the two parabolas now move to lower energy and shift to positive and negative strains. This can result in the formation of non-zero strains in the vicinity of this atom. As a magnetic field is turned on, however, the depth of the wells are reduced as a gap opens up at 0 strain, as seen in panel c). Eventually, the magnetic energy becomes larger than the Jahn-Teller energy, panel d), and the minimum vanishes completely. This will result in an average strain that goes to 0 again.



Figure 2.3: **Jahn-Teller potential for TmVO**₄. This cartoon demonstrates the effects of Jahn-Teller coupling as well as the competition between Jahn-Teller and Zeeman energies. In panel a), there's no Jahn-Teller coupling or magnetic field and as a result we see a standard harmonic potential. Turning on the Jahn-Teller coupling in panel b) results in the degeneracy breaking and the minimum of the potential moving to positive and negative strain. In panel c), a magnetic field is turned on which reduces the depth of the potential minimum until eventually destroying the local minimum at large enough fields in panel d).

Even in the case of the isolated Jahn-Teller effect, there are two additional energy scales worth discussing: the temperature and zero point energy. The temperature can affect the average strain of the atom. For example, if the thermal energy is large enough, atoms can easily be excited over the local maximum in at 0 strain into the other well. This can affect the value of the average strain seen by experimental probes, possibly resulting in 0 average strain. The second energy is the vibrational zero-point energy of the atoms. Even at 0 K, there will be an energy associated with the vibrational energy of the atoms. If this zeropoint energy is large compared to the depth of the wells, then we would expect the average strain to be 0 rather than finite. We'll discuss these energy scales more in Chapter 6 where they are important in explaining our field dependent speed of sound data. Now that we have started to develop an understanding of the Jahn-Teller effect, we will move onto the experimental techniques we use to measure this phenomenon.

CHAPTER 3

EXPERIMENTAL TECHNIQUES

The primary experimental technique used in this thesis is pulse echo ultrasound. In this technique, high frequency sound is sent through a sample by a piezoelectric transducer and the resultant echoes are measured by the same transducer [40]. This gives information about changes in the speed of sound and the attenuation as a function of some external tuning parameter. This chapter will present the experimental techniques required to perform pulse echo ultrasound measurements starting with the measurement electronics, followed by our sample preparation techniques, and finally ending with analysis of the raw data.

In this chapter we will also pay a special interest to the piezoelectric transducers used in our measurements. Transducers are, in general, one of the most important parts of a pulse echo ultrasound measurement since they both generate and detect acoustic signals. Our lab uses specialized thin film ZnO transducers, which we grow in house, and which enables us to perform many of the frequency-dependent measurements seen in this thesis. A section of this chapter will give the recipe that we use in growing our ZnO transducers and give details about the fabrication process.

3.1 Pulse Echo Ultrasound Electronics

The first piece of the experimental puzzle which we'll describe is the electronic circuit required to perform a pulse echo ultrasound experiment. The electronics



Figure 3.1: **Schematic RF circuit for ultrasound**. A circuit diagram describing our RF electronics. These electronics must generate an RF pulse, send it to the transducer, and detect the resultant echoes measured by the transducer. The RF generator (RF) generates a pulse which is amplified by Amp 1 and then goes through switch 1 (SW 1). It then travels through switch 2 (SW 2) to the sample where it is converted to sound by the attached piezoelectric transducer. The signal travels back and forth through the sample and is converted to an electrical signal again that is then sent to switch 2 again. It then is diverted to the second amplifier (Amp 2) and is read out by an oscilloscope (Scope). Arbitrary function generator 1 (AFG 1) is used for the circuit timing and to shape the RF pulse. Arbitrary function generator 2 (AFG 2) is used produce the control logic which changes the paths of the switches.

must be able to perform several primary functions. First, the electronics must generate a large RF electrical signal to drive the piezoelectric transducer. Additionally, they must be able to measure and amplify the small signal that the transducer detects from each echo without being drowned out by the driving signal. The basic schematic of this circuit is presented in Figure 3.1. In the following discussion we'll follow the path of the RF signal through the circuit, discussing the role of each element as we reach it.

The first element in the circuit is the RF generator (Tektronix TSG 4106A). Our RF generator can produce a sinusoidal RF signal with a frequency up to 6 GHz which can be shaped into pulses with either an internal or external source. We require a pulsed RF signal in this application since a continuous signal would make it impossible to resolve individual echoes in the circuit, which is key to this technique. The maximum allowed width of the pulses in a measurement is determined by the material properties of the sample being measured. We need each echo to be individually resolvable, so the width must be less than the time it takes for an echo to travel back and forth through sample. This time depends on the speed of sound and the thickness of the sample we can measure. The internal square pulse used to shape the RF signal is limited to a width of 100 ns, but by using an external arbitrary function generator we are able to send out pulses that are much narrower, so far down to 10 ns. This narrower pulse width enables us to measure ultrasound on samples which are several hundred nanometers thick. Now that we have discussed the production of the RF signal, we will talk more about the control signals used in this circuit.

The timing and logic of this circuit is controlled by two arbitrary function generators (Tektronix AFG1062). The first arbitrary function generator (AFG 1) serves multiple purposes. First, it is used to adjust the width of the RF pulse. Its second application is to control the timing in the circuit. One of the outputs of AFG 1 is connected to the clock input on both the RF generator and arbitrary function generator 2 (AFG 2). This ensures that all three outputs of these devices are in sync and that the phase of the signals don't shift relative to each other. The other function generator, AFG 2, is used to produce two square pulses which control the switches in the circuit. Details about the output of AFG 2 will be discussed in more depth when we discuss the roles of the switches.

After the RF pulse leaves the generator, it travels to a power amplifier (Amp

1; Mini-Circuits ZHL-42W+) in preparation for being sent to the transducer on the sample. The signal then travels through the first switch (SW 1; Mini-Circuits ZFSWA2-63DR+). This switch is turned on and off by one of the channels on AFG 2. This switch is only closed to allow the RF pulse from Amp 1. Otherwise it is open (connected to ground through 50 Ω) to reduce noise from the power amplifier and to prevent reflections of power into the output of the amplifier. After traveling through SW 1, the signal then propagates to switch 2 (SW 2; Mini-Circuits ZFSWA2-63DR+). SW 2 is always connected to the sample and either connects to Amp 1 or Amp 2 depending on the control logic from AFG 2. At this point, SW 2 allows the signal to propagate from Amp 1 to the transducer.

Once the electrical signal reaches the transducer, it is converted into an acoustic signal which propagates back and forth through the sample. Each time the sound finishes a complete trip across the sample, the transducer detects the acoustic signal and generates an electrical signal which can then be detected by our electronics. The echo spacing is determined by the time it takes for the sound to complete a full trip across the sample. These echoes now travel back down the coax towards the switches. The control logic from AFG 2 has by this point switched, which results in SW 1 closing and SW 2 connecting to the linear amplifier (Amp 2; Mini-Circuits ZX60-3018G-S+) instead of Amp 1. The echoes are amplified by Amp 2 and then sent to the oscilloscope (Tektronix MSO64), where they can be read by a computer to be analyzed further.

3.2 Sample Preparation

Before performing a pulse echo measurement, we first must prepare a sample suitable for this technique. In our lab, we primarily measure single crystals. This enables symmetry resolved measurements of the elastic constants, which is one of the strengths of ultrasound. In addition, we require that our crystals have two parallel faces which allows sound to continuously bounce back and forth while minimizing reflections off side surfaces. We also need to know the direction of propagation of the sound and the direction of the polarization to within a couple degrees so that we can be confident that we are measuring the correct elastic constants. Finally, we need a smooth, clean surface where we can place the transducer so we can get good coupling to the sample. Once the sample is ready, we can load it into the cryostat and begin our measurements. In the following section, we'll delve into even more depth for this sample prep process.

Outline of Sample Preparation

- Align Sample
- Polish Sample
- Clean Sample
- Sputter Transducer
- Mount Sample onto Board
- Load Sample and Measure



Figure 3.2: Flux-grown $TmVO_4$ samples. These samples grow like needles along the c-axis and also grow with crystal facets normal to the (100) axis.

3.2.1 Aligning the Sample

The process for preparing a sample first begins with determining the orientation of the crystal. In pulse echo ultrasound, as mentioned, we want to send sound along a high symmetry direction in order to isolate the behavior of a specific elastic constant. In addition, we may want to apply a magnetic field along a particular axis. Determining these axes is generically a difficult process if there are no natural facets on the crystal. However, frequently crystals grow with high symmetry axes pointing normal to crystal facets which can aid in the sample preparation process. For example, the flux grown TmVO₄ used in our measurements (Figure 3.2) typically grows with a crystal facet pointing along the (110) direction. Regardless of the initial shape of the crystal, we primarily use x-ray scattering for alignment. The main x-ray technique used is Laue backscattering diffraction. In this technique, a range of x-ray wavelengths are sent into a crystal (rather than a monochromatic beam), and we measure the elastically backscattered x-rays. The condition for elastic scattering is that the difference between the incoming and outgoing wavectors match one of the reciprocal lattice vectors of the sample [41] [42]. Laue refraction is so useful because the range of incoming x-rays means that there is practically always a wavevector difference from the scattering that matches the reciprocal lattice vector. Therefore we will always see reflections from the lattice at any orientation which simplifies the alignment process.

While the range of x-rays makes it more difficult to determine k-space indices of each peak, it allows for almost real time determination of alignment. In addition, the Laue image reflects the symmetry of the axes which is being examined. For example, a tetragonal crystal with D_{4h} point group has a 4-fold rotational symmetry around the c-axis. Similarly, the Laue image for an initial beam of x-rays along the c-axis will also have 4 fold rotation symmetry. Since this is the only direction in this crystal with such symmetry we can easily identify the c-axis with Laue diffraction. Figure 3.3 shows a Laue image for xrays sent along the (110) axis. This image was taken on the MWL120 Real-Time Back-Reflection Laue Camera System from Multiwire Laboratories. The crystal has two-fold rotational symmetry along this axis which is reflected by the 2fold rotational symmetry in this Laue image. We also can see that the alignment along this axis is very good from this image. We know this because the spots form crosses which intersect close to the center point. If the alignment were poor, these crosses would not intersect close to the center and would appear



Figure 3.3: **Typical laue diffraction pattern.** A Laue diffraction pattern for a crystal of $Y_{0.1}$ Tm_{0.9}VO₄ along the (110) crystal axis. The two-fold rotational symmetry of the crystal around this axis is reflected by the 2-fold rotational symmetry of the Laue image. Image taken on the MWL120 Real-Time Back-Reflection Laue Camera System from Multiwire Laboratories.

distorted.

As an example of our alignment procedure, we'll discuss how to align TmVO₄ samples grown by two different methods. The first method, flux growth, results in crystals that grow like needles along the c-axis and have facets along the (100) direction. The second method, image furnace growth, results in crystals that are completely unoriented. The goals for preparing both of these crystals are the same, a sample where the magnetic field can be aligned along the c-axis and where we have two parallel faces along the (110) direction for sound to travel.

The first goal is to determine the c-axis of the crystal. In the case of the flux grown crystal this is quite easy, since the crystal grows along that direction. In the case of the unoriented sample, the simplest procedure first involves mounting the sample onto a polishing block and then using a goniometer and Laue set-up to get a general idea of the location of the c-axis. The c-axis for this crystal shows a distinct signature of a 4-fold rotation symmetry enabling easy-identification. After the general location of the peak has been determined, the crystal must be reoriented on the block so the c-axis is as close to the normal of the polishing block as possible. The ultimate goal is to polish a crystal face that is normal to the c-axis so that this axes can be tracked easily.

The surface we use to mount the samples for Laue is one of our polishing blocks made out of stainless steel. These blocks attach to a precision lapping fixture that was made by South Bay Technology Inc. (now Ted Pella, Inc.). These blocks have very parallel surfaces and can be attached to a device that can used to polish samples. The samples are adhered to the block with a waxy material (crystal bond) whose viscosity changes dramatically based on temperature. At room temperatures it is a solid, but it becomes very liquid and flows easily at higher temperatures (190 °C). It cools and hardens quickly and can be used to quickly adhere a sample to a block.

If we find that the c-axis of our sample is misaligned, then we must align it by hand. This process involves first heating up the polishing block and crystal bond so that the crystal bond just barely softens. Then we poke the sample with a toothpick to try to rotate the crystal to the correct direction. We can check to see if it's aligned now with Laue. If it's aligned within a few degrees we can stop the process. If not, we repeat the alignment process until the c-axis is aligned within the desired amount. Once the c-axis is aligned, we can polish this face (to be discussed in later sections).

After the alignment of the c-axis, we now align the crystal along the desired (110) axis for this measurement. For the flux-grown sample we know that the crystal facets grow perpendicular to the (100) axis. This means that we simply must rotate the sample approximately 45° on the polishing block and repeat the alignment process for this orientation. On the other hand, this process is more complicated in the unaligned image furnace-grown samples. In these samples, we so far only know the (001) direction, though this also gives us the plane in which the (110) axis lies. Therefore, if we rotate the sample by 90° from the (001) direction we'll be in the correct plane. We can then scan in this plane to try to find a high symmetry direction. There is an additional complication in this process, however. In this plane there will be two separate axes with two-fold rotational symmetry: the (100) axis and (110) axis. Once we align the sample, so that the Laue image has a two-fold rotational symmetry, we must then determine whether is the (100) or (110) direction.

There are a few different techniques that we can use to distinguish between the (110) and (100) orientations. First, there exist automated fit procedures in software that can automatically determine the orientation. However, this software is often a black-box and doesn't lend itself to understanding easily. A simpler technique to determine the orientation is to use a monochromatic x-ray source such as a Rigaku system. Once the crystal is aligned a high symmetry direction, it's easy to use this to determine the length of the lattice vector in this direction.

The method used with the Rigaku system is to perform a $\theta/2\theta$ scan in the

direction of the normal. In this technique, as demonstrated in Figure 3.4, the x-ray source and detector maintain the same angle with the parallel as each other throughout the scan. This results in a $\Delta \vec{K}$ that points vertically during the scan of θ , which allows the detection of reciprocal lattice vectors that point normal to the mount. As the value of θ changes, the length of $\Delta \vec{K}$ changes. When this vector length is the same as a reciprocal lattice spacing, there will be a spike in intensity at the detector from Bragg reflections. Since the (110) and (100) directions in TmVO₄ have different atomic spacing in real space, there will also be different spacings between reciprocal lattice sites in momentum space. Given knowledge of the the reciprocal lattice spacing in the [100] and [110], we can determine the expected angles of peaks in scattering during a $\theta/2\theta$ scan. If we see that the crystal is indeed pointing along the (100) direction then we can rotate the crystal by 45° and repeat the alignment process. Once the crystal is aligned with the (110) direction normal to the surface of the polishing block, we can begin the process of polishing the sample in preparation for placement of the transducer.

3.2.2 Polishing the Sample

Once the crystal is oriented in the proper direction on the polishing block, we can begin to polish. In order to controllably polish the sample, however, we first must attach the polishing block to another device which allows the block to sit very parallel to a flat surface. This device also allows us to change the pressure on the crystal in a controlled manner. The key element of this design is that the rod which the block attaches to is supported by springs that are designed to compensate for its weight. As a result, without any added weight the polish-





ing block/sample barely touches the surface below. The pressure can then be adjusted by adding weights to the top of the rod. More weight results in faster polishing but may not be possible for more delicate crystals.

In addition to the polishing apparatus, we must have a proper environment for polishing before preparing a sample. The polishing station we use consists of flat lapping paper from Thor Labs with grit sizes of 30 μ m, 6 μ m, 3 μ m, 1 μ m, and a 20 nm finishing paper, a solvent/lubricant (methanol), flat glass plates, and an inflow hood to prevent inhalation of methanol fumes and stray dust. In order to prepare the station for polishing we first clean the glass plate by using methanol and a chem wipe to wipe down the surface. Then, more methanol is sprayed onto the glass and a piece of polishing paper, grit side up, is placed onto the surface. Any excess air bubbles are pushed out form underneath the polishing paper and the lapping paper should now be adhered to the glass. Now we are almost ready to polish.

Once the lapping paper is adhered to the glass surface, the polishing process can begin. Methanol is first placed on the paper as a lubricant. Then the polishing device is gently placed on the paper, while the sample rod is still held up so that the sample is not yet in contact with the paper. The sample rod and sample are lowered gently until the sample makes contact with the paper. With the sample now in contact, we begin polishing. We typically move the sample in a figure-8 pattern to get as uniform a pattern as possible. If there is a buildup of friction, more methanol is added as a lubricant. After enough passes, the sample is removed from the device and progress is checked under the microscope. This process is repeated until the desired properties are achieved.

This set-up lets us easily polish a parallel face to any flat/polished face. To do this, we first remove the crystal from the polishing block. We then flip it over so that the newly polished, flat crystal face is against the surface of the block. To get two highly parallel faces, the already polished face must sit very flat against the surface of the polishing block. This is best done by heating up the crystal bond (190 °C) so that it's very non-viscous and can flow easily. Then, when the crystal bond is non-viscous, it is possible to push most/all of the crystal bond out from underneath a flat crystal face. Once the crystal bond hardens, we can begin polishing again until we have two parallel faces for ultrasound.

The final step in our polishing procedure involves preparing a surface for the

deposition of a transducer. We want this to surface to be as smooth as possible so our transducer adheres well to the sample and we get good acoustic coupling. To ensure this, we typically polish this surface last so we avoid placing the final surface on a rough polishing block thereby scratching it. In addition, we use the final polishing paper on this surface (20 nm) to get as smooth of a surface as possible.

As a note, there are two main variables that control the rate at which a sample is polished. The first, as previously mentioned, is the pressure exerted on the sample which we control by adding weights to the top of the polishing rod. The second is the size of the grit used. Larger grit results in faster polishing but also results in a rougher surface. Typically we polish using larger grit first to remove more material and slowly decrease the size of the grit to get a smoother face.

3.2.3 Cleaning the Sample

In the next step of the sample prep process, we clean the surface in preparation for the transducer deposition. In general, we want a surface free of dust and any other organic films, since this will result in a transducer that adheres better to our sample and has a stronger mechanical response. This process is still in development, but our current chemical cleaning procedure will be described in this section. As a note, our sample cleaning process is inspired by silicon wafer cleaning techniques though technical limitations sometimes prevent us form applying certain steps in the procedure [43].

The chemical cleaning process we use is the AMI wash (acetone-methanol-

isopropanol). This three step process is used to clean organic contaminants and dirt off the surface of our samples. It begins by placing our sample in a clean beaker with high purity acetone. The beaker is then placed in an ultrasonic bath for a few minutes. If the sample is delicate, we instead swirl the sample in the beaker by hand, though this is dramatically less effective at removing surface contaminants. After this step, the acetone is poured out and methanol is quickly added to the beaker with the sample. Then the sonication/swirling is repeated. This same process is repeated with isopropanol. At the end, we finally pour out the isopropanol and let the sample dry in air.

The acetone is meant to aggressively remove material at first since acetone is a very strong solvent. However acetone tends to be dirty and there are additional contaminants in the acetone from the sample. When acetone evaporates it leaves a film on the sample from these dissolved contaminants The methanol is cleaner than the acetone and dilutes the remaining contaminants that were not poured out with acetone. Finally IPA dilutes the remaining contaminants even further while acting as a final "clean" solvent.

Recently we have begun to consider an additional non-chemical step in the process of cleaning our sample: plasma etching. In this process, the sample is placed in a chamber that is pumped out to vacuum. Then a gas is reintroduced into the chamber (either oxygen or nitrogen). A large electrical bias is placed across the chamber which ionizes the atoms in the gas, removing some electrons. The now charged ions are accelerated by the electric field towards the sample and collide with the sample, removing surface contaminants. This method is especially effective at cleaning samples resulting in films that adhere well to surfaces. Preliminary results suggest that ZnO films that are sputtered



Figure 3.5: **Example of LiNbO**₃ **transducer and ZnO transducer on a sample.** This image shows an example of a LiNbO₃ transducer in the picture on the left and a ZnO transducer in the picture on the right. The LiNbO₃ transducer must be attached to the sample with glue while the ZnO transducer is a thin film that's grown directly on the sample. The ZnO transducer can also be grown in any shape we wish. Photos taken by Florian Theuss.

after this process have a particularly large mechanical response.

3.3 ZnO Transducer Development

One of the novel approaches to pulse echo ultrasound in our lab is the use of thin film ZnO transducers instead of the use of commercially available LiNbO₃ bulk transducers. These can be grown directly onto the surface of a sample and offer multiple advantages over bulk transducers, though they still pose their own challenges. Figure 3.5 shows an example of a LiNbO₃ transducer and a ZnO transducer mounted on a sample. We'll first discuss the process to create the transducers and then discuss the advantages and disadvantages of ZnO transducers

Our ZnO transducers consist of a stack of multiple layers that include Pt electrode layers, Ti adhesive layers, and a ZnO piezoelectric layer. The electrodes



Figure 3.6: **Layers in a ZnO transducer.** This cartoon shows the all the layers and their thicknesses in a typical ZnO transducer. The ZnO layer is the active piezoelectric layer, the Ti layers act as adhesive layers, and the Pt layers act as the electrodes.

are typically 100 nm thick while the Ti layers are 7 nm. The active ZnO layer usually ranges from 1 micron to 1.5 microns. In general, for thin-plate transducers, the thickness of the piezoelectric layer sets the fundamental frequency. However, we have found that our ZnO transducers have a broad frequency response and typically work between 300 MHz and 3 GHz.

A typical stack for a ZnO transducer is shown in the cartoon in Figure 3.6. We typically start with a Ti/Pt bottom electrode layer, where the Ti helps with adhesion and the Pt provides electrical contact. This layer should be left partially exposed, so we can make electrical contact to the bottom electrode later. Then the ZnO layer is grown directly onto the Pt layer. For longitudinal transducers we want the c-axis of the ZnO to be normal to the surface of the sample. Luckily, ZnO normally grows with the c-axis normal to the surface. Finally, we follow with another Ti/Pt layer to act as the top electrode. This layer is typically made smaller in diameter than the ZnO layer to prevent shorting of the top and bottom electrodes.

We will now describe a recipe for the growth of each layer of the transducer that consistently produces high quality transducers. The recipe that we follow for our transducer is given by Table 3.1. This recipe is specific to the growth of these transducers via sputter deposition in a chamber in our lab that is dedicated primarily to the growth of ZnO. There are two separate recipes because the piezoelectric ZnO layer can be deposited either by RF sputtering with a ZnO target or by pulsed DC sputtering using a Zn target in an oxygen rich atmosphere. DC sputtering with a Zn target offers the advantage of a faster growth rate while the films grown by RF sputtering seems to be of a higher quality.

	Ti	Pt	ZnO (DC)	ZnO (RF)
Ar Flow (sccm)	15	15	15	15
O ₂ Flow (sccm)	0	0	8	5
Power (W)	60	30	24	10
Pressure (mTorr)	4	3	7	3
Target	Ti	Pt	Zn	ZnO
Thickness (nm)	7	100	1000	1000

Table 3.1: **Recipe for ZnO transducers.** This table shows the important parameters for the sputter deposition of transducers in our chamber. We include the parameters for the ZnO layer deposited via either DC or RF sputtering.

Now that we know how to grow ZnO transducers, we will discuss the advantages these thin film transducers offer over bulk transducers. Our ZnO transducers generally have better coupling to the samples since there's no intermediate glue layer. This lack of a glue layer also reduces the interference effects in the signal resulting in better data. In addition, these transducers are broadband since they aren't single crystal. They can respond over a nearly continuous range of frequencies ranging from 300 MHz to over 3 GHz. This allows for frequency dependent attenuation sweeps which can be used to extract internal time scales of a system. Finally, these transducers, since they are so thin, can respond very quickly to RF pulses. This allows for very narrow pulse widths in ultrasound that at the moment are limited by the electronics rather than by the time it takes for the transducer to respond mechanically. This results in the ability to measure pulse echo ultrasound on extremely thin samples (order of several hundred microns). A comparison of the echo patterns produced by these two types of transducers is shown in Figure 3.7. The top echo pattern is produced by the ZnO transducer and the bottom echo pattern by the LiNbO₃ transducer. The ZnO transducer produces much sharper echoes with less noise in between echoes.

3.3.1 Mounting the Sample

Once the sample is fully polished and the transducer has been deposited, we mount the sample onto a board where we make electrical contact to the transducer. However, we must take into account a few considerations before mounting the sample. First, we must ensure that the direction of the magnetic field will lie in the direction of the correct crystal axis. In addition, we don't want the portion of the surface directly opposite the transducer to be in contact with any other surface. Contact with that surface can lead to a loss of signal or additional reflections from the interface and glue layers. This can interfere with the quality of our measurements.

An example of how these samples are mounted is shown in Figure 3.8. In



Figure 3.7: Example ultrasound echo patterns generated by a LiNbO₃ transducer and a ZnO transducer. The top echo train is generated by a ZnO transducer and the bottom echo train by a LiNbO₃ transducer. The ZnO transducer can respond much more quickly to the driving voltage signal and as a result has much sharper echoes than those produced by the LiNbO₃ transducer. In addition there are less features in between the echoes with the ZnO transducer.

it, we can see that the sample is glued to a glass slide with GE varnish so that the sample stands up vertically. This is to ensure that the magnetic field will applied to the correct axis of the crystal (c-axis). In addition, though difficult to see, the transducer sits above the glass slide to try to prevent the effects just discussed.

This circuit board is also where we make electrical contact to the transducer. In this image, there are two wires directly painted onto the sample (one to the ground electrode and the other to the top electrode). The ground wire is directly painted onto an exposed portion of the Pt bottom electrode in the top portion of the sample. In this image, the ground wire can be seen going to the top of the sample and the electrical connection is made of the large blob of silver paint seen at the top of the sample. The other wire is directly painted onto the top electrode of the transducer near the center of the sample. In this lighting it's difficult to see the outline of the top electrode, but the silver paint is contained within this boundary. The other end of these wires are then painted directly to copper pads. This then leads to an MMCX connector and coax that leads directly to our pulse echo electronics.

3.4 Ultrasound Analysis

Pulse echo ultrasound is a measurement technique in which high frequency sound (MHz to GHz) is sent through a sample to measure the speed of sound and the ultrasonic attenuation. We use an interferometry technique which enables measurements of the relative change in the speed with a resolution on the order of a part in a million. The resolution from this method, however, comes at the cost of the knowledge of the absolute speed of sound. The absolute speed of sound can be measured via another method, where we measure the time between peaks and use the length of the sample to calculate the speed of sound. However, this typically only gives a resolution on the order of a part in a hundred which is much lower than if we measure the relative change.

The other quantity, the attenuation, is measured by fitting an exponential to the envelope of the echoes and then extracting the exponent. Together these quantities are related to real and imaginary part of the susceptibility of the re-



Figure 3.8: **Example of an ultrasound sample mounted on a PCB.** This image shows how we typically mount $\text{Tm}_x Y_{1-x} \text{VO}_4$ samples on a board for an ultrasound measurement. The sample is standing straight up so the magnetic field can be applied the c-axis. The two wires silver painted onto the top and bottom electrode provide electrical contact to the transducer. The signal travels from these wires to a coax that eventually attaches to an oscilloscope.

sponse of a system to an external stress. This section will now discuss in more detail how we measure these quantities.

Figure 3.9 shows the essence of pulse echo ultrasound. A pulse of sound is emitted from a transducer and travels through the sample. It reflects off the opposing surface and finally is detected by the transducer again. This process is repeated until the sound dissipates completely. The initial echo is used as a ref-



Figure 3.9: **Illustration of pulse echo ultrasound technique.** In this cartoon a RF voltage is applied across a piezoelectric transducer which is attached to a sample. The transducer converts this signal to sound and the sound propagates back and forth through the sample until dissipating completely. Each time the signal returns to the transducer, some of the sound is converted back into an electrical signal which can then be read by an oscilloscope.

erence that will be compared to all the subsequent echoes. We then measure the phase difference between the reference echo and each other echo using a digital lock-in procedure which will be described later. This phase difference extracted from this technique is the value modulo 2π radians, while the actual phase difference will be on the order of 1000 radians. The absolute phase difference can be determined by dividing the time of flight by the period of the sound. This times 2π is the phase difference. This phase can then be related to the speed of sound (v), frequency (f), and length (L) of the sample via the equation:

$$\phi = 2\pi \frac{t}{T} = \frac{4\pi fL}{v} \tag{3.1}$$

The extra factor of 2 here comes from the fact that the sound must travel back and forth through the sample to be detected by the transducer.


Figure 3.10: Echo train from pulse echo ultrasound experiment. This image shows an example of an echo train from a measurement of pulse echo ultrasound. Ideally the envelope should decay exponentially, but there are some oscillations in the envelope due to interference effects.

While we can use our knowledge of the spacing of the echoes and the length of the sample to get the absolute speed of sound from this equation, we often do not know this information to better than 1 percent. Such a low resolution is a problem when trying to examine physics that does not couple strongly to the lattice where signatures of the physics may be on the order of parts per million. Using our phase technique we are able to determine relative changes in the speed of of sound to one part in a million resolution. In exchange we lose information about the absolute speed of sound, though this information is usually not as important as the relative changes.

At the moment Equation 3.1 shows the relation between absolute phase and the speed of sound, but the power of this technique comes from looking at the relative changes in phase. First, we reference the initial phase difference as the phase at t = 0 and subtract all future values of the phase from this value. This phase difference with time will be called $\delta\phi$ and is typically fairly small. We then calculate $\frac{\delta\phi}{\phi}$ and assuming small changes $\delta\phi$ compared to the overall value ϕ , we can expand the right of equation 3.1 to first order in δL , δv and δf . This equation takes the form:

$$\frac{\delta\phi}{\phi} = -\frac{\delta v}{v} + \frac{\delta f}{f} + \frac{\delta L}{L}$$
(3.2)

The relative change in phase depends on changes in frequency, the length of the sample, as well as the speed of sound in the sample. In our measurements, we typically work at a fixed frequency so $\frac{\delta f}{f} = 0$, and we assume that changes in the length are small so $\frac{\delta L}{L} = 0$. The speed of sound is related to the relevant elastic moduli by the formula $v = \sqrt{\frac{c}{p}}$. If we assume small changes in relative speed of sound we can expand to lowest order in δc and we find the relation $\frac{\delta v}{v} = \frac{1}{2} \frac{\delta c}{c}$. Therefore we find the following equation between phase, velocity, and elastic constant:

$$\frac{\delta\phi}{\phi} = -\frac{\delta v}{v} = -\frac{1}{2}\frac{\delta c}{c}$$
(3.3)

We can now calculate $\delta \phi / \phi$. We measure $\delta \phi$ with digital lock-in, and use the spacing of our echoes and the knowledge of the frequency to calculate the approximate phase ($\phi = 2\pi t/T$). We see that ϕ is on the order of 1000 radians and we can measure $\delta \phi$ to a part in a thousand precision. Therefore, we are able to determine the relative changes in phase and speed of sound to a part per million resolution.

The other quantity we measure, the attenuation, is easier to extract. We first start with the ultrasound signal as in Figure 3.10 and then use digital lock-in to

extract the envelope. The peak amplitudes in this envelope are then fit to the function $a * \exp[-\alpha t]$. The attenuation is the quantity in the exponent α .

Now that we have an idea of what we will be measuring, we can take a look at the raw data from an ultrasound measurement. Figure 3.10 shows a typical echo pattern that we measure during a pulse echo ultrasound experiment. The transducer, as mentioned before, initially sends out a pulse of sound, and this pulse is detected multiple times by the transducer as it travels through the crystal and reflects off the surface with the transducer. As the sound travels through the crystal, it decreases in amplitude until eventually it dissipates completely. This decrease in the amplitude of the signal can be seen in our echo pattern presented in Figure 3.10. This decay should theoretically be exponential, however there are almost always oscillations in the amplitudes of the echoes around an exponential.

There are two main interference effects that we understand: interference from glue layers and interference from differences in path length between different parts of the sound wave front. These effects are illustrated in illustrated in Figure 3.11. Panel a) shows an ideal wavefront with direction given by \vec{k} . Panel b) shows that some parts of the wave front can expand out. These paths will have a different path length and will arrive at the transducer at different times. As a result, they will interfere with the signal from part a). Panel c) shows the interference effects resulting from acoustic mismatch between the sample and glue layer. The sound can reflect multiple times from the boundary of the glue layer and the sample. This will result in a difference in path length and therefore will result in the appearance of interference in our echo pattern.

The first source of interference effects that we'll discuss are glue layers. In-



Figure 3.11: **Cartoon of interference effects in pulse echo experiment.** In this image, panel a) shows the ideal path of sound of a plane wave in a pulse echo ultrasound experiment with the direction of propagation denoted by \vec{k} . Panel b) shows that part of the wavefront spreads out and travels along a different path that reflects off the sides and results in interference. Panel c) shows how interference due to glue layers arise. As a note, all these effects happen simultaneously, they are just drawn separately here for clarity.

terference from glue layers is a prominent issue with bulk transducers since the transducer must be attached to the sample via an adhesive layer. It's impossible to completely remove the glue layer between the transducer and the sample. Therefore sound that travels through the glue will be partially reflected at the glue/sample and then the glue/transducer boundary. This results in sound that, once transmitted into the sample, has a slightly different path length than the sound that was transmitted immediately. This results in an interference effect which can manifest as oscillations in the amplitude/phase of our signal. An advantage of ZnO transducers is that there is no glue layer so these effects should be minimized.

The other source of interference comes from the fact that transducers don't produce sound that's a perfect plane wave. Transducers have a finite size and as a result the wavefront of sound spreads out from the transducer. If part of the wavefront runs into a side surface it can reflect multiple times and may end up at the transducer again. This sound will have traveled a different path length and therefore has a different phase from the rest of the sound that didn't reflect off the side. This will result in interference effects in both the attenuation and speed of sound data. The severity of this effect depends on multiple factors such as the size of the transducer and the wavelength of the sound. The following equation describes the degree of spread and in particular the angle where the intensity of the signal is reduced to -6 dB:

$$\sin\left(\alpha/2\right) = .514c/fD$$

In this equation, α is the angle at which the signal is reduced to -6 dB, c the speed of sound, f the frequency, and D the diameter of the transducer. We can estimate this angle using some typical numbers for the both LiNbO₃ and

ZnO transducers. The typical lowest measurement frequency for a LiNbO₃ is f = 30 MHz while for a ZnO transducer it is f = 300 MHz. We'll compare transducers of the same size with a diameter of D = 0.5 mm. Finally, the longitudinal speed of sound in LiNbO₃ is approximately 7000 m/s [44] [45] while in ZnO it is approximately 6000 m/s [46]. This gives an angle of approximately 28° in the LiNbO₃ transducer and 2.4° in the ZnO transducer. This smaller angle means that the interference effects in the ZnO transducer should be significantly smaller due to the higher working frequency. The ZnO produces sound that looks much more like a plane wave and therefore reduces the interference effects in our samples.

The fact that we still can see interference effects from our ZnO transducers means that there must be another source of interference. At the moment we are not sure what causes these effects. However, one possible source worth investigating are imperfections in the transducer itself. ZnO transducers are not single crystals and instead consist of many grains [47]. Typically the c-axis of these domains grow perpendicular to the surface of the substrate but there's always some deviation from perfect alignment [48]. It may be possible that this misalignment can result in additional interference effects. Depending on the properties of the substrate it may be possible that annealing/growing these transducers at high temperatures can result in less interference effects [49] [50]. Now that we have discussed the quantities we can measure and some of the challenges in ultrasound, we'll follow up with how to go from a raw signal to the phase and amplitude of an echo.

3.4.1 Digital Lock-In

In order to extract the phase and amplitude the echoes from our raw data, we use a signal processing technique known as digital lock-in [51]. This technique lets us "lock-in" to data with a certain frequency and extract both the envelope and phase. We begin by digitally generating both a sine and cosine wave with the same frequency as the RF ultrasound signal. We then multiply our measured ultrasound data by the sine and cosine giving the following equations:

$$V_x = V\cos(\omega t) \tag{3.4}$$

$$V_y = V\sin(\omega t) \tag{3.5}$$

Next, we apply a low-pass filter Butterworth filter to V_x and V_y which removes their high frequency components. If we were to just apply the filter once, there would be a resultant phase shift in the data. Instead we apply the filter, reverse the filtered data and apply the same filter again. The resultant data (V'_x and V'_y) no longer has a phase shift and the high frequency components have been removed. After applying the filter to the data we can determine the envelope and phase of the signal from the following equations.

$$A = 2\sqrt{V_x'^2 + V_y'^2}$$
(3.6)

$$\phi = \tan^{-1}[V_y'/V_x'] \tag{3.7}$$

Figure 3.12 shows the results of digital lock-in on a few echoes from the data already presented in Figure 3.10. Panels b) and c) are the envelope and phase from this data extracted via the digital lock-in procedure just described. We can determine the peak amplitude and phase from these plots by finding the time



Figure 3.12: **Digital lock-in on ultrasound data.** This image shows an example of the analysis performed to extract the amplitude and phase from ultrasound echoes. Panel a) shows a sample of a few echoes from Figure 3.10. Panel b) shows the extracted amplitude envelope after performing digital lock-in with the peak locations identified by red dots. The corresponding phase is shown in panel c) with the red dots identifying the phase at the peak location.

at which the max amplitude of each echo occurs and then extracting the voltage and phase at that time. These quantities are used to determine the attenuation and speed of sound respectively.

CHAPTER 4

ULTRASONIC PARAMAGNETIC RESONANCE

This chapter is adapted from the manuscript, Measuring the Random Strain Distribution in a Dilute Jahn-Teller System, with P. Massat, I. Fisher, and B.J. Ramshaw.

4.1 Introduction

Disorder is ubiquitous in quantum materials. This is particularly true when phases of matter are tuned by chemical substitution, such as the hightemperature iron pnictide and cuprate superconductors. Disorder has a strong effect on phase transitions, sometimes even changing the nature of the ordered phase entirely [52]. A central challenge is teasing apart the direct effect of disorders from the other changes that accompany substitution, such as electron density.

In this regard, the substitution series $\text{Tm}_x Y_{1-x} \text{VO}_4$ is ideal for studying disorder. At x = 1, the 4f orbitals on the Tm^{3+} ions in TmVO_4 undergo a cooperative Jahn-Teller transition—a realization of Ising nematic order [6][21][16]. At x = 0, YVO_4 is non-magnetic. The entire series is electrically insulating, greatly simplifying the physics compared to the cuprate and iron pnictide superconductors.

Here, we study how substitutional disorder introduces long-range strains that couple otherwise isolated Tm³⁺ ions. Starting from pure YVO₄, we introduce small amounts of Tm and use ultrasonic paramagnetic resonance to measure the resulting strain distribution function. We extract the strain distributions for x = 0.01 and x = 0.03. We quantify the energy scale that substitutional disorder introduces into the Tm_xY_{1-x}VO₄ system, providing input for modeling how the Ising nematic phase is destroyed by disorder when small amount of yttrium are substituted into pure TmVO₄.

4.2 Technique

This experiment is based on the fact that ultrasonic phonons of a particular symmetry are resonantly absorbed by the 4f quadrupole on the Tm³⁺ ions. Tm³⁺ ions in Tm_xY_{1-x}VO₄ have 12 4*f* electrons that form a non-Kramers doublet that is separated from the excited states by 50 kelvin [35]. The doublet acts as an electric quadrupolar degree of freedom, with no accompanying magnetic dipole. As the the doublet is non-Kramer's, it is unstable to structural distortions, also known as the Jahn-Teller effect.

The application of a transverse magnetic field induces a magnetic dipole component to the 4*f* state and splits the quadrupole doublet. A phonon whose energy is equal to the doublet spacing can then induce a transition from one state to the other (i.e. a transition between quadrupole orientations). This "ultrasonic paramagnetic resonance" (UPR) is analogous to electron paramagnetic resonance (EPR), but using strain waves instead of electric fields [53] [54] [55]. The main advantage of UPR over EPR is that UPR can access a much lower range of frequencies and can be performed spectroscopically over a broad range of frequencies—here from 300 MHz up to 3 GHz—whereas EPR is generally performed in a fixed-frequency cavity (e.g. at 9 GHz [56] [57] [58]).

Pulse echo ultrasound is typically performed with single-crystal LiNbO₃ or

quartz transducers that are affixed to the sample with adhesives. These transducers operate only at fixed harmonics, limiting their ability to perform spectroscopy. Here, we instead sputter ZnO directly onto the sample surface, forming a thin-film transducer that operates almost broad-band, from 300 MHz up to 3 GHz. The ZnO layers consist of a Ti/Pt bottom electrode, followed by an approximately 1 μ m ZnO piezoelectric layer, followed by another Ti/Pt top electrode. The Ti/Pt layers are 7nm/100nm thick, with the Ti being used as an adhesive layer and the Pt acting as the conducting electrode. The ZnO layer is grown by using a 99.99% pure metallic Zn target in a reactive atmosphere with an argon flow of 15 sccm and O₂ of 8 sccm.

4.3 **Results**

Figure 4.1a shows the attenuation of longitudinal phonons propagating along the 110 direction in $\text{Tm}_x Y_{1-x} \text{VO}_4$, at x = 0.01 and x = 0.03, as a function of *c*-axis magnetic field from 0 to 40 mT, at frequencies ranging from 0.5 GHz up to 3 GHz, and at 1.8 kelvin. Two peaks are observed in the sound attenuation as a function of magnetic field, with the distance between the peaks first increasing as the ultrasonic frequency is increased until one peak reaches zero field, after which the peak separation remains constant with increasing frequency.

The data at x = 0.01 and x = 0.03 look qualitatively similar. As we discuss in detail below, these peaks in the attenuation arise from resonant scattering of the acoustic phonons with the Tm³⁺ quadrupoles. The main qualitative difference between the two data sets is in the width of the absorption peaks: the x = 0.03 peaks are significantly broader than the x = 0.01 peaks. We also measured a



Figure 4.1: **Ultrasonic attenuation in Tm**_{*x*}**Y**_{1-*x*}**VO**₄. Panel a) presents the normalized, vertically-shifted attenuation data from both the 1% and 3% Tm sample at many different frequencies. Plotting the peak locations on a frequency vs. field plot for both samples gives panel b). We can explain the behavior of the peaks in panel b) by the simple energy level diagram in c). The 0 field gap is due to the hyperfine coupling between the ground state and nuclear spin of the I = 1/2 Tm.

sample with x = 0.10 but found no evidence for absorption peaks. As we discuss below, this evolution of the peak width with substitution level is indicative of the local strain distributions within the material.

4.4 Analysis

g-factor. We first track the evolution of the absorption peak as a function of phonon frequency and magnetic field. Figure 4.1b shows the positions of the peaks for both substitution levels—evidently the peak positions do not vary much with the change in Tm substitution levels. By converting the frequency scale to an energy scale with Planck's constant, and the field scale to an energy scale using the Bohr magneton, the slopes of these lines give us a *g*-factor of

approximately 11.8. This is somewhat different from EPR measurements of the *g*-factor of a Tm^{3+} ion embedded in YVO₄ (10.2) [58]. This is likely due to the effect of anisotropic broadening in the lattice. In Figure 4.1, we can see that as more Tm^{3+} is added, such as in the 3% sample, the magnitude of the slope of the best fit lines to the peaks increases. Thus, the *g*-factor extracted from this fit will be larger than the actual value. This change in slope is due to the inwards broadening of the curves as the amount of Tm^{3+} is added to the lattice. In order to accurately measure the *g*-factor using this method, we would want a very dilute sample where the anisotropic broadening is minimized. Despite the small difference in value, we can conclude that the absorption lines are related to the splitting of the Tm^{3+} quadrupole energy levels, just as they are in the EPR experiment.

Hyperfine coupling. Given that the Tm³⁺ quadrupoles are not ordered at low Tm concentrations in Tm_xY_{1-x}VO₄, one would expect the energy scale for the resonant absorption of phonons to go to zero at zero magnetic field, i.e the two quadrupole configurations should be degenerate at B = 0. Figure 4.1b, however, has a resonant absorption peak at around 1.9 GHz as $B \rightarrow 0$. This zero-field energy scale comes from the hyperfine interaction between the Tm³⁺ quadrupole and the spin 1/2 of the ¹⁶⁹Tm nuclei (100% abundance).

The Hamiltonian governing both the Zeeman and hyperfine physics is

$$H_{\rm ion} = -\frac{1}{2} \mu_B g_c B S^z - A S^z I^z, \qquad (4.1)$$

where μ_B is the Bohr magneton, g_c is the *c*-axis *g*-factor of the quadrupole, *A* is the hyperfine coupling strength, and S^z and I^z are Pauli matrices for the quadrupole and nuclear spin, respectively. As both g_a and g_b are zero for the quadrupole, only S^z couples to the nuclear moment. We extract a hyperfine cou-

pling of 1.94 GHz, which is close to EPR measurements (1.73 GHz) [58]. There is a slight difference in value which may be due to differences in the strain environment.

Figure 4.1c illustrates the energy level diagram of the coupled quadrupolenuclei states as a function of magnetic field. Four states initially split into two doublets by an amount equal to the hyperfine exchange interaction. An applied magnetic field couples to the induced magnetic dipole moment on the Tm³⁺ and splits the doublets further. An incoming phonon can flip the sign of the quadrupole, resulting in two distinct transition energies (the other transitions are forbidden because the phonons cannot flip the nuclear spin).

The effect of strain on the absorption lines. The model described thus far has a single, sharp pair of absorption lines for a given magnetic field and measurement phonon frequency. The experimental data, however, shows absorption lines are both broadened and "filled in", as shown in Figure 4.2b (low frequency) and c (high frequency). As is well known in the EPR literature [59], absorption lines in Jahn-Teller systems are modified by strains in the crystal—each substituted Tm³⁺ ion produces a long-range acoustic strain field that is felt by all other Tm³⁺ ions. These random strains are a mixture of $\epsilon_{xx} - \epsilon_{yy}$ ($\epsilon_{B_{1g}}$) and ϵ_{xy} ($\epsilon_{B_{2g}}$) and couple to the B_{1g} and B_{2g} quadrupoles (S^{y} and S^{x} , respectively), as

$$H_{\text{strain}} = -\mu_x \epsilon_{\text{B}_{2g}} S^x - \mu_u \epsilon_{\text{B}_{1g}} S^y.$$
(4.2)

The parameters μ_x and μ_y give the strength of the couplings between the quadrupoles and strains in the different symmetry channels. Diagonalizing the sum of the bare ion (Equation 4.1) and strain coupling (Equation 4.2) contributions gives the following energy eigenvalues:

$$E = \pm \sqrt{\frac{1}{4}\mu_B^2 g_c^2 B^2} \pm \mu_B g_c B A + A^2 + \left(\left(\mu_x \epsilon_{B_{1g}}\right)^2 + \left(\mu_y \epsilon_{B_{2g}}\right)^2\right).$$
(4.3)



Figure 4.2: **Strain broadening of the phonon absorption.** This image shows the effects of B_{1g} and B_{2g} strains on the phonon absorption curves. Panel a) shows how the introduction of strains results in a shift of the energy level differences. The purple curve is what we expect for 0 strain. However as strain is introduced, an avoided crossing emerges around 12 mT and the curves shift up in energy. Panel b) and panel c) show some examples of the data from the 1% and 3% data at 1 GHz and 3 GHz. The lower halves of these panels then present an example of the theoretical predictions of the attenuation curve for a Gaussian distribution of strains in the low-frequency and high-frequency cases.



Figure 4.3: **Fits to attenuation data.** This image shows our current best fits to the low-frequency and high-frequency data in both the 1% and 3% Tm samples. The points are the data while the solid curves represent the fits to the data. We can find very high-quality fits for the low frequency data though the high-frequency seem to be of lower quality. This likely due to the much larger uncertainty in the high-frequency data.

Figure 4.2a shows the modified transition energies for different values of the strain-induced gap at a Tm³⁺ ion. For a fixed measurement phonon frequency, Tm³⁺ ions with different strain-induced gaps will have absorption lines at different values of magnetic field. Figure 4.2b compares data measured at 1 GHz to theoretical curves for two different sizes of strain-induced gaps. As the gap increases in strength, the absorption lines are brought together. This is the "low-frequency" regime. Figure 4.2c compares data measured at 3 GHz again with theoretical curves. In this "high-frequency" regime—where the phonon frequency is larger than the zero-field gap—both absorption lines move toward lower field with increasing strain. These two regimes produce qualitatively distinct lineshapes, as is clearly seen in the data. Note that the we model the ab-

sorption lines as lortenzians—this will be discussed in further detail later.

Modeling the strain distribution. It is clear from Figure 4.2 that strains can explain the broad attenuation feature, at least at a qualitative level, but more can be learned with a quantitative analysis. Each Tm^{3+} ion has its own absorption energies, set by the magnitude of the local B_{1g} and B_{2g} strains. The total measured UPR lineshape is the sum of the absorption from all ions. Evidently, the exact shape of the measured absorption lines should then depend on the distribution function of strains, and one can, in principle, back out the strain distribution from the data. As seen in Figure 4.2b, the two Tm concentrations have different lineshapes, suggesting different strain distributions. For strain gaps larger than the energy of the probing phonons, there will be no absorption lines. This means that our UPR measurement is sensitive to strain gaps as large as our highest measurement frequency.

We construct a minimal model that best describes the data at all frequencies and magnetic fields. Schematically, the model at each ion consists of a lorentzian lineshape (we use the same lineshape for each ion), a phonon-induced transition matrix element (that depends on the local strain), a Bose occupation factor for phonon absorption and emission, and an amount of B_{1g} and B_{2g} strain. The strain is assumed to come from a gaussian distribution, and the total measured absorption signal is a convolution of this distribution function with the other factors at each lattice site. Qualitatively, these lineshapes in the low and high frequency regimes are shown in Figure 4.2.

We model the single-ion absorption as a lorentzian—this "intrinsic" broadening accounts for effects such as finite measurement bandwidth and dipolar coupling to the dipole component of the other Tm³⁺ ions. The transition rate itself depends on the local strain—with no local strain, the S^z states are pure field-induced dipoles. With local strain, these dipole states are mixed with the quadrupoles, changing the rate at which phonons induce transitions between them. The transition rate Γ is modeled using Fermi's golden rule,

$$\Gamma \propto |\langle f|S^{x}|i\rangle|^{2}\rho, \qquad (4.4)$$

where the final and initial states are obtained by diagonalizing the sum of Equation 4.1 and Equation 4.2. The occupation factor that multiples the transition rate is

$$\rho = \left[\exp(-E_i/kT) - \exp(-E_f/kT)\right]/Z.$$
(4.5)

Finally, we model the strain distribution $w(\epsilon_{B_{1g}}, \epsilon_{B_{2g}})$ as a Gaussian distribution. Because the magnitude of the gaps induced by the strains depends only on the total strain $\epsilon_r^2 = \epsilon_{B_{1g}}^2 + \epsilon_{B_{2g}}^2$ (see Equation 4.3), it is convenient to write the strain distribution in polar coordinates, ϵ_r and ϵ_{θ} . The distribution is then

$$w(\epsilon_r, \epsilon_\theta) = \frac{1}{2\pi \sqrt{\sigma_r \sigma_\theta}} \exp(-\frac{(\epsilon_r - \epsilon_{r0})^2}{2\sigma_r^2}) \exp(-\frac{(\epsilon_\theta - \epsilon_{\theta 0})^2}{2\sigma_\theta^2})/\epsilon_r,$$
(4.6)

where ϵ_{r0} is the center of the distribution for the magnitude of the strain, σ_r is the width of the distribution in the radial direction, $\epsilon_{\theta 0}$ is the center of the distribution in the angular direction (i.e. setting the ratio of $\epsilon_{B_{1g}}$ to $\epsilon_{B_{2g}}$, and σ_{θ} is the width in the angular direction. Note that, despite the strain gap only depending on ϵ_r , both strains do not enter equally into the final expression for the attenuation: the initial and final eigenstates are modified differently in the presence of each strain, and the transition rate between them (given by Equation 4.4) only contains $\epsilon_{B_{2g}}$ since that is the strain we apply with our ultrasound. Equation 4.6 gives us the strain distribution in terms of ϵ_r and ϵ_{θ} , but what we actually want to fit the field-dependent data is to replace ϵ_r with the magnetic field at which our particular phonon frequency can induce transitions between the states. This can be done using Equation 4.3, setting the left-hand side equal to the phonon energy and solving for the magnetic field *B* for a given $\epsilon_r^2 = \epsilon_{B_{1g}}^2 + \epsilon_{B_{2g}}^2$. This gives us the strain distribution as a function of the field variable B_0 , where B_0 is the field at which our phonon energy is equal to the energy splitting of the two states in the presence of the strain ϵ_r . The total expression is then

$$\alpha(B) = \int \int \gamma(B - B_0) w[\epsilon_r(B_0), \epsilon_\theta] \Gamma[\epsilon_r(B_0), \epsilon_\theta] \epsilon_r(B_0) dB_0 d\epsilon_\theta, \qquad (4.7)$$

where γ is the intrinsic linewidth of a transition centered around B_0 , w is the strain distribution solved numerically in terms of B_0 and the angular strain variable, and Γ is the transition rate between states as modified by the strain. We integrate over the angular distribution variable and the field variable B_0 to obtain the total sound attenuation as a function of applied magnetic field.

Fitting the data. With all the pieces in place, we are equipped to fit the attenuation data to a distribution of random strains. While Equation 4.7 is intractable analytically, the fits can be done numerically. Because the model is somewhat computationally intensive but contains a relatively small number of free parameters, we do a "grid search" of the entire parameter space to determine the best fit parameters. We discuss different regions of the parameter space in turn, describing how our data constrains the shape of the strain distribution.

We start by examining the lowest four frequencies—0.5 GHz, 0.7 GHz, 0.85 GHz, and 1 GHz—where removing the background attenuation from the data is the most straightforward. We find that, for both samples, the strain distribution is centered around $\theta = \pi/4$, i.e. the strain at each site contains, on average, an



Figure 4.4: Extracted strain distribution from fits. This image shows the strain distributions extracted from our fits to the 1% and 3% Tm samples. In the 1% sample we find a strain width of 0.7 GHz while in the 3% sample it appears uniform. In both samples we find equal contributions from both B_{1g}

equal amount of B_{1g} and B_{2g} strain. This is reasonable on physical grounds, as there is no reason for a random distribution of Tm ions to produce more shear strain in one channel than the other. We can show that the uncertainty on this angle is approximately $\pm \pi/16$. The best fits to the data are shown in Figure 4.3.

We next examine the high frequency data at 2.45GHz, 2.75 GHz, and 3GHz data (the data between 1 GHz and 2.45 GHz is more difficult to to analyze because one of the transitions goes to zero field, making the background removal ambiguous). These data more strongly constrain the radial part of the strain distribution, since they probe higher energies. We find that the 1 % Tm sample has a radial strain distribution width of 0.7 GHz—a flat distribution fills in the attenuation curve, particularly at these high frequencies. The 3 % Tm sample, on the other hand, has a nearly flat distribution of strains up to 1.5 GHz, which is clearly reflected in the more "filled in" structure of the attenuation peaks.

4.5 Discussion

Figure 4.4 summarizes the main findings of this work. First, the strain distributions. We find that the ratio of B_{1g} and B_{2g} strains is roughly 1, i.e. the angle of strain distribution in the radial direction is $\theta = \Pi/4 \pm \Pi/16$. The width of this distribution is not tightly constrained by our data—as long as B_{1g} and B_{2g} strains are represented equally *on average*, we cannot distinguish whether they are equal for all Tm ions (i.e. the distribution is a delta function in the θ direction) or whether there Tm ions that experience much more of one strain than the other. Given the random nature of the Tm substitution and the long-range nature of the strains, we suspect that the distribution is tightly peaked around $\pi/4$.

In the radial direction, we find that the strain distributions are roughly centered around zero, meaning that there are strains all the way down to zero. Further, we find that the strain distribution in 1% $\text{Tm}_x Y_{1-x} \text{VO}_4$ falls off above 1 GHz, whereas it appears flat up to at least 1.5 GHz for the 3% $\text{Tm}_x Y_{1-x} \text{VO}_4$. The physical picture is that each Tm ion in 1% $\text{Tm}_x Y_{1-x} \text{VO}_4$ is far enough from its neighbors that only small strain gaps are induced on average. By 3%, there are enough Tm ions nearby that much larger strain gaps are present. By 10%, the disorder is so large that the UPR signal is wiped out entirely.

In addition to the strain distribution, our data also provides insight into the intrinsic broadening of the UPR peaks. As can be seen in Figure 4.3, not only is the 3% $\text{Tm}_x Y_{1-x} \text{VO}_4$ "filled in" between the peaks, it also has a broader tail outside of the two transitions. This indicates that the intrinsic linewidth the width that would be measured for a single Tm ion with a particular strain configuration—is broader in the 3% sample compared to the 1% sample. Further, the asymmetry of the peak heights suggest that the intrinsic width is itself dependent on magnetic field. We suggest that one contribution to the intrinsic width could be random, long-range magnetic dipolar interactions between the Tm ions. As the magnetic field increases the dipole on each site, the strength of the random interaction increases, further broadening the peaks [60].

Perhaps the most remarkable aspect of the data is that any UPR signal is visible at all at low temperature: even isolated quadrupoles are susceptible to Jahn-Teller distortion at low temperature, and one might expect that each Tm ion distorts into a state with a strain gap of order the size of the Jahn-Teller interaction strength in the pure compound—of order 2 kelvin. However, a 2 kelvin strain would only be visible by 40 GHz ultrasound, making it impossible to observe in our experiment. This suggests that the majority of the Tm ions remain in a symmetric, undistorted state down to at least 1.8 kelvin.

4.6 Conclusion

The confluence of the 100% abundance of the spin-1/2, ¹⁶⁹Tm isotope, plus the quadrupolar ground state of the f electrons in its Tm³⁺ configuration, provides a natural experiment for investigating the effects of long-range strains in a substituted system. We use broad-band ultrasound spectroscopy to investigate the phonon-induced transitions between the four quadrupolar/nuclear moment states, and find that we can measure the distribution of random strains experienced by the Tm ions.

On their own, our measurements provide microscopic insight into how sub-

stitutional disorder introduces long-range interactions between otherwise isolated ions through lattice strains. Even with only 3% substitution, the strain distributions reach out to energy scales beyond a few kelvin (our estimate of the width of the distribution for the 3% sample. By 10% substitution, the induced strains are so large as to wipe out the UPR signal entirely.

Our measurements also provide insight into the other end of the substitutional series—starting with pure TmVO₄ and introducing a few percent yttrium. While UPR is not possible in these materials, the series has a "mirror symmetry" when viewed from either end: one expects that 1%Tm substituted YVO₄ should have strains that are the same order of magnitude and with roughly the same distribution as 1%Y substituted TmVO₄ (given that the crystal structures and elastic moduli are very similar). Thus our measurements provide new understanding as to why the cooperative state is destroyed by 20% Y substitution into TmVO₄. We find that even 3% substituion introduces long-range, random interactions between Tm ions with an energy scale of order a few kelvin—the same size as the exchange coupling between Tm ions that drives the cooperative phase transition. Thus the destruction of the long-range ordered state can be viewed as a competition between the random energy scale introduced by substituional disorder with the energy scale of exchange—once disorder dominates, the phase transition no longer occurs.

Finally, our work has implications for other substitutional alloys with nematic tendencies, particularly the cuprates and iron pnictides, where nematicity is thought to interact with superconductivity. If even 3% substituion can have effects with energy scales of order a few kelvin, substitution levels around 30%, where both pnictides and cuprates have proposed nematic quantum critical point, should have long-range, strain-induced disorder that could approach several tens of kelvin—of order the size of the superconducting transition. Thus these materials should not be viewed as pure "nematic" systems, but rather as strongly disordered alloys with local tendencies toward rotational symmetry breaking.

CHAPTER 5 INTERACTION OF JAHN-TELLER IONS

Pulse echo ultrasound not only give us information about how the internal distributions of elastic strain and magnetic field evolve in the dilute systems, it also can give us detailed information about the nature of the interactions between quadrupoles. In a generic material, there are multiple channels through which quadruples can communicate. For example, this communication may happen via acoustic and optical phonons or via conduction electrons through an RKKY-like interaction [39] [61]. However, since TmVO₄ is a non-magnetic insulator, this limits the channels by which quadrupoles can communicate, leaving interactions by phonons as dominant. As a result, this is an ideal environment to examine in depth the nature of phonon interactions in these materials.

The primary physics driving the quadrupolar physics in this material is the Jahn-Teller effect as previously discussed. A simplified Hamiltonian describing this physics takes the form:

$$H = \frac{1}{2}N\Omega c_{66}\epsilon^2 - V_s\epsilon \sum_n S^x(n) - \frac{1}{2}\sum_{nm} J(n-m)S^x(n)S^x(m) - \frac{1}{2}\mu_B g_c B \sum_n S^z(n)$$
(5.1)

This Hamiltonian is written in the same notation as in Gehring and Gehring [6]. In this Hamiltonian, we are ignoring interactions of the B_{1g} quadrupole components since they are subdominant to the B_{2g} Jahn-Teller energies. The first term is the elastic energy, with *N* representing the number of unit cells and Ω the unit cell volume. The second term couples the long-range, uniform strain of the appropriate symmetry and the quadrupole S^x with coupling strength V_s . The third term is the quadrupolar-quadrupolar coupling. The coefficient J(n - m) describes the coupling between quadrupoles by all phonons besides

the k = 0 acoustic phonons (the uniform strains). This is a sum over all pairs of quadrupoles and does not assume a particular form for J(n - m). The final term is the Zeeman energy.

Due the relative simplicity of the Hamiltonian in this material, examinations of the coupling parameters in this model has been very thorough. The 70's and 80's in particular were a time of extensive studies into the problem of the Jahn-Teller effect on this paradigmatic material. Many types of measurements were conducted to examine the strength of the phonon coupling parameters each with their own specialties. Since phonons couple the quadrupoles, experimental techniques that probe the behavior of phonons are particularly valuable in this problem. For example, inelastic neutron scattering can give momentum-resolved information of the behavior on finite-*k* phonons [62], Raman spectroscopy can examine k = 0 optical phonons [63], and ultrasound can provide information about k = 0 acoustic phonons as well as as zone-averaged information about other phonons [24] [23]

In this study of the Jahn-Teller effect in TmVO_4 we use ultrasound to examine the coupling strengths, but we take a different approach compared to previous studies. We measure across the whole series $\text{Tm}_x Y_{1-x} \text{VO}_4$ ranging from the dilute 1% Tm sample all the way to the fully cooperative 100% Tm sample. We then examine how the parameters describing the uniform strain-quadrupole coupling, the quadrupole-quadrupole coupling, and the magnetic field coupling evolve as the concentration of Tm^{3+} ions changes. This evolution, as well as the role of each parameter in the Hamiltonian, will give us detailed information about the nature of the interactions between quadrupoles.

Data

The main set of data in our study is presented in Figure 5.1. Panel a) of this figure shows all the temperature dependent data taken. This data was taken in samples with different Tm concentrations ranging from the pure sample $TmVO_4$, to $Tm_{0.1}Y_{0.9}VO_4$, to $Tm_{0.03}Y_{0.97}VO_4$, and to $Tm_{0.01}Y_{0.99}VO_4$. This data was taken over a temperature range from approximately 1.8 K to 12.5 K. Additional low temperature data will be presented later in this chapter. The vertical axes of all these plots are multiplied by a factor so that they can sit on approximately the same vertical scale. In pulse echo measurements, the leading cause of uncertainty in measurements is often due to interference effects either from non-ideal transducers or samples that are non-ideal. In these measurements we found that the 1% Tm sample shows variations on the order of a few parts in 10^{-6} , the 3% sample shows variations on the order of 10^{-5} , the 10% sample shows variations on the order of 10^{-4} , and the 100% sample shows variations on the 10^{-4} . These uncertainties arising from interference effects are much smaller (100 times smaller) than the overall changes of $\delta v/v$ for each sample and thus don't contribute significantly to the uncertainty in the overall fits.

As can be seen, the data in all samples is qualitatively similar, though the magnitude of the changes in the speed of sound are very different. For example, the relative changes in the speed of sound in the 1% Tm sample are approximately 100 times smaller than in the 100% Tm sample, 10 times smaller than in the 10% sample, and 3 times smaller than in the 3% sample. The overall magnitude appears to be proportional to the percentage of Tm in the sample. This effect shows that the softening of the lattice originates directly from the Tm ions, in particular the Jahn-Teller effect from the 4f electrons. The origin of this

softening will be discussed in further detailed in the analysis section.

The other prominent behavior that can be seen in the data is how the softening of the speed of sound changes with magnetic field. As the magnetic field along the c-axis increases, the gap between the once degenerate ground state levels increases, suppressing the Jahn-Teller effect. Therefore, we see large softening at lower fields, but at higher fields the softening becomes less prominent. At 6 T, for example, the speed of sound barely changes since the gap is now so large that at the temperature scale of the measurement, the energy levels no longer appear degenerate. Theoretically, at large enough fields the only contribution left to changes in the speed of sound should be due to the anharmonicity of the lattice. At low temperatures, this results in a speed of sound that is roughly temperature independent, similar to the data at 6 T. We can also measure the speed of sound in the pure YVO₄ to confirm that there are no unexpected anomalies in the speed of sound from the host lattice.

The background temperature dependence of the speed of sound in pure YVO_4 is shown in Figure 5.2. This data was measured with a longitudinal transducer sending sound along the (110) direction, similar to the measurements in our other samples. Panel a) shows the temperature dependence from approximately 1.8 K to 200 K with changes referenced to the speed of sound at 200 K. The temperature dependence seen is the normal background from the anharmonicity of the lattice [64] [65] [66]. Panel b) shows the speed of sound from about 1.8 K to 12.5 K which is the range for our other measurements. We see that there are variations on the order of 10^{-5} which is very small compared to the scale of changes in Figure 5.1. This basically flat background below 12.5 K agrees with the mostly temperature independent speed of sound at 6 T for the

other samples in Figure 5.1. When fitting the speed of sound data in Figure 5.1, we will be able to model the background as a constant.

The Hamiltonian in Equation 5.1 will be the basis for deriving a formula for the elastic constants in all of our Jahn-Teller materials. We'll examine this derivation in more detail later in this chapter but for now we'll use the following mean-field result for the speed of sound [6]:

$$\frac{\delta v(T,B)}{v} = \left(\frac{\delta v}{v}\right)_0 - \frac{\mu' \tanh(\Delta/kT)}{\Delta - \lambda \tanh(\Delta/kT)}$$
(5.2)

In this equation $\Delta = \frac{1}{2}g_c\mu_B B$ is the Zeeman energy, μ' the mean-field, strainquadrupole coupling strength, λ the mean-field, quadrupole-quadrupole coupling strength, and $\left(\frac{\delta v}{v}\right)_0$ a constant vertical offset. This formula is only correct in the approximation that we can ignore the effect of fluctuations of the quadrupolar moment. This is typically a good approximation, especially since long-range strains are important in these systems. However, it might be possible that the varying levels of disorder throughout the series affects the validity of the meanfield approximation. This concern does not seem too important though, since the data is qualitatively similar in all samples regardless of the amount of disorder

We will now use Equation 5.2 to fit our data and extract how μ' , λ , and the magnetic *g*-factor, *g_c*, change with Tm substitution. The data above 12.5 K is removed to avoid contributions from higher energy crystal field levels. We fit the data for each sample separately, but for each sample's field and temperature dependent data we only use the 4 free parameters. Panel b) of Figure 5.1 shows the fits superimposed on the data. The fits match the data extremely well over all fields and temperatures and for all substitution values.

Table 5.1 shows the values of the extracted fit parameters for all samples.



Figure 5.1: **Temperature-dependent speed of sound data for all substitutions with fits.** Panel a) presents the speed of sound data for TmVO_4 , $\text{Tm}_{0.1}\text{Y}_{0.9}\text{VO}_4$, $\text{Tm}_{0.03}\text{Y}_{0.97}\text{VO}_4$, and $\text{Tm}_{0.01}\text{Y}_{0.99}\text{VO}_4$ as a function of temperature at multiple magnetic field values. The data is taken between approximately 1.8 K and 12.5 K. Additional low temperature data will be shown later in this chapter. Panel b) shows the same data with the fits to Equation 5.2 plotted on top it in black. The fits and the data show excellent agreement. The extracted parameters are presented in Table 5.1.

	μ(K)	λ (K)	g_c
TmVO ₄	-0.16	-1.23	10.9
Tm _{0.1} Y _{0.9} VO ₄	-0.018	-1.16	10.3
Tm _{0.03} Y _{0.97} VO ₄	-0.0057	-0.73	10.1
Tm _{0.01} Y _{0.99} VO ₄	-0.0016	-0.24	10.3

Table 5.1: **Fit parameters for temperature-dependent** $\delta v/v$ **sweeps.** The three parameters here shows different evolutions with Tm substitution. The magnetic *g*-factor, *g_c*, stays constant across the series, the strain-quadrupole coupling parameter, μ , scales with the concentration of Tm, and the quadrupole-quadrupole coupling parameter, λ , rises rapidly with increasing Tm concentration until it saturates at 10 % Tm.



Figure 5.2: **Temperature-dependent speed of sound data in YVO**₄. Panel a) presents the speed of sound data in the YVO₄ from 1.8 K up to 200 K. The temperature dependence follows the typical behavior due to the anharmonicity of the inter-atomic potential. At low temperatures (below 25 K) the speed of sound does not vary significantly. In particular, panel b) shows that below 12.5 K (the temperature range of our other measurements), variations in the speed of sound are on the order of 10^{-5} .

The constant offset term $\left(\frac{\delta v}{v}\right)_0$ from Equation 5.2 is not included in this table and will not be discussed further. It's an arbitrary offset that just depends on the initial measurement location in phase space and doesn't give any insight into the physics of the system. The first parameter we'll discuss is the magnetic *g*-factor along the c-axis, g_c . As can be seen, this quantity does not vary with changing Tm concentration. This agrees intuitively with the fact that the *g*factor is a local property that describes the microscopic energy level splittings in a magnetic field, and this should not change if there are more Tm atoms in the sample.

The next parameter we extract is the uniform strain-quadrupole coupling term μ' . This parameter changes dramatically between samples, and in fact appears to scale linearly with the percentage of Tm in the sample. This behavior with Tm concentration agrees with our expectation from theory. In the theory, the term in the Hamiltonian that describes the coupling between the uniform strain and quadrupolar moment is a sum over all possible Tm ions as in Equation 5.1. While the coupling strength itself should be inherently independent of the number of Tm ions, what we measure with ultrasound isn't the coupling strength directly. Instead, this quantity depends on the concentration of Tm in the material as will be seen in more detail in the next section.

The final parameter λ is the most difficult parameter to extract reliably but gives the most interesting and detailed information about this system. In the microscopic Hamiltonian, λ describes the strength of an Ising-like interaction between nearby quadrupoles. A priori, we don't know much about the extent of this interaction, but with our data it will be possible to extract information about the range of this interaction.

We'll now perform a more careful analysis of the parameter λ since it's effect on the data is subtle in some regions of parameter space. For example, this parameter is difficult to extract reliably at higher temperatures since the magnetic *g*-factor g_c and the uniform strain coupling μ' working in tandem can easily compensate for changes in this parameter. However, measurements at low temperatures tend to do a better job at constraining λ and require more dramatic "unphysical" changes of μ' and g_c to compensate for a change in λ . The consequences of changing λ can be seen most prominently for field sweeps at He3 temperatures. Panel a) of Figure 5.3 shows a plot of a model of the speed of sound based on Equation 5.2 which keeps g_c , μ , and $\left(\frac{\delta v}{v}\right)_0$ constant for several different values of λ . This data is plotted at a temperature of 300 mK over a field range of 0 T to 6 T with $g_c = 10.2$, $\mu = 0.3$ K, and $\left(\frac{\delta v}{v}\right)_0 = 0$. The field dependent curves are plotted for $\lambda = 0$ K, $\lambda = -0.5$ K, and $\lambda = -1$ K. The plots show that a change in the value of λ results in the changing location and sharpness of a characteristic "knee" in the data. As the value of λ becomes more negative the sharpness of this knee decreases and changes in the speed of sound become less prominent.

We now examine how the parameters μ and g_c can act together to compensate for changes in λ . Panel b) of Figure 5.3 presents plots of the same model Equation 5.2, but now we use the $\lambda = -0.5$ K curve as "data" to be fit. For these two fits, we constrain the values λ to $\lambda = 0$ K and $\lambda = -1$ K and see how the parameters μ and g_c can compensate for these changes. We find that the curves of these fits for these different λ 's can be forced to be quite similar. However, the values of μ and g_c required for these fits show dramatic changes that are not physical. For example, we know from other measurement techniques (UPR/EPR in chapter 4) that $g_c = 10.2$. However the fits for when $\lambda = 0$ K and $\lambda = -1$ K require the values $g_c = 5.2$ and $g_c = 15.1$ respectively. This value is dramatically different than the measured value in other techniques suggesting that these fits aren't the best. Therefore, it seems that the low temperature field-sweep data can be used to strongly constrain the values of λ .

Panel a) in Figure 5.4 shows additional field sweep data for a range of temperature values from 400 mK to 12.3 K in the 3% Tm sample. Before attempting



Figure 5.3: **Speed of sound models for field sweeps from** 0 **T to** 6 **T at** 300 **mK.** Panel a) shows how altering the value of λ qualitatively changes the behavior the model given fixed values of the other parameters. Panel b) shows the same $\lambda = -0.5$ K plot as before. The other curves are generated by fixing $\lambda = 0.0$ K and $\lambda = -1.0$ K and letting the other parameters vary to find the best fit to the $\lambda = -0.5$ K curve. Changing the values of g_c and μ can mostly compensate for changes in λ but this requires dramatic changes in both μ and g_c that are very large.



Figure 5.4: **Speed of sound data with fits for field sweeps from** 0 **T to** 6 **T in Tm**_{0.03}**Y**_{0.97}**VO**₄**.** Panel a) shows the raw field-dependent data. At low fields there is an upturn in the data from the formation of spontaneous Jahn-Teller Strains. This effect will be discussed more in the next chapter. Panel b) shows the same data with the low-field upturn removed. Panel c) shows the fits to all data from panel b) using Equation 5.2. The extracted parameters are $\lambda = -0.48$ K, $\mu = -0.0057$ K, and $g_c = 10.1$ which is in decent agreement with Table 5.1
to fit the model to this data, there are some prominent low field features that are worth discussing. The low field upturns in the data deviate from the meanfield theory (Equation 5.2) in the case where there is no spontaneous Jahn-Teller strain. However, these upturns occur at a field range where the field energy is comparable to the Jahn-Teller energy. This corresponds to the formation of potential wells at non-zero strain, suggesting that these features are related to the formation of Jahn-Teller strains. These features will not be discussed extensively in this chapter and instead will be the focus of Chapter 6. When fitting this data to Equation 5.2, the data will be cut off well above these upturns when the magnetic field energy is dominant over the Jahn-Teller energies.

Panel b) of Figure 5.4 presents the same data as before but instead with the low field data removed. We now fit the mean-field, zero-strain theory to the data. As before, the data and the theory are in excellent agreement. The values of the parameters extracted from these fits are similar to those found in Table 5.1 and take the values $\lambda = -0.48$ K, $\mu = -0.0057$ K, and $g_c = 10.1$. The values found for μ and g_c are in excellent agreement with the previous results, while λ has a significantly larger variation from the previously extracted value in Table 5.1. This is likely caused by the inability of the high temperature data to constrain this parameter as strongly.

Ideally, we would have low temperature field dependent data for all samples, but at the moment we lack that data for the other samples. However, we believe that the value of λ in the 3% sample is very well constrained. We can see it is approximately half way in value between the completely dilute sample where λ has to be 0 K and in the fully cooperative system where $\lambda = -1.23$ K.

Many of the conclusions we will draw in the next few sections of this chap-

ter will depend on the doping dependence of λ . In particular, the rapid rise of this value from -0.24 K in the dilute sample to the fully saturated value of approximately -1.2 K by 10% will be a major focus. Even if we only trust the low temperature fits in the 3% Tm sample, we still see this parameter is half-way to it's saturation value that is known from literature. The fact that this already happens by 3% Tm concentration is extraordinary and will result in the same conclusions being drawn.

5.1 Analysis

In this section, we will discuss in more depth the behavior of the measured parameters across the substitution series and the origins of this behavior . The first parameter, the magnetic *g*-factor g_c , was already discussed in the previous section and will not be discussed further here. The next parameter from our definition of the speed of sound, μ' , provides information about the strength of the coupling between quadrupolar moments and the uniform strain in a material. The extracted values from our fits show that this parameter μ' varies proportionally to the number density of Tm ions in the crystal. In order to understand this variation, we'll examine the uniform elastic energy term and the strain-quadrupolar coupling term from Equation 5.1 in more detail:

$$H_{\epsilon} = \frac{1}{2} N \Omega c_{66} \epsilon^2 - V_s \epsilon \sum_n S^x(n)$$
(5.3)

The variables here are the same as the defined in Equation 5.1. Minimizing with respect to the strain and the applying mean-field theory results in the Hamiltonian of the form:

$$H_{\mu} = -\mu \langle S^{x} \rangle \sum_{n} S^{x}(n)$$
(5.4)

This formula follows the derivation given by Gehring and Gehring [6] where:

$$\mu = V_s^2 / c\Omega \tag{5.5}$$

This parameter μ is not necessarily the same as the parameter μ' that appears in our fits for the elastic constants. We will see that the parameter we call μ' is in fact related to μ but with an additional scaling due to the concentration of Tm ions in the sample. However, first we'll examine whether the definition of μ in Equation 5.5 can account for any of the variation seen in μ' .

The parameter μ consists of three different terms, two of which may change between different crystals in the doping series (c and Ω). For example, the lattice parameters in YVO₄ are a = 7.1183(1) Å and c = 6.2893(1) Å and in TmVO₄ are a = 7.0682(1) Å and c = 6.2593(1) Å [67]. This results in a unit cell volume in YVO₄ that is $\Omega_Y = 318.68$ Å³ and in TmVO₄ that is $\Omega_{Tm} = 314.31$ Å³. The unit cell volume of YVO4₄ is approximately 1.4% larger than the unit cell volume of TmVO4₄. The scale of this change in the unit cell volume across the series is not nearly large enough to account for the factor of one hundred change in μ' .

The other parameter that can change is the bare elastic constant across this series of materials. In our experiments we send longitudinal sound along the (110) orientation which measures the elastic constant $(c_{11} + c_{12})/2 + c_{66}$ [68]. The elastic constant in the Hamiltonian describing the Jahn-Teller effect and the equation for μ (Equation 5.5) however only depend on the shear modulus c_{66} , which is the channel for the Jahn-Teller effect. Examining the literature, we find that the bare elastic constant $c_{66,0}$ in YVO₄ is experimentally measured as 16.2 GPa [69], and values up to approximately 22 GPa are theoretically determined [70]. From ultrasound measurements, the bare elastic constant $c_{66,0}$ in TmVO₄ is determined to be 16.4 GPa [24]. Even when using the much larger theoretical

value for YVO₄, the elastic modulus $c_{66,0}$ in YVO₄ is 36% larger than in TmVO₄. Again, this small percent difference isn't nearly large enough to account for the 2 orders of magnitude change see in our extracted value of μ'

The definition of μ given in Equation 5.5 by Gehring and Gehring [6] is not able to account for the dramatic change seen in the extracted value of the parameter μ' from our measurements. However, a more careful examination of the uniform strain terms in the mean-field theory show that the theory is able to explain this change. As before, the uniform strain terms before applying the mean-field theory are written as:

$$H_{\epsilon} = \frac{1}{2} N \Omega c \epsilon^{2} - V_{s} \epsilon \sum_{n} S^{x}(n)$$
(5.6)

The first term describes the total elastic energy of the sample and *N* is the number of unit cells. The second term describes the Jahn-Teller energy from the uniform-strain coupling, and here the sum is over the number of Jahn-Teller active sites (the rare earth sites with Tm ions). In the pure TmVO₄ sample, the sum over Tm ions will have 2*N* terms since there are two Tm ions per unit cell. However, as Y replaces Tm, sites with Y no longer contribute to the sum in the Jahn-Teller energy term. The number of terms in the sum is now *x* * 2*N* rather than 2*N* where *x* is the percentage of sites occupied by Tm. Minimizing the free energy with respect to strain gives $\epsilon = (V_s/N\Omega c) \sum_m S^x(m)$. The Hamiltonian in equation (5.6) can then be written as:

$$H_{\epsilon} = -\frac{1}{2} \frac{\mu}{N} \sum_{nm} S^{x}(n) S^{x}(m)$$
(5.7)

The Hamiltonian now takes a form that describes an effective long-range Isinglike interaction between quadrupolar moments. In such a system, we would expect the system to be well approximated by a mean-field Hamiltonian, even though the Tm ions are not situated on a regular lattice. The mean-field Hamiltonian now takes the form:

$$H_{\epsilon} = -x\mu \langle S^{x} \rangle \sum_{n} S^{x}(m)$$
(5.8)

We replaced one of the quadrupolar moments by the mean-field value and summed over the number of sites which as already mentioned is x * 2N. Now, the mean-field Hamiltonian used to calculate the speed of sound has a term in it that depends on the fraction of rare earth sites occupied by Tm ions. We now see that $\mu' \propto x\mu$ as expected. As a note, there are additional constant prefactors in this relation which are related to the conversion from the elastic moduli to the speed of sound. However, these won't be affected by changing Tm substitution and are ignored for this analysis.

In the equation for the speed of sound Equation 5.2, the value of the parameter μ' changes according to the fraction of rare earth sites occupied by Tm, which explains the evolution of the parameter μ' in Table 5.1. Another way of thinking about it is that the measured μ' is directly proportional to the the *x* in the chemical formula Tm_{*x*}Y_{1-*x*}VO₄. This effect appears to be a very long-range effect associated with the susceptibility of the mean field at each Tm ion. As more and more Tm ions are added to the lattice, they contribute linearly to the susceptibility. This suggests that the understanding that this parameter describes a long-range, uniform strain coupling is valid.

5.1.1 Evolution of λ

The final parameter we will examine, λ , is also the one with the most complex dependence on the density of Tm. As described before, this parameter describes all other symmetry-allowed phononic interactions between quadrupoles except for the k = 0 acoustic phonons. The saturation of this parameter to its most negative value by the 10% Tm sample is quite different than the behavior of μ' , which scales linearly with the density of Tm. Despite the difference in behavior, we'll take a similar approach to our analysis of μ' . We'll examine the λ term in the Hamiltonian in more detail and see if the mean-field theory is able to explain its evolution with Tm concentration

Our analysis of λ will begin with a more thorough examination of the Isinglike interaction between quadrupoles in Equation 5.1:

$$H_{Q-Q} = -\frac{1}{2} \sum_{nm} J(n-m) S^{x}(n) S^{x}(m)$$
(5.9)

Writing the quadrupole-quadrupole interaction into this form is actually a nontrivial task. The review by Melcher [21] or Gehring and Gehring [6] can show the full derivation of this term. However, we are interested only in the step right before, where this term is written in momentum space as:

$$H_{Q-Q} = -\frac{1}{2} \sum_{\mathbf{q}} J(\mathbf{q}) S^{x}(\mathbf{q}) S^{x}(\mathbf{-q})$$
(5.10)

The Fourier transform can convert between the momentum-space and positionspace versions of this term:

$$J(n-m) = (1/N) \sum_{\mathbf{q}} J(\mathbf{q}) \exp[-i\mathbf{q} \cdot (\mathbf{R}_n - \mathbf{R}_m)]$$
(5.11)

In this equation, N gives the number density of Tm ions and \mathbf{R}_n are the positionspace locations of the Tm sites. This analysis was preformed for the fully cooperative system, assuming no disorder that might change the form of the Fourier transform (Equation 5.11). Reducing the occupation of Tm sites will affect equation Equation 5.11 by changing the value of N to x * N where x is the fraction of rare earth sites occupied by Tm. Since the occupation is random, we no longer have a purely periodic lattice of Tm ions. However, in this analysis we will ignore that detail. We'll assume that the Tm sites are occupied in a perfectly periodic manner, so we can naively use this formula. This assumption might be partially justified since ultrasound is a long-wavelength probe. It is possible that averaged over many unit cells, the randomness might appear averaged out to the ultrasound. Applying the new form of the Fourier transform to Equation 5.10, we find the new formula:

$$H_{Q-Q} = -\frac{1}{2x} \sum_{n,n} J(n-m) S^{x}(n) S^{x}(m)$$
(5.12)

If we now apply mean-field theory to this term, it becomes:

$$H_{Q-Q} = -\frac{1}{x} \langle S^x \rangle \sum_{n,m} J(n-m) S^x(n)$$
(5.13)

We now assume that $\lambda = \sum_{m} J(n - m)$ is a constant. The Hamiltonian then becomes:

$$H_{Q-Q} = -\frac{1}{x} \lambda \langle S^x \rangle \sum_n S^x(n)$$
(5.14)

This formula takes a form similar to the strain-quadrupole coupling term from Equation 5.8.

In order to develop a more quantitative understanding of how the measured λ depends on Tm concentration, we must come up with a simple model for J(n - m). In particular we'll need a model of J(n - m) as a function of distance. The simplest model for J(n - m) is that it takes a constant value of J inside some



Figure 5.5: $\operatorname{Tm}_{x} Y_{1-x} \operatorname{VO}_{4}$ with interaction sphere. This figure shows the lattice of $\operatorname{Tm}_{x} Y_{1-x} \operatorname{VO}_{4}$ for x = 0.1 decorated with Y atoms (red) and Tm atoms. The black Tm atom is the center of the interaction sphere, the blue atoms are outside this sphere, and the green atoms are inside the sphere and therefore interact with the central Tm atom.

effective interaction distance R_0 and is 0 outside this distance. This model is illustrated in Figure 5.5.

In Figure 5.5, we present the tetragonal lattice of the $Tm_xY_{1-x}VO_4$ series with only the Tm/Y ions decorating the lattice. In this image, each rare earth site has a 10% chance of being filled by Tm (blue/green) and 90% by Y (red). In addi-



Figure 5.6: **Probability of a Tm neighbor vs interaction distance for multiple Tm concentrations.** This figure shows the likelihood that a Tm ions interacts with at least one other Tm ion given some effective interaction distance. Notice that as the percent of Tm in the sample increases, this value quickly saturates with interaction distance. The interaction distances at which we plot the data points are when new neighbors fall into the interaction sphere.

tion, one Tm site (black) is chosen as the center, around which a sphere of radius R_0 is drawn. This sphere represents the maximum distance for quadrupoles to interact in our model, beyond which there interaction strength is 0. On average, each central Tm ion will interact with $x * N_1$ other ions (green) where N_1 is the number of rare earth sites within the interaction sphere. If we combine the prefactors at the front of Equation 5.14 into one parameter λ' we find:

$$\lambda' = (1/x)\lambda = (1/x)\sum_{i} J = (1/x) * xN_{1}J = N_{1}J$$
(5.15)

Naively, this equation suggests that the parameter λ' , as measured by ultrasound, should not depend on the percent of Tm in this sample. However, this is still not the complete quantity measured by ultrasound. We assumed that all ions in this model contributed to this sum. However, there will be some ions



Figure 5.7: **Probability of a Tm neighbor vs Tm concentration for multiple interaction distances.** This figure shows the likelihood that a Tm ion interacts with at least one other Tm ion given the concentration of Tm. This is plotted for a variety of different interaction distances. We can use this plot and our measured values of λ to determine an effective interaction distance of the quadrupoles.

that do not have other ions within their interaction distance. These ions will not be part of the double sum and will not contribute to its value. This means that the effective measured value of λ' is the value from Equation 5.15 times the probability that the ion has a Tm neighbor within its interaction sphere. This becomes more obvious in the case where all the Tm ions are completely isolated. In this situation, Equation 5.15 would predict a value that is the same as the fulling interacting case. However, we know that this term should be 0 since there is no interaction between ions. We will account for this effect by examining how the second sum in Equation 5.14 changes when some ions are not interacting.

At the moment, the sum in Equation 5.14 is over all the rare earth sites with Tm ions. However, we shouldn't include the terms that represent Tm ions that don't interact with any other Tm ions. This means that we'll have to subtract out of this sum the number of Tm sites that don't interact. This analysis is aided by re-examining Figure 5.5. In this figure, a Tm ion will contribute to this second sum if there is another Tm ion within this radius of sphere R_0 . This is equivalent to saying that it will not contribute if there isn't at least one Tm ion within this radius. Assuming a uniform distribution of Tm ions, we can easily calculate the probability that there isn't a Tm ion within the interaction sphere. The value x in the chemical formula for the series $Tm_xY_{1-x}VO_4$ gives the probability that it's not. If there are N_1 rare earth sites within the interaction sphere then the probability that none of them are occupied by Tm is given by:

$$p_{no} = (1 - x)^{N_1} \tag{5.16}$$

The probability that at least one site is occupied by a Tm site is:

$$p_{one} = 1 - (1 - x)^{N_1} \tag{5.17}$$

This probability can be multiplied by the sum in Equation 5.14 to determine the true average form of the sum. We also plug in Equation 5.15 into this formula to get:

$$H_{Q-Q} = -N_1 J * (1 - (1 - x)^{N_1}) \langle S^x \rangle \sum_n S^x(n)$$
(5.18)

This equation is now the effective average term in the Hamiltonian describing the interactions between quadrupolar moments. The sum in Equation 5.18 is now technically over all Tm sites, not just sites with interacting Tm ions as before. The number of terms in the sum in Equation 5.18 is now consistent with the number of terms for the μ' parameter in Equation 5.8. Since these terms will be combined in the derivation of the speed of sound, they must be the same sums.

If we go back to the mean-field form given by Gehring and Gehring we can identify the equivalent λ :

$$H_{Q-Q} = -\lambda \langle S^x \rangle \sum_n S^x(n)$$
(5.19)

From this equation, the equivalent λ measured by ultrasound will be everything that appears in front of $\langle S^z \rangle \sum_n S^z(n)$. From Equation 5.18, it becomes apparent that ultrasound will measure:

$$\lambda = -N_1 J * (1 - (1 - x)^{N_1})$$
(5.20)

We now will investigate how this parameter evolves with changing values of N_1 and x. Recall that N_1 is the number of rare earth sites (Tm and Y atoms) within the interaction sphere, and x is the fraction of rare earth sites occupied by Tm ions. The value of N_1 will not change as the Tm density, x, changes, but it will change as the interaction distance changes. In this analysis, we'll focus on the factor $(1 - (1 - x)^{N_1})$ rather than the term $-N_1J$. We will do this because while changing N_1 in $-N_1J$ will change the value of λ , it will change the same in all samples regardless of concentration. We are most interested in the ratio of the values of λ at different concentrations compared to the pure sample and why it saturates as early in the 10% Tm sample. The $-N_1J$ term will not affect this saturation. Instead, the term $(1 - (1 - x)^{N_1})$ will be responsible for this saturation.

Figure 5.6 plots the probability of a Tm ion interacting with at least one other Tm ion $(1 - (1 - x)^{N_1})$ versus effective interaction distance up to 25 Å. This model is plotted for multiple values of Tm concentration ranging from x = 0.01 up to the x = 1. The interaction distance is directly related to the number of rare earth

ions in the interaction sphere N_1 . As the interaction distance (R_0) increases, N_1 also increases approximately as R_0^3 , though we can also model the lattice and see how this number changes exactly with R_0 . For the rest of this discussion, we will primarily discuss how the interaction probability changes compared to R_0 rather than N_1 but recall that they are related. As a note on Figure 5.6, the points plotted in this graph correspond to when the interaction sphere intersects with a new set of neighbors. Since the sets of near neighbors are not regularly spaced on the lattice and the number of new neighbors changes between set of neighbors, we see an irregular jumps in the plot.

This plot (Figure 5.6) demonstrates how quickly the interaction probability saturates with interaction distance. For some context, we see that the pure sample (x = 1) is immediately saturated to its maximum value. This happens because the smallest point plotted is for an interaction sphere of radius given by the nearest neighbor distance, and all sites are occupied by Tm in this sample. As we decrease the occupation of rare earth sites by Tm, we increase the interaction distance required before this term fully saturates. However, this saturation occurs relatively quickly even in the x = 0.01 sample at a value of approximately 20 Å. In the x = 0.10 sample, it happens at the smaller value of 10 Å. Recall that this interaction probability factor will scale the value of λ that we measure with pulse echo ultrasound. For example, when this quantity is fully saturated, λ will have the same value as the pure, x = 1 sample. On the other hand when it is 0, then $\lambda = 0$ K. From our model in Figure 5.6, and the knowledge that λ is fully saturated in the x = 0.1 sample at 10 Å, we can see that the interaction distance is around 10 Å. We can gain more insight into the interaction distance by plotting the probability of interaction vs Tm fraction for different values of interaction distance (Figure 5.7) and comparing this to the our extracted values of λ from Table 5.1.

The plots in Figure 5.7 show how the interaction probability evolves with increasing Tm occupation. We have plotted the data up to x = 0.2 and for interaction distances up to $R_0 = 9.25$ Å. Recall that the values of the parameters λ at different values of Tm fraction are: $\lambda = -1.23$ K for x = 1, $\lambda = -1.16$ K for x = 0.1, $\lambda = -0.73$ K/-0.48 K for x = 0.03, and $\lambda = -0.24$ K for x = 0.01. The ratio of these values of λ at any concentration to the value of λ_1 at x = 1 should be the same as the probability of interaction. These values are given by: $\lambda/\lambda_1 = 1$ for x = 1, $\lambda/\lambda_1 = 0.94$ for x = 0.1, $\lambda/\lambda_1 = 0.59/0.4$ for x = 0.03 and $\lambda/\lambda_1 = 0.20$ for x = 0.01. Comparing this evolution of the ratio of λ 's to the interaction probability in our plots, we see that we can constrain the effective interaction distance rather effectively. For example, the near saturation of the x = 0.1 value eliminates values of the interaction distance that are below 6 Å. Then, the range of λ seen in the x = 0.03 sample constrains the value to a value between 6 Å and 8 Å.

The results of these constraints may change as we take additional highquality, low-temperature data in the x = 0.01, x = 0.1, and x = 1 sample similar to the data in the x = 0.03 data. However, the preliminary results suggest that the interaction distance is between 6 Å and 8 Å, which is approximately the length of the unit cell in these materials. Despite the possible changes, we do not expect the upper constraint on the distance to change dramatically with the new data. For one, our value of λ in the x = 0.03 sample did not change dramatically between the two fits and is still 40% of the saturated value. This means that the interaction distance can't be too large, otherwise we would expect a nearly saturated value. This limits the interaction range to approximately a distance of one unit cell. The nature of this analysis, with its rapid rise in interaction probability, means that it is very robust in its ability to constrain the interaction distance. For example, we can, with a high degree of confidence, constrain the effective interaction distance to approximately one unit cell. This can be done with just one value of λ and the fact that it is not fully saturated to its x = 1 value. Additional data should further constrain our extracted values of λ and build further confidence in our inferences.

Finally, we can discuss the implication of this effective interaction distance for the Jahn-Teller effect. We see that all other terms besides the acoustic strain have an effective interaction distance that is on the order of only one unit cell. This is consistent with the short travel distance of optical phonons, suggesting that this coupling is dominated by optical phonons. In addition, these are likely k = 0 phonons, since this transition is a k = 0 transi

CHAPTER 6

SPONTANEOUS JAHN-TELLER STRAIN

As a disclaimer, some of the ideas and arguments presented in this chapter are still in development and will be expanded upon in the future.

6.1 Introduction

The Jahn-Teller effect directly couples the electronic and structural degrees of freedom in a crystal. There are two different regimes of the the Jahn-Teller effect, the single ion effect and the cooperative effect. In the single ion effect, Jahn-Teller strains emerge gradually as the temperature is lowered and the atoms fall into the local potential minimum. On the other end, in the cooperative effect, there is no mean strain above a critical temperature. Below this temperature, a phase transition occurs, after which a non-zero mean strain will emerge continuously, in the case of a second order phase transition.

In this chapter, we will study perturbations from the limiting cases of the completely isolated effect and the completely cooperative effect. On the isolated end, we'll examine what happens to the the speed of sound as more and more Tm ions are allowed to interact. We'll see what this can tell us about the effect of interactions on the properties of the system. On the cooperative side, we will see the effect that disorder has on the behavior above the cooperative transition. Ideally from our understanding on the dilute side we can develop intuition for the "non-ideal" features in the cooperative system.

6.2 Data

Our data in this chapter will be presented in two separate subsections. In the first part, we'll show the speed of sound vs. field data for all the dilute samples. We'll also plot the attenuation and discuss difficulties associated with interpreting this data. In the next subsection, we'll present the speed of sound vs. field data and attenuation vs. field data in the cooperative samples. Then we'll discuss the similarities and difference in our data between these two regimes and how the dilute data might help us interpret the cooperative data.

6.2.1 Dilute Systems

The speed of sound data from the dilute side of the series is presented in Figure 6.1. In particular, this figure shows the field-dependent speed of sound measured at various temperatures in the Tm_{0.01}Y_{0.99}VO₄, Tm_{0.03}Y_{0.97}VO₄, and Tm_{0.1}Y_{0.9}VO₄ samples. The field sweeps are performed at approximately the same temperatures in all samples, with a high temperature of approximately 12.5 K. As can be seen, the data is qualitatively similar for all samples. As the field is lowered from 6 T, the speed of sound decreases until it eventually undergoes an upturn at low field, after which it continues increasing until 0 T. These measurements were performed at several frequencies and no frequencydependence was found in the upturn. The location and width of these upturns appear to be dependent on both the temperature of the measurement and the concentration of Tm. However, they all occur roughly around the same field value, where the Zeeman energy ($\mu_{Bgc}B_c = 3.4$ K for $B_c = 0.5$ T) is comparable to the Jahn-Teller energy ($\mu = 3.15$ K). This suggests that the upturns may be associated with the emergence long-range, uniform strains and a nonzero quadrupolar moment due to the Jahn-Teller effect. An intriguing feature to notice is that the upturns are wider for samples with more Tm and at larger temperatures. These upturns are one of the main focuses of study in this chapter. In particular, we'll examine the origins of these features, and why they are different between samples with different Tm concentrations.

The other interesting measurement in these samples is the field-dependent attenuation data. As a warning, this data is much more difficult to interpret than the speed of sound data in this context. This is primarily due to interference effects, which are often more problematic in attenuation measurements than in speed of sound measurements. The attenuation data from the 10% Tm sample is not included here because the interference effects in this sample were significant, making it even more difficult to interpret. We will not attempt to draw many conclusions from this data, but hopefully the conclusions we do draw will be useful in our discussion on disorder in the cooperative systems.

Figure 6.2 presents the attenuation data for the 1% and 3% sample. In panel a), the data below 50 mT is removed since the sweep rate is 0.1 T/min in this plot and the finer features of the hyperfine resonances would be severely distorted. Panel a) presents attenuation data that was taken at the same time as the speed of sound data in Figure 6.1. This data is only presented at one temperature since interference effects make it difficult to extract more detailed conclusions from additional temperatures. As can be seen in panel a), the changes in the attenuation are much smaller in the 1% sample than in the 3% sample. Another important feature, especially in 3% data, is that attenuation starts to increase dramatically around 1 T. Comparing this to the speed of sound data, we see



Figure 6.1: $\delta v/v$ vs *B* at multiple temperatures in the samples Tm_{0.01}Y_{0.99}VO₄, Tm_{0.03}Y_{0.97}VO₄, and Tm_{0.1}Y_{0.9}VO₄. These plots show upturns in the speed of sound around 0.5 T, which for $g_c = 10.2$ is approximately an energy of 3.4 K. This is a similar energy scale to the Jahn-Teller coupling energy $\mu = 3.15$ K, suggesting that these upturns are due to the Jahn-Teller effect. We'll examine in more detail the reason for the differences between samples.



Figure 6.2: Changes in the ultrasonic attenuation ($\delta\Gamma$) in the dilute samples. Panel a) shows some of the attenuation corresponding to the speed of sound sweeps in Figure 6.1. The data is constrained to the range B = 0.05 T to B = 3 T for clarity. Panel b) and panel c) present the attenuation data in the 1% and 3% Tm samples at two different frequencies. This data is from the set of data taken in chapter 4 on the hyperfine absorption, and the low field spikes in attenuation are the features studied in chapter 4. A constant background is subtracted from all of the data. There are two main features that will be important for this chapter. First, the attenuation "activates" near the same field value as the upturns in the speed of sound. Second, changes in the attenuation in the 3% sample are dramatically larger than in the 1% sample.

that the rise in the attenuation occurs around the same field value as the upturn in the speed of sound. All of our attenuation measurements, regardless of temperatures, display these same features, even though they all have different interference patterns.

Panel b) and panel c) of Figure 6.2 present the attenuation data in the same 1% and 3% samples as before, now just taken at a slower sweep rate. This data is part of the same set of data from chapter 4, just up to a maximum field of 0.25 T. The field sweeps from panel b) and c) were both taken at 1.8 K and at the frequencies 0.7 GHz and 1.0 GHz. The UPR absorption at low fields is not removed from this data, since the field sweep rate was so slow that all features are resolved properly. In particular, the sweep rate was 0.004 T/min rather than 0.1 T/min in this measurement. This slower field sweep rate lets us examine the data more closely and ensure that the features we saw in the faster sweeps are qualitatively correct. Since this data only goes up 0.25 T, we can't see where the attenuation starts to rise dramatically. However, we can see that the attenuation in the 3% sample is much larger than in the 1% sample, similar to panel a).

The shared features in the attenuation data gives us more insight into what might be happening in these systems. The first feature we'll discuss is the rise of the attenuation in the 3% sample around 1 T from panel a) of Figure 6.2. This rise in the attenuation roughly corresponds to the location of the upturn seen in the speed of sound in Figure 6.1. This suggests that these effects may be related and may both originate from the emergence of a non-zero strain/quadrupole moment due to the Jahn-Teller effect. However, the 1% sample also shows a similar upturn in the speed of sound, but it doesn't show a significant rise in the attenuation, which complicates this interpretation. Naively, we might expect that the changes in the attenuation in the 3% sample would be 3 times larger than changes in the attenuation in the 1% sample if the Tm ions are driving the attenuation. However, changes in the 3% sample seem to be more than 3 times greater than changes in the 1% sample, suggesting that there may be additional physics to understand. We'll delve into more depth about the possible origin of this phenomena in the discussion section.

6.2.2 Cooperative Systems

The insights gained from examining the speed of sound and attenuation in the dilute samples can be used to aid us in our examination of the cooperative samples. On the cooperative end, we currently have field-dependent data in both $TmVO_4$ and $Tm_{0.95}Y_{0.05}VO_4$. We have much less data in the pure sample at the moment, so we will primarily focus on the features seen in the 95% Tm sample. Then, we'll examine the data from the 100% Tm sample to compare and contrast the features.

We will now briefly talk about the cooperative transitions in these materials. These materials both undergo cooperative Jahn-Teller transitions, with the addition of Y suppressing the transition temperature. In the pure x = 1 sample, the transition occurs at 2.15 K, while in the x = 0.95 sample, the transition occurs at 1.8 K. In addition, this transition can be suppressed to 0 K with a magnetic field placed along the *c*-axis. Our measurements lie well outside the low-temperature, ordered phase, in the region of higher temperature and field. This is mostly for practical reasons since the attenuation becomes very large at small temperatures and small fields.

$Tm_{0.95}Y_{0.05}VO_4$

Figure 6.3 presents our field-dependent speed of sound data at multiple frequencies and temperatures in $Tm_{0.95}Y_{0.05}VO_4$. One of the most immediately striking features is that this data shows an upturn at fields below 1 T, similar to data from samples at the dilute end of the series. Figure 6.4 shows a closer look at this region of interest, only showing the data below 2 T. Unlike the upturns in the dilute data, the locations of these upturns show a striking frequency dependence. As the frequency increases, the field value of the minima also increases. This seems to be a real effect rather than an artifact due to interference. If we examine the variation in the speed of sound curves due to interference by choosing different echoes in the echo train, we see that this variation is much smaller than the variation due to changes in frequency. If interference effects were the culprit, we might see variations in the minima location between echoes that were as large as the shifts due to changing the frequency. Another piece of evidence supporting that this frequency dependence is real is the systematic dependence of minimum location with frequency. For all temperatures, we see that increasing the frequency results in the minima increasing in field. With an interference effect, we would expect the change to be random.

The frequency-dependent speed of sound in this cooperative system shares similarities with the speed of sound in the dilute systems but also shows some stark differences. The most obvious feature, the upturn in the speed of sound, appears to be a common feature in all of the samples that we have measured so far. In the dilute system, we believe that this upturn is due to the formation of Jahn-Teller strains once the Jahn-Teller energy scale and Zeeman energy are comparable. This may be the case in the cooperative 5% Y sample as well, though there are complicating factors. The first is the frequency dependence of the speed of sound at low fields. It appears that at least some of the upturn comes from the frequency-dependent behavior that is seen in this system and not the dilute systems. The second is the cooperative nature of the transition. Naively, we expect that there should not be a mean Jahn-Teller strain above the transition temperature in a completely cooperative system. However, if the upturn in the speed of sound is due to long-range strains, then we know that at least some of the Tm ions see a non-zero strain above the transition. This also suggests that the quadrupole moment/order parameter may be non-zero above the transition.

The attenuation data corresponding to the speed of sound data from Figure 6.3 is presented in Figure 6.5. This data is measured at the same temperatures as before and at the same frequencies, except for the highest frequency of 2.45 GHz. This higher frequency data is excluded because there is a large amount of interference at this frequency, which results in difficulty interpreting the data. The data is vertically shifted for clarity since we are more concerned with changes in attenuation than with absolute values of the attenuation. The attenuation curves at all temperatures and frequencies are qualitatively similar. At larger fields (> 1 T), the attenuation is approximately field-independent except for interference effects. These effects cause wiggles in the data, which are especially prominent at 5 K. Around approximately 1 T, the attenuation "activates" and starts to rise dramatically. The magnitude of this rise is greater for larger frequencies, which is a typical behavior of attenuation. The behavior of the attenuation in this cooperative system is qualitatively similar to the behavior of the attenuation seen in the dilute systems. The attenuation curves in both are temperature independent at high fields, but they rise dramatically at a similar field value to where we see upturns in the speed of sound.

This similarity between the speed of sound and attenuation in the dilute and cooperative systems suggests that similar physics is driving the behavior seen in these samples. From the dilute samples, we associate the rise in the speed of sound and the activation of the attenuation with the emergence of Jahn-Teller strains. In the cooperative system, this feature may also be due to the emergence of Jahn-Teller strains. However, this behavior is mildly unexpected for the co-operative system. In a purely cooperative system Jahn-Teller system, we would only expect the formation of a static strain below the transition temperature. However, the 5% Y sample surely has disorder, and it seems that this disorder pre-strains a population of Tm ions.

TmVO₄

The speed of sound vs field data measured in TmVO₄ at 10 K is presented in Figure 6.6. This data is taken over a wide range of frequencies, ranging from 0.946 GHz to 2.703 GHz. The signal was lost below 0.3 T for most frequencies, so we removed that data for all frequencies. This data shows several features in common with the data from the 95% sample. We see that both sets of data show an upturn in the speed of sound around the 0.5 T. In addition, the overall magnitude of the changes in this region are comparable (approximately 1.5×10^{-3}). However, the differences in the data between samples are also significant. Perhaps the most important difference is that the dramatic frequency dependence seen in the 95% sample is not seen in the pure sample. While there is some variation in the speed of sound measured at different frequencies in the pure sample, the variation is smaller than the variation seen in the 95% sample. The change



Figure 6.3: **Speed of sound vs field in Tm**_{0.95}**Y**_{0.05}**VO**₄. These plots show the speed of sound vs field at 5 K, 7.5 K, and 10 K. At each temperature, data was taken at multiple frequencies ranging from 0.65 GHz to 2.45 GHz. At high fields the data is frequency independent, but at higher temperatures a frequency-dependent upturn emerges.



Figure 6.4: Speed of Sound vs Field up to 2 T in sample $Tm_{0.95}Y_{0.05}VO_4$. This is the same data as in Figure 6.3 but with the data above 2 T removed in order to emphasize the frequency dependent upturn. The systematic increase of the field value of the upturn with increasing frequency suggests that this is an intrinsic effect rather than due to interference.



Figure 6.5: Attenuation vs field in $Tm_{0.95}Y_{0.05}VO_4$. This is the attenuation data corresponding to the speed of sound data from Figure 6.3. The 2.45 GHz data was removed since interference effects are especially large at that frequency in this sample. The attenuation is also vertically shifted for clarity. At high fields, the attenuation is field independent, but "activates" around 1 T.

with frequency in the pure sample also is not systematic and appears to change randomly with increasing frequency. In addition, the change in frequency does not result in the field value of the minimum changing. These two observations suggest that the frequency-dependent variations seen in the 95% sample do not exist or are not observable in the pure sample. Any frequency dependence seen in the pure sample appears to be due to artifacts from interference effects. This also suggests that the upturn in the pure sample is not a frequency-dependent effect and may be due to the emergence of Jahn-Teller strains similar to the dilute samples. This likely means that some of the upturn in the 95% Tm sample is also frequency independent and due to Jahn-Teller strains as well.

The attenuation data corresponding to the speed of sound data in the pure sample is presented in Figure 6.7. This data is qualitatively similar to the attenuation data in the 95% Tm sample. At high fields, the attenuation is relatively constant with field, except for interference effects which are especially prominent in the 1.597 GHz data. Around 0.6 T we see that the attenuation "activates' and begins to rise rapidly with decreasing field until we lose the signal. The attenuation also changes most rapidly for the highest frequency data, as is typical for attenuation data. These behaviors are all quite similar to the attenuation data in the 95% sample, though the main difference is quite interesting. The "activation" field in the 95% sample appears to be at a larger field value (1 T) than the "activation" field in the 95% sample occurs at a larger field value than in the pure sample. However, the frequency dependence in the 95% complicates this interpretation, and we will attempt to examine this more quantitatively in the next section.



Figure 6.6: Speed of sound vs field in TmVO_4 for multiple frequencies at 10 K. This plot shows the speed of sound vs field data in the pure Tm sample at 10 K and below 2 T. The measurement is performed at many frequencies ranging from 0.946 GHz to 2.703 GHz. There is a slight frequency dependence in the data, though this is likely from interference effects. Similar to the dilute samples, this data shows an upturn at low fields (< 0.5 T).



Figure 6.7: Attenuation vs field in TmVO_4 for multiple frequencies at 10 K.. This is the attenuation data corresponding to the speed of sound data from Figure 6.6. The data is vertically shifted for clarity. This data is mostly field independent above 0.6 T except for interference effects. At 0.6 T, the attenuation starts to rise rapidly and we quickly lose the signal.

6.3 Analysis

In this section, we'll explore the upturns in the speed of sound in more theoretical depth and attempt to give a more quantitative description for their emergence. We'll first examine them in the dilute side of the series. For these materials, we'll attempt to understand why the location and width of these upturns change with Tm concentration. Then, we'll take these insights to the cooperative end of the system and explore what we can learn about the effect of disorder in the cooperative Ising model. In addition, we'll explain how to understand the frequency dependence in the 95% Tm sample. In this discussion, we'll primarily focus on the speed of sound data, but we'll also discuss the attenuation data when particularly relevant.

However, before examining the physics which results in the formation of Jahn-Teller strains, we'll generalize the formula for the speed of sound from chapter 5 (Equation 5.2) to allow for finite strains. The speed of sound in the presence of the Jahn-Teller can be generically written as [6]:

$$\frac{\delta v}{v_0} = -\frac{\mu' g_{\gamma}}{1 - \lambda g_{\gamma}} \tag{6.1}$$

In this equation μ' and λ are the strain-quadrupole coupling and the quadrupole-quadrupole coupling respectively, and g_{γ} is the quadrupolar susceptibility. This quantity is defined as:

$$g_{\gamma} = \left(\frac{\partial \langle S^x \rangle}{\partial h^x}\right)_{\gamma} \tag{6.2}$$

 $\langle S^x \rangle$ is the average value of the quadrupolar moment in the appropriate symmetry channel while $h^x = \lambda \langle S^x \rangle + V_s \epsilon$ is the mean field at the location of the ion. This quantity describes how easily the quadrupolar moment changes from variations in the mean field h^x . In addition, we may apply a magnetic field B_c along the c-axis. The average quadrupolar moment from the mean-field theory then takes the form:

$$\langle S^{x} \rangle = \frac{h^{x}}{[(h^{x})^{2} + \Delta^{2}]^{1/2}} \tanh\left(\frac{[(h^{x})^{2} + \Delta^{2}]^{1/2}}{kT}\right)$$
(6.3)

In this equation $\Delta = \frac{1}{2}\mu_B g_c B_c$ is the Zeeman energy. Previously, to calculate the susceptibility, we took the derivative of this equation with respect to h^x and then set $h^x = 0$. Now, however, we no longer assume that the mean field h^x is 0 and instead will allow for it to be finite. Instead of a single term in the susceptibility, we have several:

$$g_{\gamma} = \frac{1}{kT} \frac{(h^{x})^{2}}{(h^{x})^{2} + \Delta^{2}} sech^{2} \left[\frac{\sqrt{((h^{x})^{2} + \Delta^{2})}}{kT} \right] + \frac{\Delta^{2}}{((h^{x})^{2} + \Delta^{2})^{3/2}} \tanh\left[\frac{\sqrt{(h^{x})^{2} + \Delta^{2}}}{kT} \right]$$
(6.4)

This equation goes into the formula Equation 6.1, which now gives the formula for speed of sound in the presence of finite strain. Since the full form of this equation is particularly complicated, we will plot this equation vs field for different values of the parameters h^x in Figure 6.8 to gain an intuition for their effect. This data is plotted for several values of the mean field h^x at T = 0.3 K, with $\lambda = -1.0$ K, $\mu' = 0.03$ K, and $g_c = 10.2$. This plot shows that we expect there to be an upturn at low fields when the mean field h^x becomes comparable to the temperature of the measurement. This supports our intuition that the upturn in the speed of sound is related to the emergence of Jahn-Teller strains and therefore a non-zero mean field. We'll explore this strain more in the next subsection.

6.3.1 Dilute Systems

Our analysis of the emergence of Jahn-Teller strains will begin with a reexamination of the Jahn-Teller Hamiltonian for isolated ions. We will di-



Figure 6.8: Theoretical model of speed of sound vs field for finite values of the mean field h^x . This image shows how changing h^x affects our the predicted form of the speed of sound. The main takeaway is that when the mean field h^x is comparable to the measurement temperature, an upturn at low field may occur.

agonalize this Hamiltonian to determine the eigenvalues as a function of strain/displacement coordinate. These eigenvalues are the upper and lower potentials in which the nuclei/4*f* electrons live, and from these potentials, we can determine the average strain. Up to now we have been ignoring the nuclear kinetic energy. However, if we want to determine the strain distribution, we must include the kinetic energy since there will always be some zero point energy even at T = 0 K. We can now solve for the eigenvalues and eigenfunctions of this position space Hamiltonian. The key insight is that at T = 0 K, the Jahn-Teller strain distribution will be given by the probability distribution determined by the ground state wavefunction of this Hamiltonian. This wavefunction is the probability that an atom will be found at a specific value of strain, which is what we mean when we talk about the strain distribution.

The Hamiltonian describing the Jahn-Teller effect is given by:

$$H = \frac{1}{2}c\epsilon^2 - V_s\epsilon \sum_n S^x(n) - \Delta \sum_n S^z(n)$$
(6.5)

In this equation, the first term is the standard elastic energy, the second is the Jahn-Teller coupling with V_s giving the strength of the coupling, and the third term is the Zeeman coupling with $\Delta = \frac{1}{2}g_c\mu_B B_c$ as before. This Hamiltonian describes the potential landscape of the combined nuclear/electronic system. Up to this point, we haven't allowed for the possibility of a nuclear kinetic energy term. However, its inclusion, the Hamiltonian becomes:

$$H = \frac{p^2}{2M} + \frac{1}{2}c\epsilon^2 - V_s\epsilon \sum_n S^x(n) - \Delta \sum_n S^z(n)$$
(6.6)

In this Hamiltonian, p represents the momentum of the nuclear/electronic system while M is the mass of the system (primarily the nuclear mass). This Hamiltonian has two different components to it. The first are the electronic levels which are represented by a $2x^2$ matrix and the second are the momentum and strain which must be treated as operators if we wish to determine the vibrational wavefunctions/spectrum. The Hamiltonian in Equation 6.6 can also be written as:

$$H = \begin{pmatrix} \frac{p^2}{2M} + \frac{1}{2}c\epsilon^2 - \Delta & -V_s\epsilon \\ -V_s\epsilon & \frac{p^2}{2M} + \frac{1}{2}c\epsilon^2 + \Delta \end{pmatrix}$$
(6.7)

At this point, this matrix is written in the spin basis. We first diagonalize the matrix to determine the electronic eigenstates before attempting to solve the position-basis Hamiltonian. The energy levels take the form:

$$H_{\pm} = H_K + H_U = \frac{p^2}{2M} + \frac{1}{2}c\epsilon^2 \pm \sqrt{\Delta^2 + V_s^2\epsilon^2}$$
(6.8)

Now that we have written the matrix in diagonal form, we see that there are two separate Hamiltonian that depend on position/momentum. At T = 0

K, the atoms/electrons will fall into the lower energy state H_{-} and the strain distribution will be determined by the ground state of this lower energy state. Using this Hamiltonian, we can write down the time-independent Schrodinger equation:

$$\frac{\hbar^2}{2M}\frac{\partial^2\psi}{\partial\epsilon^2} + \frac{1}{2}c\epsilon^2 - \sqrt{\Delta^2 + V_s^2\epsilon^2} = E\psi$$
(6.9)

Now that we have the form of this differential equation, it's worth discussing some qualitative expectations and building some intuition from the form of the potential. Since the potential is complicated, this is best done by plotting the potential vs for different values of V_s and Δ as seen in Figure 6.9. In panel a), both the Jahn-Teller coupling and the magnetic field coupling are set to zero resulting in a purely quadratic elastic potential. As the Jahn-Teller coupling is turned on in panel b), the two once-degenerate states split and lower in energy and their minima shift to finite strain. If the temperature is low enough and the wells deep enough, we might expect the equilibrium positions of the atoms to now lie at finite strain. As the magnetic field is turned on such as in panel c), a gap opens up at 0 strain and the minima become shallower. Eventually, when the Zeeman energy is larger than the Jahn-Teller energy such as panel d), the bottom potential becomes completely flat and the equilibrium position of the atoms will be 0 once again. We can use this simplified picture to develop an understanding of what is happening in field sweeps in different samples. At high fields, the energy levels are flat and the mean strain is 0. However, as the magnetic field becomes comparable to the Jahn-Teller energy scale, we expect the formation of spontaneous strains in the system due to the emergence of potential wells away from zero strain. This behavior suggests the possibility that the upturn in the speed of sound is due to the emergence of spontaneous Jahn-Teller strains.



Figure 6.9: **Jahn-Teller potential for TmVO**₄. This cartoon demonstrates the effects of Jahn-Teller coupling as well as the competition between Jahn-Teller and Zeeman energies. In panel a), there is no Jahn-Teller coupling or magnetic field and as a result we see a standard harmonic potential. Turning on the Jahn-Teller coupling in panel b) results in the degeneracy breaking and the minimum of the potential moving to positive and negative strain. In panel c), a magnetic field is turned on which reduces the depth of the potential minimum until eventually destroying the local minimum at large enough fields in panel d).

Our next goal in this analysis is to develop a quantitative understanding of the emergence of these strains by numerically solving for the wavefunction at multiple fields. Then we will evaluate how this wavefunction evolves as the field changes. This is the current state of our research on the dilute systems, but we will continue with this analysis in the future to develop a further understanding of these Jahn-Teller strains and why they are different in each of the dilute samples.
6.3.2 Cooperative systems

The examination of Jahn-Teller strains in the cooperative systems is still a workin-progress. However, what we do see so far is quite intriguing. In both cooperative samples measured so far, x = 1 and x = 0.95, we see upturns in the speed of sound. From the dilute systems, we identify these upturns as being caused by the emergence of Jahn-Teller strains. However, in a purely cooperative system, we would not expect these strains to emerge outside the ordered state. What we see however, is that there appears to be a population of Tm that is strained due to the Jahn-Teller effect even before the cooperative transition. This occurs even in the nominally pure system. At this stage, we believe that this pre-strained population of Tm is due to the effect of random strains. However, we are still working to gain further insights into these strains as well as the percentage of Tm affected before the transition.

Relaxation Time

The frequency dependence of the speed of sound in the 95% Tm sample adds another interesting complication to the physics of the cooperative systems. In the case of the dilute materials, the entirety of the upturn can be attributed to the formation of Jahn-Teller strains at low field. However, the strong frequency dependence of the upturn in the speed of sound in the 95% Tm sample means that there is additional physics that must be explained. Typically, the speed of sound can show frequency-dependent behavior when there is an internal time scale that is comparable to the period of the sound [71] [72]. The simplest theory that allows for a time-dependent speed of sound/elastic constant is a simple modification of the normal theory of elasticity known as anelasticity.

The theory of anelasticity is one of the simplest modifications to standard elasticity that allows for a time-dependent speed of sound. Figure 6.10 [2] shows an example of some simple ways in which standard elasticity can be modified. Anelasticity modifies standard elasticity by allowing for time dependence but preserving linearity and complete recoverability. This effect can be intuitively understood by examining the response of the strain to an external stress. When a static stress is suddenly applied, the entirety of the strain cannot respond instantaneously as in Figure 6.11. Instead, some portion of the strain responds immediately, while the rest takes time to reach its equilibrium value. Similarly, once the stress is released some component of the strain responds instantaneously, but there is also a part that takes time to respond. After a long enough time, the strain returns back to its initial value (complete recoverability). The time scale for the strain to respond is known as the relaxation time.

Now that we have intuitive idea of what is meant by anelasticity, we want to examine how anelasticity might emerge. These sort of relaxation-type dynamics can emerge when there is an internal degree of freedom in the material that is linearly proportional to the strain. For example, this internal degree of freedom could be a quadrupolar moment that couples linearly to strain in the Hamiltonian. The standard relation between stress and strain is them modified by the addition of this internal variable:

$$\epsilon = J_U \sigma + \chi \xi \tag{6.10}$$

In this equation, ϵ is the strain, J_u the elastic compressibility, σ the stress, ξ the internal degree of freedom, and χ the coupling strength to the internal degree of freedom. We make the approximation that the rate at which this variable returns

	Unique equilibrium relationship (complete recoverability)	Instantaneous	Linear
Ideal elasticity	Yes	Yes	Yes
Nonlinear elasticity	Yes	Yes	No
Instantaneous plasticity	No	Yes	No
Anelasticity	Yes	No	Yes
Linear viscoelasticity	No	No	Yes

DIFFERENT TYPES OF MECHANICAL BEHAVIOR, CLASSIFIED ACCORDING TO THE CONDITIONS OBEYED BY THE STRESS-STRAIN RELATIONSHIP

Figure 6.10: **Modifications of the theory of elasticity.** This table shows some of the assumptions of the theory of elasticity, and the theories that result when these assumptions are broken. We are particularly interested in anelasticity, which preserves linearity and a unique equilibrium position but is no longer instantaneous. Reproduced from the book *Anelastic Relaxation in Crystalline Solids* [2]

to its equilibrium value is proportional to its deviation from equilibrium:

$$\frac{d\xi}{dt} = -(1/\tau)(\xi - \bar{\xi}) \tag{6.11}$$

This time dependent relaxation of the internal degree of freedom is what introduces the relaxation behavior to the strain.

The differential equation describing an anelastic solid is given by:

$$\sigma + \tau_{\epsilon} \dot{\sigma} = c(0)\epsilon + c(\infty)\tau_{\epsilon} \dot{\epsilon} \tag{6.12}$$

In this formula, τ_{ϵ} is the strain's relaxation time. c(0) the zero-frequency elastic constant, and $c(\infty)$ the high frequency elastic constant. As can be seen, in the limit that $\tau_{\epsilon} = 0$, we return to the standard theory of elasticity where strains and stresses respond instantaneously. If we assume a strain proportional to $\exp[i\omega t]$, we can derive the basic form of the frequency-dependent elastic constants and



Figure 6.11: **Anelastic response to applied stress.** This plot shows the elastic and anelastic response to a stress that is turned on at time t_{on} and turned off at t_{off} . In the elastic theory, the strain can respond instantaneously. In the anelastic theory, part of the strain responds instantaneously and part takes time to reach its max value. This time scale is known as the relaxation time (τ).

attenuation:

$$c(\omega) = c(\infty) - \frac{c(\infty) - c(0)}{1 + \omega^2 \tau^2}$$
 (6.13)

In Equation 6.13, there are several regimes of behavior. In the low frequency regime, defined by $\omega \tau \ll 1$, we find $c(\omega) = c(0)$. On the other hand, when $\omega \tau \gg 1$, we then see that $c(\omega) = c(\infty)$. While the values of $c(\infty)$ and c(0) depend on the particulars of the theory, we expect there to be some universal behavior. For example, as the relaxation time increases and passes through the value $1/\omega$, the behavior of $c(\omega)$ should switch from more like c(0) to more like $c(\infty)$. A simple model demonstrating this behavior is presented in Figure 6.12. This figure shows $c(\infty)$, c(0), and $c(\omega)$ as a function of magnetic field for multiple frequencies. In panel a), the dashed lines represent a particular model of $c(\infty)$ and c(0)that are based on the Jahn-Teller effect but whose details are not particularly important at this point. Panel b) shows the field-dependent relaxation time which at 0 T is 4 ns and decays exponentially with increasing field. We plot $c(\omega)$ for multiple frequencies and see behavior that is reminiscent of our speed of sound data in the 95% sample from Figure 6.3. The behavior of $c(\omega)$ changes from c(0)at high fields where the relaxation time is small compared to $1/\omega$ towards $c(\infty)$ at low fields when the relaxation time is large compared to $1/\omega$. We see that a minimum in the elastic constant develops around this crossover region and that it decreases in field value as the frequency is lowered similar to Figure 6.3 motivating further examination of the 95% data.

The model we used here is motivated by what we might expect in the cooperative TmVO₄ samples. In the case of the TmVO₄ series, the internal degree of freedom that is linearly proportional to the strain is the quadrupolar moment. This means that the relaxation time here describes how quadrupoles relax back



Figure 6.12: $c(\omega)$ vs field for multiple frequencies.. This figure demonstrates how the elastic constants can cross over between c(0) and $c(\infty)$. In this figure, c(0) and $c(\infty)$ are based off a field dependent Jahn-Teller model with different sets of parameters though the details of the model are not important for this image. What we can see in panel a) is that crossover between c(0) and $c(\infty)$ occurs when the relaxation time scale is comparable to the measurement frequency as seen in panel b). Therefore the high frequency data crosses over before the low frequency data for this model.

to equilibrium when perturbed. Our model of a relaxation time that increases with decreasing field seems to be able to capture the correct frequency dependence of the data. It shows minimums in the elastic constant that increase in field with increasing frequency though the exact functional form is difficult to know. At this point we still don't fully understand the model for c(0) and $c(\infty)$ which complicates extracting quantitative insights into the behavior of the relaxation time. However, we do know that c(0) is probably less than $c(\infty)$. The elastic constant c(0) shows softening from the bare value due to the Jahn-Teller effect and should be similar to what we have seen in other samples. However, it is typically thought that $c(\infty)$ will not show as much softening if any, since there is not time for the quadrupoles to respond to the perturbation. Therefore $c(\infty)$ is probably closer to the bare elastic constant. As a result, $c(\omega)$ should go from a smaller value to a larger value of elastic constant as it passes through $1/\omega$ as we included in our model. The model presented may not capture quantitative features of our data, but it might allow us to gain some physical insights into the cooperative end of the TmVO₄ series.

The behavior of the relaxation time is particularly interesting in the context of the random field Ising model [73] [74] [75], which is the model likely describing our cooperative samples. The random field Ising model predicts that with increasing disorder from random fields, there should be critical slowing of time scales [76]. While at this stage we are still working to see if we can extract the quantitative behavior of the relaxation times from the 95% sample, what we see so far can gives us some insight into this critical slowing down. Primarily, we know that the time scale of the relaxation of the quadrupolar moments is on the ns scale in our measurements of the 95% Tm sample since we see frequency dependence in the speed of sound. In addition, it's likely that the relaxation time increases with decreasing field as previously discussed. This contrasts with the pure sample and the samples on the isolated end of the series, where we do not see frequency dependence at the same field and temperature value which suggests that the time scale is smaller. In the isolated Jahn-Teller samples, the quadrupole moments are able to fluctuate independently and as a result their time scales may be faster than what we can detect with out measurement frequency. However, in the 95% Tm sample, disorder may result in groups of quadrupoles fluctuating together which significantly slows down the time scales. This should be more prominent in samples with more disorder which can explain why we aren't able to see the slower time scales in the pure Tm sample.

CHAPTER 7 CONCLUSIONS/OUTLOOK

This thesis investigates several aspects of the Jahn-Teller effect in the model system $\text{Tm}_x Y_{1-x} \text{VO}_4$. There are three main studies in this thesis. The first, in chapter 4, utilizes a technique known as Ultrasonic Paramagnetic Resonance to drive resonant transitions between localized energy levels associated with the 4*f* electrons of the Tm. Since we know the microscopic Hamiltonian describing isolated Jahn-Teller ions, we can extract detailed information about the internal strain distribution in both the 1% and 3% Tm samples. Intriguingly, we find a finite width to the strain distribution in the 1% sample but can not resolve the width in the 3% sample (it appeared uniform). Another interesting feature of the analysis is the ability to resolve the symmetry of the strains present and their relative importance compared to each other. Since ultrasound is a symmetry sensitive probe, we extract the ratio of the magnitude of B_{1g} and B_{2g} strains. We find that these strains occur in equal magnitudes.

The next study, in chapter 5, examines the effective interaction distance of quadrupoles in our Jahn-Teller system. We do this by first measuring the speed of sound in samples across the series $\text{Tm}_x Y_{1-x} \text{VO}_4$: for x = 0.01, x = 0.03, x = 0.10, and x = 1.00. In each of these samples, we fit a well-known mean-field formula (Equation 5.2) for the speed of sound to our data and extract the parameters from these fits for each sample. Of particular interest is how the parameter describing the quadrupole-quadrupole interaction (λ) evolves with Tm substitution. This parameter describes how these quadrupoles interact via all channels besides k = 0 acoustic strain. We find that the value for small Tm concentrations (x = 0.01) was very near 0, but by x = 0.10, it nearly saturates

to its x = 1.00 value of $\lambda = -1.23$ K. With some simple modeling, we see that this rapid rise in this parameter can tell us the effective interaction distance of quadrupole moments. In this system, we determine that the effective interaction distance is on the order of one unit cell. This effective interaction distance is consistent with interactions mediated by optical phonons

Finally, in chapter 6, we examine a feature in our field-dependent speed of sound data that appears in all samples we have measured. Below 1 T, and at all temperatures, we see that the speed of sound begins to increase again. This upturn can't be described by the equation used for the speed of sound used in chapter 5 (Equation 5.2). However, it can be understood by first noticing that this upturn occurs when the Jahn-Teller energy is comparable to the magnetic Zeeman energy. This suggests that these upturns are associated with the formation of Jahn-Teller strains. In the dilute samples, we see that there are qualitative differences in the width and location of these upturns between different samples. We believe that this is due to the effects of interactions, though this requires more study. On the cooperative end of the series, we see these upturns even in the pure sample. This is likely due to the effect of random strains pre-straining the Tm before the cooperative transition. This again, will be interesting to examine in more depth, since it may give us insight into the effect of disorder on a cooperative transition.

The studies presented in this thesis have opened up several avenues of investigation into other Jahn-Teller systems. Starting with ultrasonic paramagnetic resonance, we may be able to use this technique in other dilute Jahn-Teller systems. This can give an extremely detailed investigation of the strains at relatively small values in more complicated systems, such as those with conduction electrons or magnetism. In addition, the technique we use to examine the effective interaction distance can also be used in more complicated system. It would be interesting to see the effect of magnetism on quadrupolar interaction distance, such as in the system DyVO₄ [6]. Also, how would the addition of conduction electrons, such as in TmAg₂ [39] affect the interaction distance? Would it result in much longer-range interactions, and would we see the parameter λ saturate much more quickly as a result? Finally, we hope to be able to extract information about the Jahn-Teller strain distributions from the upturns seen in our field-dependent speed of sound data. In the dilute side of the series, this could tell us how interactions change this distribution, and in the cooperative systems, it could tell us about what disorder does to the phase transitions. There are still many interesting topics of research left in this material and in related materials, and we are excited to see where they take us.

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