Effects Of DC Electric Field On Ferroelectric Phase Transitions In Potassium Tantalate Niobate Studied By Ultrasound Pulse-Echo

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A thesis submitted for consideration for the degree of Bachelor of Science with Honors in Physics

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Submitted & Defended May 2019
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Abstract

The ultrasound pulse-echo technique is used to investigate the bulk ferroelectric crystal $KTa_{0.92}Nb_{0.08}O_3$ as it is cooled to and warmed from its ferroelectric phase in the presence of an external DC electric field. Measurements are performed using a homodyne ultrasound apparatus with phase-sensitive detectors, and a DC electric field which varies from 0 V/cm to $>2$ kV/cm. The speed and attenuation of ultrasound are both measured as functions of temperature to model changes in the crystal. The observed behavior includes dependence of transition temperatures on applied voltage, strong effects associated with the coercive field, and possible evidence of a metastable polarization that exists in the material’s paraelectric temperature regime, a phenomenon previously unpublished.

I. THEORY

A. Ferroelectric Crystals

1. Basic Properties

A ferroelectric material has certain crystal phases wherein the material possesses a spontaneous, long-range electric polarization even when an external electric field is not present. Ferroelectrics are broadly classified as either displacive or order-disorder. For displacive ferroelectrics, structural phase transitions at low temperatures shift ions, misaligning the centers of positive and negative charge in the crystal, and thereby creating an intrinsic electric dipole moment. For order-disorder ferroelectrics, ions may be displaced even in the material’s non-ferroelectric phases, but the random orientation of the dipoles makes the material electrically neutral on average. These dipoles are then ordered as the material approaches its ferroelectric phase. Many ferroelectric materials exhibit both displacive and order-disorder behaviors. A ferroelectric material may be further polarized or polarized in a different direction by an external field, and will exhibit hysteresis in the dependence of the polarization on the applied electric field. As with ferromagnets, the polarization disappears above the Curie point (a label for the transition temperature when it is approached from below), where the thermal motion overcomes the order of the polarization. [1] In general, the ferroelectric phase
of a given material will be of lower symmetry than the non-polar phase, because ferroelectricity is caused by anisotropic interactions between atoms in the crystal lattice, and is dependent upon specific crystallographic directions. [2] Some ferroelectric materials undergo multiple transitions, which each decrease the symmetry of the crystal in favor of stronger electric dipole moments. [3]

2. Structural Phase Transitions & Soft Modes

Continuous phase transitions occur when the structure of a crystal changes without producing latent heat. The lack of latent heat signifies that the change in entropy is continuous across the entire transition. Continuous transitions are also called second-order phase transitions, according to Ehrnfecht’s classification, because the second derivative of the Gibbs free energy with respect to temperature is discontinuous at $T_C$. This is distinct from first order phase transitions (e.g. solid to liquid, liquid to gas, etc.), which possess a discontinuity in the first derivative of the Gibbs free energy at $T_C$. [4]

One important concept used to explain continuous transitions is that of mode softening. A soft mode is a normal vibrational mode in a lattice structure which tends to zero amplitude as $T \rightarrow T_C$. [5] Out-of-phase oscillations with nonzero frequency at the center of the Brillouin zone are referred to as optical phonons, because they are of sufficiently high frequency to perturb electromagnetic radiation. These optical phonon modes are distinct from acoustic phonon modes in that acoustic modes are in-phase oscillations (in which atoms in neighboring unit cells travel in the same direction) with low frequency caused by an outside disturbance. Continuous phase transitions may be described as the softening of optic modes which have eigenvectors very similar to the shifts that occur at the phase transition. When the frequency of the oscillations approaches zero, the restoring force vanishes, and the material will deform along the direction of the corresponding eigenvector as a result. Ferroelectric phase transitions are associated with the softening of a particular transverse optical (TO) phonon. The soft optic modes of interest are those which become unstable either at the center ($q = 0$) or at the boundary ($q = \frac{\pi}{a}$) of the Brillouin zone. [6] The temperature dependence of this soft phonon frequency as $T_C$ is approached from above may be expressed by:

$$\omega^2_{TO}(q_s, j) = A(T - T_C),$$  \hspace{1cm} (1)
where $\omega_{TO}$ is the frequency of the transverse optical phonon, $q_s$ is the wavevector, $j$ is the branch index, and $A$ is a material-specific constant. \[7\] \[8\]
As $T \to T_C$, $\omega_{TO} \to 0$, creating an instability in the crystal. The restoring force approaches zero, and ions are displaced to create states of lower crystal symmetry. \[1\]

Continuous ferroelectric phase transitions are accompanied by a divergence of the static dielectric constant $\epsilon(0)$, which depends on factors such as temperature and the frequency of a plane-wave electric field propagating through the material. The dielectric function $\epsilon(\omega, \mathbf{K})$ is dependent on polaritons - quasiparticles arising from interactions between electromagnetic radiation and the electric and magnetic dipole-carrying vibrations of the ions in the lattice. \[9\] The static dielectric constant is defined as the dielectric constant as $\omega \to 0$, or in the limit of a static electric field. The Lyddane-Sachs-Teller relation states:

$$\frac{\omega_{LO}^2}{\omega_{TO}^2} = \frac{\epsilon(0)}{\epsilon(\infty)},$$ \hspace{1cm} (2)

where $\omega_{LO}^2$ is the frequency of a longitudinal optical phonon, and $\epsilon(\infty)$ is the high-frequency limit (in the limit of an oscillating external electric field with $\omega \to \infty$) of the dielectric constant, which is not temperature-dependent. From this equation, and Equation (1), we may see that, for a TO frequency approaching zero, the static dielectric constant $\epsilon(0)$ will obey a Curie-Weiss law:

$$\epsilon(0) \propto \frac{1}{T - T_C},$$ \hspace{1cm} (3)

and will diverge at the transition temperature. This is characteristic of a ferroelectric material as it enters its polarized phase. \[1\]

3. Dipole Alignment, Polar Regions, & Crystal Energy

Many of the useful properties of ferroelectric materials rise from the polar regions that form in the ferroelectric phase. These regions contain sets of electric dipoles ordered along a particular axis, and they may be enlarged when an external electric field moves the domain wall. Applications of microscopic domain wall motion include fast, high-density, non-volatile random access memory. \[10\] With no external field present, polar regions form spontaneously, but an external field may both enlarge the domains and nucleate
new domains, since the electric field makes those domains aligned with the field most energetically favorable. Ferroelectrics exhibit hysteresis in polarization, typically having two or more stable states within their ferroelectric phase which may be induced by a sufficiently high field known as the coercive field. [11] At this degree of polarization, a particular dipole will remain aligned with its neighbors due to the torque it will experience if it rotates away from this alignment. Much theoretical and computational work has been done on hysteresis and dipole alignment, including treatments of polarization as rotational Brownian motion, [12] and Monte Carlo methods used with first-principles Hamiltonian calculations. [13] [14]

As the applied field increases, the sample’s net polarization increases, due to the increased size of polar nanoregions whose net dipoles point along the direction of the electric field. As these regions increase in size, a greater total number of dipoles will be aligned along the same axis, decreasing the free energy of the crystal (the low-temperature limit as $T \to 0 K$ is complete alignment, which shows that greater alignment corresponds to lower free energy [13]). These polar nanoregions form while the sample is cooling. While the sample is warming toward its Curie point, the thermal motion of the ions increases until it eventually scatters the dipoles within the domains.

4. Relaxor Ferroelectrics

Relaxor ferroelectrics have a broader peak in dielectric susceptibility at their transition temperatures than conventional ferroelectrics. Additionally, this peak in susceptibility is often not accompanied by crystal realignment. Because of the wide range of temperatures over which susceptibility is high, ferroelectric relaxors (usually with lead cations) are often used in capacitors. [7]

Though ferroelectric relaxors often do not undergo the same types of transitions as conventional ferroelectrics do, both types of transitions are characterized by a divergence of the dielectric constant. [15] Relaxors may exist in random field states, due to their formation of polar nanoregions, and often undergo three total transitions. The three relaxor transition temperatures have been interpreted in previous literature. According to Toulouse, [16] the first transition temperature (sometimes called the “Burns temperature” because of the temperature-dependent measurements of the optic refractive index by G. Burns [17]) leads to the onset of polarization regions which have
very short lifetimes, and cause no asymmetry in the crystal. The second transition temperature begins the onset of more stable polarized regions, and the third temperature (sometimes called the “freezing temperature”) is where polarization fluctuations cease. [18]

While relaxors exhibit long-range order, their ferroelectric phase also exhibits short-range order consistent with glass phases. This mixed state has been theorized because relaxors such as KTN have been found to follow the Vogel-Fulcher law, with dipole reorientation frequencies given by:

\[ \nu = \nu_0 \exp \left[ \frac{-U}{T_m - T_f} \right], \]

where \( U \) is the activation energy associated with jumping out of the potential well created by the dipole alignment, \( T_m \) is the temperature of maximum dielectric permittivity, and \( T_f \) is the freezing temperature. [19] [20]

B. Potassium Tantalate Niobate

1. Structure & Ferroelectricity

Potassium Tantalate Niobate (\( KTa_{1-x}Nb_xO_3 \), abbreviated KTN) is a ferroelectric perovskite. In general, the perovskite structure allows for many useful properties, such as ferroelectricity, ferromagnetism, and superconductivity. This is because the \( ABO_3 \) lattice structure allows for ions to exist in a geometry wherein the central ions (the “B sites”) may shift away from their positions when the sample is subjected to the right external conditions, such as temperature, pressure, or applied electric or magnetic fields. These shifts are caused by realignments of the lattice (e.g. from cubic to tetragonal), which redistribute the crystal’s electronic energy. To gain an initial understanding of the transitions in KTN, we may imagine that the central Ta/Nb\( ^{4+} \) ions (which we refer to as “Nb sites”) are incrementally confined by three separate phase transitions. The cubic to tetragonal transition shifts the Nb sites along the [100], the tetragonal to monoclinic transition shifts the Nb sites along the [110], and finally, the monoclinic to rhombohedral transition shifts the Nb sites along the [111], after which they reside at a single corner of the lattice. These transitions may also be understood according to a model wherein the randomly oscillating Nb sites lose a degree of freedom for each successive transition: the cubic lattice allows the ion to undergo three-dimensional oscillations between the eight corners of the lattice.
(the expectation value of the ion is still at the center), the tetragonal phase allows two-dimensional oscillations on a single face, the monoclinic phase allows one-dimensional oscillations along an edge, and the rhombohedral phase allows no oscillations. In this model, each crystal realignment corresponds to an optic mode softening. A diagram of these transitions may be seen in Figure 1. The previous publications have argued that the ferroelectric behavior in KTN is primarily driven by order-disorder (see section I.A.1) rather than displacive characteristics. The Nb sites have been found off-center at room temperature, and are displaced only by about 20% when cooled to liquid nitrogen temperatures. [21] The literature is largely divided as to the nature of KTN's transitions, but they are shown as displacive in Figure 1 for ease of visualization.

KTN has a wide variety of compositions, characterized by differing values for $x$ in the formula $KTa_{1-x}Nb_xO_3$. KTN is sometimes referred to as a "mixed ferroelectric" because both Nb and Ta occupy the B sites, though the ferroelectric behavior is largely driven by the presence of niobium. [22] The sample studied herein is a KTN 8% crystal, meaning $x = 0.08$. Different compositions have different transition temperatures, and differing ferroelectric behavior. Previous work by DiAntonio shows that the transition temperatures for this composition should be close to the $T_C$ values shown in Figure 1. [23] The 8% composition is in the lower range of Nb concentration for which three distinct transitions are observable. For $0 < x \leq 0.05$, only one transition is observable, which suggests that the cubic crystal realigns directly to rhombohedral. Correspondingly, a single divergence of the static dielectric constant is observed as temperature decreases. [24] This illustrates the tendency toward relaxor behavior as more Nb is added.

2. Uses & Reasons for Study

KTN is a useful and popular ferroelectric to study for several reasons. Firstly, the material itself is used in many applications. The crystal structure of KTN gives it high electrostrictive and piezoelectric effects, and also strong electro-optic effects. For example, the quadratic Kerr effect modulates the index of refraction according to:

$$\delta n = -\frac{1}{2} n^3 \epsilon^2 g_{11} E^2,$$

(5)
where \( n \) is the index of refraction, \( \epsilon \) is the dielectric constant, \( g_{11} \) is the electro-optic constant of the material, and \( E \) is the applied electric field. Because the dielectric constant of KTN follows a Curie-Weiss law:

\[
\epsilon \propto \frac{1}{T - T_C},
\]

it may be seen that, by varying the temperature and electric field with precision, the index of refraction may be changed precisely. [25] Thus, the material is often used as a beam deflector. Since KTN modulates its index very quickly, it is a good choice for a swept light source. The swept light source is used in optical coherence tomography (OCT), a technique which uses coherent light of varying wavelengths to capture three-dimensional images in optical-scattering media, such as biological tissue. KTN beam deflectors have been used for a variety of purposes in recent publications. [26] [27] [28] KTN’s electrostrictive and electro-optic effects also make it useful as a varifocal lens, which has also been used in recent publications. [29] [30] Studies of KTN’s aforementioned properties without an explicit application have also been a
subject of recent research. [31] [32] [33] It is especially of interest in thin film research. [34] [35] [36]

KTN is also a useful material for modeling more complicated ferroelectrics, such as lead relaxors. This is partially because KTN itself exhibits slight relaxor behavior, seen in its formation of polar nanoregions. [37]

C. Ultrasound Pulse-Echo Technique

The ultrasound pulse-echo technique is a non-destructive means of exploring materials and determining their elastic constants. The technique has been used for more than 50 years, including in studies on ferroelectrics in general, and KTN in particular. [38] The basic setup consists of two transducers mounted at opposite, flattened ends of a sample along the direction of interest. One transducer sends a short pulse of ultrasound - a pressure wave of a frequency above the range of human hearing (i.e. \( > 20,000 \) Hz). The receiving transducer senses the pulses and reflects them back toward the first transducer. The pressure wave will bounce between the two transducers, losing energy at each reflection until it eventually decays. The receiving transducer may provide information about the pulses, such as the amplitude and phase of the ultrasound\(^*\). Additionally, through measurement of the time between reflections, the speed of sound in the material may be very easily obtained. If the sample is of length \( L \), and we define \( \tau_{\text{echo}} \) as the time it takes for a pulse to travel back through the sample from the receiving transducer and then return to the receiving transducer, then the speed of sound in the material will be given by \( v = \frac{2L}{\tau_{\text{echo}}} \). For increased accuracy, the times in between each reflection from the receiving transducer may be measured and averaged, since the reflections are periodic. A diagram of this basic setup is shown in Figure 2.

D. Elasticity Tensors & the Christoffel Equation

1. Hooke’s Law

One of the most useful applications of the ultrasound pulse-echo technique

\(^*\)It is somewhat unfortunate that the term “phase” at once refers to the state of the ferroelectric crystal, and the phase of the ultrasound, two phenomena which must here be discussed side-by-side. The lone word “phase” will refer to the phase of the ultrasound, and the phase of the crystal will be mentioned in tandem with terms like “ferroelectric”, “transitions”, and “crystal” for clarification.
Figure 2: The basic ultrasound pulse-echo probing apparatus, with the sending transducer pictured on the left. The setup in this study has an additional receiving transducer mounted at the opposite end of the sample. Reprinted from Fisk & Migliori [39] with author permission.

is finding the elastic constants of a material via the Christoffel equation. The entire set of elastic constants may be obtained if the speed of sound is known along the different directions of the crystal, and the density of the material is known.

The elasticity tensor is obtained by applying Hooke’s Law along the different directions of the crystal. Hooke’s Law assumes that a strain is linearly related to the applied stress producing the strain (a valid assumption for stresses as small as ultrasound pulses). The most generalized version of Hooke’s Law states:

$$
\epsilon_{ij} = s_{ijkl} \sigma_{kl},
$$

where $\epsilon_{ij}$ represents components of the strain, $s_{ijkl}$ gives the compliances of the crystal along different directions, and $\sigma_{kl}$ represents components of the stress. The indices are as such because, for any homogeneous stress, every component of the homogeneous strain will depend linearly on every component of the stress. For example:
\[
\epsilon_{11} = s_{1111}\sigma_{11} + s_{1112}\sigma_{12} + s_{1113}\sigma_{13} + \\
s_{1121}\sigma_{21} + s_{1122}\sigma_{22} + s_{1123}\sigma_{23} + \\
s_{1131}\sigma_{31} + s_{1132}\sigma_{32} + s_{1133}\sigma_{33}.
\] (8)

The stress and elasticity are both represented by second-rank tensors. Thus, the generalized Hooke’s Law in equation 7 represents nine equations, each with nine added compliance terms. \(s_{ijkl}\) is a fourth-rank tensor with 81 terms, relating each strain component to every stress component.

For many purposes in solid state physics, it is more convenient to define the stiffness as the inverse of the strain: \(c = \frac{1}{s}\). \(c\) is also a fourth-rank tensor, such that:

\[
\sigma_{ij} = c_{ijkl}\epsilon_{kl}.
\] (9)

This is a more easily interpreted equation, since the strain is a consequence of the applied stress, and \(c_{ijkl}\) is analogous to the spring constant \(k\) in the simplest version of Hooke’s Law for a spring displaced from equilibrium: \(F_{\text{spring}} = -k\Delta x\).

2. Elasticity Tensor for Isotropic Materials

The tensor \(c_{ijkl}\) may be reduced to a 6x6 matrix in the case of a uniaxial stress, since, for such a stress, the off-diagonal elements of the stress tensor obey \(\sigma_{ij} = \sigma_{ji}\), implying that:

\[
c_{ijkl} = c_{jikl}.
\] (10)

Likewise, the uniaxial nature of the stress means that the off-diagonal elements of the strain tensor will obey \(\epsilon_{kl} = \epsilon_{lk}\), implying that:

\[
c_{ijkl} = c_{ijlk}.
\] (11)

These two relations imply that only 36 elements of the fourth-rank stiffness tensor are independent, and these may be expressed in a 6x6 matrix:
This matrix $c_{ij}$ contains the full set of information regarding axial and shear stress and strain. Elements with subscript $i$ ranging from 1 to 3 indicate components of the stress acting along an axis, while elements with subscript $i$ ranging from 4 to 6 indicate shear stress. Likewise, elements with subscript $j$ ranging from 1 to 3 indicate strain along an axis, while elements with subscript $j$ ranging from 4 to 6 indicate shear strain. [3]

This matrix may be further simplified for an isotropic material, for which the stiffness constants are the same along the three coordinate axes. Thus:

$$c_{11} = c_{22} = c_{33}.\quad (12)$$

Because the $x$ direction corresponds to the $yz$ plane, the $y$ direction corresponds to the $xz$ plane, and the $z$ direction corresponds to the $xy$ plane, the same argument applies to the constants associated with these planes:

$$c_{12} = c_{13} = c_{23}.\quad (13)$$

By a similar logic, a shear stress acting on a coordinate plane will produce the same shear strain no matter the plane on which it acts:

$$c_{44} = c_{55} = c_{66}.\quad (14)$$

A more nuanced argument, shown in Figure 4, demonstrates that the requirement for the properties of an isotropic material to be invariant under a $180^\circ$ rotation reduces several matrix elements to zero, specifically, those representing the shear strain in a coordinate plane caused by a uniaxial stress:

$$s_{14} = s_{15} = s_{16} = s_{24} = s_{25} = s_{26} = s_{34} = s_{35} = s_{36} = 0.\quad (15)$$

The same arguments may be applied to all other elements not yet mentioned, reducing them to zero as well.
Figure 3: Symmetry argument demonstrating that invariance under a 180° rotation requires that $s_{61} = -s_{61}$ for an isotropic medium, and thus that $s_{61} = 0$. Reprinted from Auld, *Acoustic Fields and Waves in Solids, Volume I* (2015). [40]

By convention, the equivalent matrix terms are labeled according to the term with lowest index, i.e. $c_{11}$, $c_{12}$, and $c_{44}$. Because of the equalities outlined above, the stiffness matrix for an isotropic material is:

$$
c = \begin{pmatrix}
    c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\
    c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\
    c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\
    0 & 0 & 0 & c_{44} & 0 & 0 \\
    0 & 0 & 0 & 0 & c_{44} & 0 \\
    0 & 0 & 0 & 0 & 0 & c_{44}
\end{pmatrix}.
$$

(16)

Since each rank of this matrix describes all components of the strain
caused by a particular stress, we may interpret this stiffness matrix in the following way: for an isotropic material, any stress applied along an axis will cause a strain along this same axis, and two equal strains along the other axes. Any shear stress will produce a shear strain only in the direction corresponding to the shear stress.

Because, for a cubic crystal, only three stiffness terms are independent, the longitudinal modulus $c_{11}$, and the shear moduli $c_{44}$ and $c_{12}$ are of greatest interest to problems involving plane waves.

3. Christoffel Equation & Speed of Sound

For a uniform plane wave $\mathbf{K}$ with polarization $\mathbf{U}$ freely propagating through a solid, the wave equation may be expressed as:

$$(k^2 c_{ijkl} s_j s_l - \rho \omega^2 \delta_{ik}) u_k = 0 \quad (17)$$

where $k$ is the plane wave magnitude, $c_{ijkl}$ are the components of the elastic tensor, the $s$ and $u$ terms are the direction cosines for the plane wave $\mathbf{K}$ and the polarization $\mathbf{U}$, respectively, $\rho$ is the density of the material, $\omega$ is the frequency of vibrations, and $\delta_{ik}$ is the Kronecker delta function. It is useful to define the Christoffel matrix:

$$\Gamma_{ik} = \sum_{i,k=1}^{3} c_{ijkl} s_j s_l, \quad (18)$$

whose terms account for the stiffness constants of the material and the plane wave propagation direction. Because of the tensor ranks involved in defining this matrix, it has 9 terms. When the Christoffel matrix is substituted in Equation (17), we obtain the Christoffel equation.

We apply the Christoffel equation to a freely propagating plane wave induced by a uniaxial stress applied for a very short time (a good approximation of an ultrasound pulse) in an isotropic crystal. Since the Kronecker delta function in Equation (17) will be satisfied by the isotropic conditions, we may now express the Christoffel equation as:

$$k^2 \Gamma_{ik} \mathbf{u} = \rho \omega^2 \mathbf{u}. \quad (19)$$

When the Christoffel equation is expressed this way, it becomes clearer that it is an eigenvalue equation. The eigenvectors represent the speeds and directions of the plane waves.
We then assume that the plane wave propagates in the direction:

\[ \vec{s} = s_x \hat{x} + s_y \hat{y} + s_z \hat{z}. \]  

(20)

Using the stiffness tensor as previously defined for an isotropic material, we find the Christoffel matrix to be:

\[ \Gamma_{ik} = \begin{pmatrix} c_{11}s_x^2 + c_{44}(1 - s_x^2) & (c_{12} + c_{44})s_x s_y & (c_{12} + c_{44})s_x s_z \\ (c_{12} + c_{44})s_x s_y & c_{11}s_y^2 + c_{44}(1 - s_y^2) & (c_{12} + c_{44})s_y s_z \\ (c_{12} + c_{44})s_x s_z & (c_{12} + c_{44})s_y s_z & c_{11}s_z^2 + c_{44}(1 - s_z^2) \end{pmatrix} \]  

(21)

which, when substituted in the Christoffel equation, yields:

\[ k^2 \begin{pmatrix} c_{11}s_x^2 + c_{44}(1 - s_x^2) & (c_{12} + c_{44})s_x s_y & (c_{12} + c_{44})s_x s_z \\ (c_{12} + c_{44})s_x s_y & c_{11}s_y^2 + c_{44}(1 - s_y^2) & (c_{12} + c_{44})s_y s_z \\ (c_{12} + c_{44})s_x s_z & (c_{12} + c_{44})s_y s_z & c_{11}s_z^2 + c_{44}(1 - s_z^2) \end{pmatrix} \begin{pmatrix} u_x \\ u_y \\ u_z \end{pmatrix} = \rho \omega^2 \begin{pmatrix} u_x \\ u_y \\ u_z \end{pmatrix} \]  

(22)

If we assume the plane wave is propagating along only one direction, for example: \( \vec{s} = s \hat{z} \), then all terms in the matrix not dependent on \( z \) vanish, and with the definition \( v = \frac{\omega}{k} \), it is easily seen that:

\[ v = \sqrt{\frac{c_{\text{eff}}}{\rho}}, \]  

(23)

where \( c_{\text{eff}} \) is the effective elastic constant (labeled as such because it depends on both \( c_{11} \) and \( c_{44} \)). Thus, we may find the stiffness of the material along a particular direction by knowing only the density of the material and the speed of a sound wave propagating uniaxially along the direction of interest. A diagram of the sound wave orientations required to find each of these elastic constants may be seen in Figure 4.
Figure 4: Orientations of sound waves required to find each of the three independent elastic constants in a cubic crystal: the longitudinal constant $c_{11}$, and the shear constants $c_{44}$ and $c_{12}$. In this study, the ultrasound is applied longitudinally, so the softening of $c_{11}$ is observed. Reprinted from Fisk & Migliori [39] with author permission.

II. EXPERIMENTAL APPARATUS & METHODS

A. KTN Sample & Low-Temperature Apparatus

This study is performed on a single-crystal [100] cut KTN 8\% sample grown by Lynn A. Boatner at Oakridge National Labs. Transducers are glued to either end of the sample so that ultrasound pulses may be sent through longitudinally, and the crystal is placed in a sample holder shown in Figure 8, where the electric field is applied across the crystal transversely. This sample holder is mounted at one end of a long, hollow metal tube, which has the input and output for the ultrasound and the input for the temperature controller at its opposite end. Also at this end is the valve and the hose used for achieving a vacuum throughout the metal tube, including within the sample holder. Before taking measurements, the vacuum pump is used to achieve a $\approx 10\text{mTorr}$ vacuum in the metal tube, and then the tube is filled with helium, which is used as the gas for heat exchange. The tube is sometimes pumped and filled with helium again to prevent sparking at high
During measurements, the sample holder is mounted on a 50 liter liquid nitrogen tank using an improvised Dewar adapter. After the desired voltage is applied across the sample, the sample holder is gradually lowered into the liquid nitrogen, while the temperature is monitored with the temperature controller, and the rate of change of temperature is kept under $3K$ per minute to obtain a representative number of data points for each temperature.$^\dagger$ While the sample cools, a program written by Kuo Lu in IGOR Pro records data for temperature, amplitude of ultrasound, phase of ultrasound, a mirrored version of amplitude of ultrasound (for when monitoring attenuation is more convenient than monitoring amplitude), and phase of ultrasound shifted by $90^\circ$ (see section II.C for details). Once the sample has been cooled close to the temperature of liquid $N_2$ ($77K$), the liquid $N_2$ tank is put under a vacuum to further cool the sample, usually to $65K$.

Once data has been taken for the duration of the cooling process, another

$^\dagger$Since complete cooling and warming of the sample often takes several hours, sometimes the sample is left overnight, usually while warming. This slows and sometimes temporarily halts the temperature change, but does not affect data.
data set is obtained while the sample is warming. First, the vacuum is let out of the $N_2$ tank, and then the sample holder is slowly lifted out of the nitrogen. The temperature rate of change still does not exceed $3K$ per minute.

B. Electronics

A Stanford Research Systems SG382 signal generator is used to generate ultrasound of frequency $50MHz$ for regular field measurements, and frequency $34MHz$ for reversed field polarity measurements. The ultrasound is sent along two different paths: one is used for the probe signal (the signal sent to the sample - to “probe” it), and the other will be used for the reference signal. To generate the probe signal, a pulse width modulator divides the ultrasound into $1\mu s$ long pulses with a frequency of $10kHz$. The pulses of ultrasound are then sent to the sample, and the echoes from the sample are sent to a preamplifier. The amplified signal is sent to a power splitter with two outputs: one is the unaltered input, and the other is the input altered with a shift of $90^\circ$ (see section II.C for a detailed explanation). To generate the reference signal, the unaltered ultrasound signal from the SG382 is sent to an attenuator set at $-16dBm$, and then to a power splitter identical to that used for the probe signal. One detector then measures the relative ultrasound amplitude and phase of the probe signal, and the other detector measures the relative amplitude and phase of the shifted signal. The two detectors thus provide the in-phase and quadrature components of the phase gain (see section II.C for more detail). A schematic of all the electronics described thus far may be seen in Figure 6.

The detectors are based on a design created by Grossman et al. for ultrasound pulse-echo measurements.\cite{38} The homodyne principle for signal processing (i.e. the probe and reference signals are derived from the same

\footnote{For data runs with a $500V$ or greater potential applied across the sample, the electronics are disconnected, the field is applied, and the sample is then cooled. Then, the field is turned off and data is taken only for the warming of the sample. This is to avoid destroying electronics, and since the sample retains polarization while in the ferroelectric phase, the data is unaltered.}

\footnote{The sample was taken out of the holder for maintenance before the reversed field polarity measurements were taken. When the transducers were remounted, the resonance of the system (i.e. KTN sample, transducers, glue, etc.) changed. After testing a wide range of frequencies, $34MHz$ was selected because of its strong first echo, the property of greatest interest for measurement.}
source) is used instead of the traditional heterodyne approach, due to the relative simplicity of the homodyne setup. The design is based on the Analog Device Inc. AD8302 gain and phase detector microchip. This chip has a high sensitivity of $-60$ dBm, according to manufacturer specification. Due to the weakness of the echo signal coming from the receiving transducer, this sensitivity is desirable.

These amplitudes and phases are sent to a Harshaw boxcar averager, which ensures that measurements are taken uniformly and consistently. Outputs from the boxcar averager are sent to analog oscilloscopes so the phase and amplitude of the echoes may be monitored while data is taken. The boxcar averager also outputs to a National Instruments digitizer, which provides data to the program in IGOR Pro. The gate on the boxcar averager is set to take measurements upon the first echo at the receiving transducer. See section II.C for details on this measurement selection.

Data for amplitudes $A_1$ and $A_2$ (mirrored amplitude), phases $\phi_0$ and $\phi_{90}$ and temperature are processed by an IGOR Pro script written by Kuo Lu. Two graphs are then produced: one with $A_1$ and $A_2$ plotted versus temperature, and one with $\phi_0$ and $\phi_{90}$ plotted versus temperature. Example graphs of unprocessed data are shown in Figure 9 and Figure 10 (only $A_1$ is shown in these graphs, as $A_2$ is merely a mirrored version of $A_1$). In Figure 11, an oscilloscope display shows the unprocessed measurements of both transducers, as well as the gate of the boxcar averager, and the phase of the ultrasound pulses.

### C. Data Processing

A large number of data points are collected, so the phase and amplitude curves appear as smooth trends. To process the phase data shown in Figure
Figure 7: Realization of electronics diagram in Figure 6: 1) Stanford Research Systems SG382 signal generator, 2) Box containing pulse-width modulator → probe → phase detector outputs, 3) Harshaw boxcar averager, 4) Tektronix analog oscilloscopes, 5) Conductus LTC-10 temperature controller. Note: An additional function generator is shown beneath the temperature controller, but it is used to communicate with the computer program only, and it doesn’t send signals to the probe.

Figure 8: Sample Holder: 1) Valve & hose for vacuum pumping, 2) input / output for pulse-echo, 3) input for temperature controller, 4) sample mounted at end of metal tube. The connection between the sample holder and DC voltage source is not pictured.
Figure 9: Sample unprocessed amplitude and phase (in-phase and quadrature components) data plotted versus temperature. Large dips / peaks in the amplitude data and dramatic changes in the rate of phase gain are associated with phase transitions (see Figure 10 for a closer analysis). Note that, as the crystal realigns to states of lower symmetry, the ultrasound amplitude is attenuated significantly, and the phase gain increases much more quickly.

9 and Figure 10, straight line segments from the 0 and 90 degree phase curves must be alternated so that the absolute value of the phase gain for every temperature is obtained. The maxima and minima of the phase curves must be avoided, because, near the continuous phase transitions, smaller ultrasound phase oscillations occur, which must be visible in the processed data. We associate these repeatable smaller oscillations with phase transitions. These segments are then joined to show total phase gain with respect to temperature, with the slopes of these segments set so they always show increasing phase with decreasing temperature. This is because the material softens as it undergoes structural phase transitions, and its speed of sound therefore decreases. The inverse relationship between phase gain and speed of sound change is discussed in future paragraphs.

In the graphs shown, phase is labeled with arbitrary units. To show phase gain, the AD8302 detectors output oscillating voltages with a peak of just

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Phase transitions must be inferred from the data rather than directly observed because ultrasound does not provide a direct way to measure the transitions. Ferroelectric phase transitions are often observed by dielectric constant measurements, though a more direct way to observe structural transitions is by single-crystal x-ray diffraction.
Figure 10: A closer look at the graph in Figure 9 near the transition temperatures, showing the amplitude and phase behavior associated with different phase transitions. From previous work by DiAntonio and Pilgrim [23], the phase transitions should be expected to occur roughly at the temperatures indicated here.

Figure 11: Unprocessed signals shown on an oscilloscope. Channel 1 (yellow) is from the transducer which sends the pulse (note the very large first amplitude pulse), channel 2 (blue) is from the receiving transducer, channel 3 (green) shows the gate (note that it is set at the first received echo), and channel 4 (purple) shows the phase of the ultrasound.
above 4V. Considering that one full voltage oscillation corresponds to a phase gain of $2\pi$ radians, we may obtain the phase gain corresponding to a particular change in voltage by simply taking a straight line section of one of the phase curves with a known gain (e.g. $\frac{\pi}{8}$ radians), and measuring the absolute value of the slope of this line. In the data presented, phase gain is shown in degrees, and the method described gives a voltage / gain relationship of $0.047 \frac{V}{\text{degrees}}$. During phase gain data processing, all data points of the phase gain curve are divided by 0.047 to display phase gain in degrees. When the detector oscillations representing phase gain reach an amplitude smaller than $\approx 3V$, the straight line method described above becomes difficult to follow, due to the shortening of the straight segments of the phase curves, in addition to oscillation patterns that often leave little to no straight sections to manually process. A method outlined by Toulouse and Launay [42] is then used to determine the echo’s relative phase by comparing the probe signal’s in-phase and quadrature components with respect to the reference signal. Since the two phase curves already represent both of these components, the following method is used:

$$\phi_{\text{echo}} = \arctan(\frac{\phi_0}{\phi_{90}}) \times \frac{180}{\pi}. \quad (24)$$

This method also gives the sign of the phase gain, which is important due to the phase gain reversal that occurs past the transition temperatures. This arctangent method is always employed before the last transition temperature so that the phase gain reversal after the last transition is displayed accurately. This phase gain reversal signifies the material is approaching its final structure, wherein its speed of sound will reach a steady state.

The phase gain data must then be processed to show the relative speed of sound change in the material. Assuming that the length of the sample does not change during the entire procedure (the sample exhibits electrostriction, but the magnitude of this effect is negligible), the phase gain of the constant frequency ultrasound signal may be entirely attributed to a change of the speed of sound in the material. The relative speed of sound change may then be found by a simple relationship to the relative phase gain:

$$\frac{\Delta v}{v_0} = -\frac{\Delta \phi}{\phi_0}, \quad (25)$$

where the left side of the equation represents relative speed of sound change with $v_0$ being the speed of sound in the material at room temperature.
(which is measured on a digital oscilloscope to be $7383 \pm 13 \text{m/s}$), and the right side of the equation represents relative phase gain with $\phi_0$ being the total phase gain across the sample at room temperature. A positive phase gain signifies a decrease in the speed of sound, since a gain in phase indicates a greater number of complete oscillations are required to traverse the sample. Positive phase gain is seen as the material approaches its transitions and softens, while negative phase gain is seen after the material has reached its ferroelectric phase, and the crystal phase transitions have ceased. $\phi_0$ may be found easily by taking the length of the sample, which is measured with an electronic caliper as $9.10 \pm 0.01 \text{mm}$, and dividing it by the wavelength $\lambda$ of the ultrasound. To find $\lambda$, the definition $v_0 = \lambda f$ may be used. For example, a $50 \text{MHz}$ ultrasound wave in this sample has wavelength $\lambda = \frac{\lambda}{f} = \frac{7383 \text{m}}{50,000,000 \text{Hz}} = 1.447 \times 10^{-4} \text{m}$. Then, $\phi_0$ (in degrees) is $\frac{9.10 \times 10^{-3} \text{m}}{1.447 \times 10^{-4} \text{m}} \times 360 = 22,180$ degrees. To convert phase gain to relative speed of sound change, all values of the finished phase gain curve are divided by $-\phi_0$.

The major reason the first echo is chosen for data collection is that this measurement makes for efficient data processing. Other echoes sensed by the receiving transducer may also be used for measurement, and will result in more precise phase gain data, but will require much more intensive processing. For example, if the 3rd echo at the receiving transducer is chosen (where the ultrasound has made 5 complete trips across the sample), the phase gain across the sample will be 5 times as great as when the 1st echo is chosen. This means that $\phi_0$ will have 5 times the value, but also that the phase gain will increase 5 times more quickly. Because the detectors will only output a periodic signal of just above 4V (peak, as seen in Figure 9 and Figure 10), this means the phase curves seen in these graphs will oscillate with 5 times the frequency, and many more straight line segments will have to be individually processed and added in order to obtain phase gain. Due to the increased sensitivity of this method of phase gain processing, future work may include closer investigation of particular phenomena explored in section III.
III. DATA & ANALYSIS

All data was collected with ultrasound applied to the sample along the [100] direction, and the electric field applied transversely. For a more complete analysis of the sample’s behavior, three electric field orientations were used. The following table shows the data collected, arranged by orientation of electric field with respect to the sample, range of applied voltages, and start and end dates for the data collections:

<table>
<thead>
<tr>
<th>E Field Orientation</th>
<th>$V_{\text{min}}$</th>
<th>$V_{\text{max}}$</th>
<th>Start Date</th>
<th>End Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regular (Summer)</td>
<td>0V</td>
<td>550V$^\dagger$</td>
<td>6/12/18</td>
<td>7/17/18</td>
</tr>
<tr>
<td>Regular (Fall)</td>
<td>0V</td>
<td>1700V</td>
<td>9/6/18</td>
<td>11/22/18</td>
</tr>
<tr>
<td>Reversed Polarity</td>
<td>50V</td>
<td>2500V</td>
<td>12/5/18</td>
<td>3/22/19</td>
</tr>
<tr>
<td>90° Flip</td>
<td>0V</td>
<td>1200V</td>
<td>4/3/19</td>
<td>5/14/19</td>
</tr>
</tbody>
</table>

A. Voltage-Dependent $T_C$ Change

As applied voltage increases past a certain threshold, all transition temperatures appear to decrease$^{**}$ changing more slowly as the voltage increases past this threshold. This is seen in both amplitude and speed of sound data trends. The $T_C$ change per added voltage is most significant in between 50V and 150V, seen in Figure 17. This $T_C$ decrease is observed in both warming and cooling data sets. This at first appears inconsistent with the theory in section I.A.3, which predicts that, as the energy of the crystal decreases with increased alignment, greater thermal energy would be required to scatter the

$^\dagger$Data was collected in the summer with the DC power supply set above 700V (with a maximum of 2500V), but the field was later found to be grounded for these higher voltage runs. Above 550V, the trends level off suddenly, and the summer data bears little to no resemblance to the fall data, which was collected with the correct voltages. Thus, any data from the summer with voltage nominally above 550V, we ignore. Since the sample’s residual polarization does not change much at high voltages (see section III.D), this confusion has likely had negligible effect on the data.

$^{**}$Because transitions are inferred rather than observed (see section II.C), claims of observed $T_C$ changes are supported by a visible temperature shift of the entire phase and amplitude trends, as well as a shift in the phase and amplitude characteristics shown in Figure 9 that appear to signify the onset of transitions.
ordered polar nanoregions. However, a possible fulfillment of this prediction is seen in section III.D.1.

Previous work on the perovskite relaxor $PbTiO_3$ found that an electric field in the direction of spontaneous polarization favors the ferroelectric phase, and increases the temperature of the ferroelectric-paraelectric transition, while a field applied in the opposite direction of spontaneous polarization has the opposite effect. [43] This data may then have an explanation in terms of the glassy behavior discussed in section I.A.4. Previous work has also shown that varying the composition of $Ba(Ti_{1-x}Zr_x)O_3$ ceramics changes whether transition temperatures increase or decrease with applied DC electric fields. [44] In this study, ceramics with lower concentrations of Zr ($x=0.21$) were shown to have increasing $T_C$ with increased fields, and ceramics with higher concentrations of Zr ($x=0.42$) were shown to have decreasing $T_C$ with increased electric fields. The authors considered as a possible explanation that, as Zr is added, the potential well decreases. This is consistent with the behavior of KTN. Its potential well decreases as Nb ions are substituted for the larger Ta ions. As the potential well decreases, less thermal motion should be required to scatter the electric order in the crystal, which corresponds to lower transition temperatures. Our sample is of a high Ta concentration, so the decreased transition temperatures we observe as electric field increases may be expected in light of this previous research.

B. Relaxation Time

Both sound and amplitude data appear to demonstrate a long-term relaxation of the sample’s polarization. Comparisons of sound and amplitude curves from the summer and fall are shown in Figure 12. It may be seen that the 0V curves from the fall more closely resemble the mid-range voltage curves from the summer (i.e. between 100V and 150V) than the 0V curves from the summer. The sample was subjected to a maximum voltage of 550V on July 16, 2018, and left at room temperature until fall data taking began with a 0V run on September 6. Despite the sample’s 52 day-long rest at $\approx 200K$ above its Curie point, it appears to have retained noticeable electric polarization. This finding appears to reflect hysteresis in the sample, though the hysteresis loop of ferroelectrics shrinks with increasing temperature, and should become a curve with zero area above the Curie point. [45] It is then surprising that this polarization exists even in the material’s paraelectric phase. This may indicate that the material has an electrically metastable
phase wherein a remnant polarization induced by a threshold voltage remains above the Curie point in a setting with little disturbance (i.e. a chamber filled with helium at $\approx 100\text{mTorr}$). If it is, in fact, a metastable phase, then a slight disturbance (i.e. a weak electric field) may spontaneously return the material to its original, non-polarized state. This is observed in Figure 13, where the sample appears to return to an earlier, non-polarized state, even when simply realigned, with no field yet applied.

In previous studies, authors have induced metastable ferroelectric phases by applying high external electric fields to materials which are antiferroelectric. [46] [47] However, these studies consider the temperature range of the antiferroelectric phase only, and not the paraelectric phase.

It does not appear that substantial work exists detailing the existence of a metastable ferroelectric phase existing within a material’s paraelectric temperature range.

C. Dual Peak

One immediately observable phenomena is the splitting of the peak shown in Figure 14. As is seen in the complete amplitude trend up to $\approx 250 K$ in Figure 9, this dual peak is the first significant attenuation the sample experiences, and occurs very near the expected $T_{C1}$. Additionally, the shoulder (labeled “1” in Figure 14) that increases to meet and eventually overtake the other peak occurs at a higher temperature. Thus, an electric field induces an augmentation of the very first precursor effect which occurs a few Kelvin above the first expected transition temperature. Figure 15 shows a possible interpretation of each peak, and the reasons for their dramatic dependence on applied voltage.

Figure 15 also shows that the amplitude of both peaks significantly decreases when higher voltages are applied.

D. Coercive Field

There are several phenomena which allow us to approximate the coercive field of the sample (see section I.A.3 for theory regarding the coercive field), above which enough of the nanoregions are ordered along the same axis that they tend to keep each other aligned. The energy of this alignment may prohibit thermal motion from scattering the dipole alignment entirely.
Figure 12: Speed of sound and amplitude data demonstrating the sample’s long-relaxation time. The 0V data set taken on September 6, 2018 shows characteristics of data sets taken with lower-mid voltages across the sample, and has little resemblance to the 0V data set taken on June 28, 2018. All data shows that the 0V Fall trend falls at temperatures in between those of the 100V and 150V runs done during the summer. Additionally, both parts of the dual peak are prominent in the amplitude graph for the 0V Fall run, while the 0V summer run shows only one strong peak with a shoulder. This prominence of both parts of the dual peak resembles lower-mid voltage runs from the summer.
Figure 13: The sample’s metastable polarization appears to vanish with very slight disturbances. This may be observed mainly in that peak 1 of the dual peak recedes upon a mere reorientation of the sample. Summer reference data is shown above, as well as data from the last experiment performed on the sample before its 90° reorientation. The polarization appears to be lost with no electric field yet applied. However, the amplitude trend still shows at a lower temperature range than that of the summer data, and the attenuation appears to be less dramatic. Similar behavior was also observed upon the application of -50V following the field reversal.

1. Warming vs. Cooling $T_C$ Change

The voltage-dependent $T_C$ changes have been discussed in previous sections, but there is also a transition temperature change between warming and cooling data sets collected with the same applied voltage. These changes appear suddenly at 150V, and the trend remains relatively constant for higher voltages. In general, cooling data shows the same trends at lower temperatures than warming data, but at 150V, the temperature difference between cooling and warming data trends increases by about a factor of 20 (the temperature difference jumps from $\approx 0.2K$ to $\approx 4K$). This may be seen in Figure 16. This data fits our expectations, as the data is consistent with the explanation of dipole behavior and hysteresis given in section I.A.3. A higher voltage induces greater dipole order, which can only be scattered by greater thermal motion. During cooling, the disordered sample transitions into its ferroelectric phase, while during warming, the sample must transition out of
Figure 14: Two extremes of the dual peaks, labeled 1 and 2. Peak 1 increases in magnitude, growing from a shoulder in the 0V data to a peak of larger magnitude than peak 2 in the 350V data.

its ordered ferroelectric phase. Thus, only warming runs are affected by this increased order caused by the coercive field, and the warming $T_C$ (the Curie point) are higher than the cooling $T_C$.

2. Residual Polarization

For voltages higher than 150V, the voltage-dependent transition temperature changes discussed in section III.A slow significantly (see Figure 17). The retained polarization above the Curie point discussed in III.B appears to lie approximately between the polarization caused by an applied 100V potential difference, and the polarization caused by an applied 150V potential difference. Thus, the unexpected, seemingly metastable hysteresis behavior discussed in section III.B implies that the coercive field for this sample is reached when a potential difference between 100V and 150V applied across the sample’s 9.10mm length. This corresponds to a field between approximately $110 \frac{V}{cm}$ and $165 \frac{V}{cm}$.

E. High-Field Behavior

For high electric fields (i.e. >700V), both relative speed of sound change
and attenuation of ultrasound are much less significant in magnitude. This is seen in data collections at all orientations for which the effects of these high fields were measured, but an example is shown in Figure 18. A decrease in the change of $c_{11}$ of KTN compositions in the ferroelectric phase with high electric fields (i.e. several kilovolts per centimeter) has been observed in previous work. [48]

F. Electric Field Reversal

Due to residual polarization effects which exist well above the Curie point and with no external electric field present, the polarity of the field was reversed in an attempt to return the material to its original state. These trials require further analysis, as initial data processing has produced inconclusive results (see Figure 19 for details). However, the apparently metastable polarization induced by the original field (which went up to 1700V) appeared to be lost after the first field of -50V was applied. This was observed in a similar way as for the data shown in Figure 13.

G. 90° Sample Reorientation

While the sample was in its previous two orientations, the applied field enlarged and nucleated polar regions in the material along one of the sample’s [100] axes, and then enlarged and nucleated polar regions in the opposite direction along this same axis. We now rotate the sample by 90°, and perform more measurements. Given that many of the domains were likely aligned along the axis of the previous fields, a field oriented perpendicular to the original field was utilized to exert maximum torque on the dipoles in the sample, and thus to reorient them with maximum efficiency. A diagram of this explanation may be seen in Figure 20.

Assuming the sample was in a random field state before any measurements described here were taken, this last sample orientation should be expected to produce the most immediate results at the lowest fields of any data sets, because the greatest alignment changes should take place when the domains are already aligned in a direction perpendicular to the applied field.

Data for these trials is still being processed, and the results are as of yet inconclusive. However, Figure 13 demonstrates evidence for the metastable polarization hypothesized in section III.B.
Figure 15: The red and blue curves show the amplitudes of each respective peak. Note that this graph relies on a flipped version of the amplitude curves where a positive slope represents increased attenuation. The red peak shows a significant spike in attenuation even when no electric field is present. The lattice diagrams below the graph show one possible interpretation, for which the peak that increases dramatically with applied voltage is associated with Nb oscillations parallel to the electric field, while the peak that shows little voltage dependence is associated with Nb oscillations perpendicular to the field.
Figure 16: The $T_C$ difference between warming and cooling data becomes significant at 150V. For a simple visualization of the magnitude of the $T_C$ change, the arrows compare the locations of the second dual peak for each trial.

Figure 17: Noticeable changes in peaks associated with $T_C$ occur between 100V and 150V. At 100V, the temperature difference between the major peaks is $\approx 0.2K$, while at 150V, this temperature difference jumps to $\approx 4K$, and remains large through higher voltage runs. Additionally, above 150V, the $T_C$ change associated with any given peak is smaller than the temperature changes below 150V. After the sample reaches this threshold voltage, the transition temperatures remain relatively stable.
Figure 18: Speed of sound and amplitude data demonstrating the decreased ultrasound attenuation and $c_{11}$ softening that occurs at high electric fields.
Figure 19: Speed of sound and amplitude data demonstrating the effects of a reversed electric field. Softening of $c_{11}$ increases quickly with applied field, decreases above 300V, then increases again at high fields above 900V, though this final decrease may be the typical softening seen with high fields (see Figure 18). The dual amplitude peak disappears immediately upon an applied field, and ultrasound attenuation increases, starting with increased attenuation peaks, such as the attenuation maximum at $\approx 88K$ for the 100V amplitude curve increasing to the near-total attenuation seen in the maximum at $\approx 85K$ for the 900V amplitude curve.
Figure 20: As an example of the theory discussed in section III.G, consider a crystal which has nanoregions aligned in the direction of the coercive field, $E_1$. If the field is reversed, the nanoregion realignment may be minimal, but if $E_2$ is used instead, the 90° rotation of the field results in maximum torque on the dipoles. This is experimentally accomplished by keeping the same field polarity and rotating the sample by 90°.
IV. CONCLUSIONS & FUTURE WORK

Temperature-dependent ultrasound pulse-echo measurements have been performed over several months on a KTN 8% sample for a wide variety of electric field magnitudes and three different field polarities. Phase and amplitude of ultrasound have been measured to characterize the changes in ferroelectric phase transitions as dependent upon the external DC field. Both cooling and warming data have been collected for voltages ranging from 0V - 500V, and warming data have been collected for voltages above 500V. A variety of phenomena have been observed in the attenuation and relative speed of sound change in the sample, many of which are consistent with or may be explained by existing literature. These include field-dependent $T_C$ changes, some behaviors associated with the coercive field, and the behavior of the sample under high electric fields (i.e. up to multiple kilovolts per centimeter). One phenomena not yet discussed in the literature is the possible existence of a metastable polarization that survives into the paraelectric temperature regime. This finding may be legitimized by the data’s previously discussed agreements with the existing literature.

Due to the large number of data sets collected (more than 100 total, though some of these are duplicates), future work may include further processing and analyzing of data sets obtained as part of the work detailed herein. Many of the described data trends will also require more robust theoretical and experimental efforts to be properly explained. Further research may also incorporate KTN samples with varying compositions, different ultrasound directions (e.g. transverse instead of longitudinal), and measurements with a range of DC voltages or with an AC field while the sample is in its ferroelectric phase. Single-crystal x-ray diffraction measurements may also be also be of interest.

V. ACKNOWLEDGEMENTS

I would like to thank my research advisor and principal investigator Dr. Oleksiy Svitelskiy for his continued mentorship in all facets of the learning involved in this project. I thank him for entrusting me with many aspects of
this research, including the electronics setup, experimentation, data processing, literature review, and data interpretation. I also thank him for informing me of various presentation opportunities that have given me invaluable experience.

I thank Dr. David Lee for his role as my academic advisor, and for the many ways in which he has encouraged and guided me in my study of physics, including in my various presentations of this research, and in my writing of this thesis. Thank you to Dr. Wang for the same kinds of constructive feedback, and for continual encouragement and practical advice that has helped me through the challenges of undergraduate physics study. I also thank Dr. Siaw for teaching me many of the physical principles underlying much of this research in her Materials Science course, and for her support that has been instrumental in my development as a physics student.

I also thank program director Tania Paskova for funding under National Science Foundation Division of Materials Research award #1709282, and the Gordon College Undergraduate Research Council for funding to present this work at ASME IMECE 2019 in Pittsburgh, PA.

I thank my parents and family for their support in all areas of my life, and for their unmatched love and understanding through my twenty-three years of life.
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