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ULTRASONIC ATTENUATION IN KC1

by

Robert W. Timme

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CHAPTER I

Introduction

Within the past decade, the paraelectric defect in alkali halides has been discovered and extensively investigated. The paraelectric defect is a crystal imperfection having a permanent electric dipole moment which can exist in one of several equivalent but geometrically different positions. Two types of paraelectric imperfections are known. One type is the polyatomic molecule such as OH⁻ or CN⁻ which occupies an anion vacancy in the host lattice, and the other type is the single ion such as Li⁺ or Na⁺ which occupies an off-center position in a cation vacancy.

The paraelectric defect exhibits its presence in a variety of ways. In an attempt to better understand the defect, measurements have been made on the thermal conductivity¹, anelastic relaxation², ultraviolet absorption³, dielectric susceptibility⁴, paraelectric cooling⁵, paraelastic cooling⁶, infrared spectra⁷, specific heat⁸, ultrasonic velocity and attenuation⁹, and paraelectric resonance¹⁰ properties of various pure and doped alkali halides. The results of these investigations plus the theoretical calculations of others¹¹ have produced realistic models to describe the paraelectric defect in its host lattice environment.

The investigations and calculations just mentioned gave strong evidence that the defect had not only an electric
dipole moment but an elastic tensor moment also. In other words, the defect interacted with stresses as well as with electric fields. Thus it was expected that paraelastic resonance was possible. Furthermore, a mixture of paraelectric and paraelastic resonance was expected which could be called acoustic paraelectric resonance in a rough analogy to acoustic paramagnetic resonance.

With the interesting and unexplored possibilities of paraelastic and acoustic paraelectric resonance awaiting, it was decided that this thesis problem would be to investigate the somewhat less technically complicated acoustic paraelectric resonance characteristics of the relatively well-understood KCl:Li$^+$ system.

However, briefly put, the project could not be completed at this time, primarily because an unexpectedly high acoustic attenuation was found in KCl which precluded the necessary transmission of a coherent beam of 9 GHz phonons. Therefore, the project was redirected toward achieving a better understanding of the acoustic attenuation mechanisms in KCl.

This thesis is presented in five parts. In the remainder of this first part the paraelectric and acoustic paraelectric resonance properties of KCl:Li$^+$ will be discussed in order to explain better the initial interest in this system. In the second part will be discussed the theory of acoustic attenuation in dielectric crystals with attention being given to the most probable mechanisms which may be
responsible for the acoustic attenuation observed in KCl. The third part will concern the apparatus and experimental procedures used in this investigation, and the fourth part will present the experimental data and the analysis. A fifth part will discuss preliminary measurements of the attenuation as a function of electric field at 1 GHz.

Paraelectric Resonance in KCl:Li$^+$

The paraelectric defect has been defined as having an electric dipole which can exist in one of several equivalent but geometrically different positions. These positions correspond to potential energy minima which arise from electrostatic interactions between the defect and the ions of the host crystal lattice. Because of the symmetry of the crystal, the positions of the potential wells are related by the point operations characteristic of the octahedral site point symmetry group. In each potential well, the defect can be in a state similar to that produced by a three-dimensional harmonic oscillator. Between each of the potential wells is an energy saddle point known as the energy barrier, and, if this energy barrier is of finite height, the polar imperfection can tunnel from one well to another even though it cannot surmount the barrier. The tunneling mixes the states associated with each individual potential well thus producing a splitting of the degenerate states and allowing transitions between the mixed states. A further splitting can be produced by
applying a static electric field to the crystal. With the energy levels of the imperfection now split by tunneling and the Stark effect, a microwave electric field can induce transitions between the different energy levels. This is the type of spectroscopy known as paraelectric resonance.

The specific case of the KCl:Li$^+$ system consists of the KCl host crystal with a 10 - 100 ppm concentration of Li$^+$ ions replacing the K$^+$ ions. The lithium ion is appreciably smaller than the potassium ion (1.36 Å as compared with 2.66 Å), and so fits into the potassium vacancy with room to spare. At first thought, one might expect the lithium ion to occupy the exact center of the vacancy where the electrostatic attractive forces of the six nearest-neighbor chlorine ions would exactly cancel, but this would be an unstable equilibrium point. Hence, the lithium ion is expected to lie in an off-center potential energy minimum somewhere in the cavity left by the potassium ion. The definitive work of Byer and Sack$^9$ and the calculations of Dienes et al.$^{11g}$ and Quigley and Das$^{11h}$ have shown the lithium ion to have its lowest energy minimum in a [111] direction. The electric dipole moment results from the off-center position of the lithium ion. The potassium ion vacancy has an effective negative charge centered at the on-site position while the lithium ion contributes an off-center positive charge. The net result is an electric dipole with its vector directed toward the lithium ion and a magnitude
of approximately one electronic charge times the lithium ion
displacement distance; hence, the name, the eight-<111>-di-
pole model.

Figure 1 illustrates the eight-<111>-dipole model for
the KCl:Li⁺ system. There are eight potential wells arranged
with one on each of the diagonals extending from the center
to the eight corners of a cube. The dipole thus formed by
a lithium ion in one of the potential wells can be repre-
sented by a vector along the appropriate [111] direction.
Eight dipoles are shown because in an isolated crystal the
lithium ion can exist equally well in any one of the eight
wells, and, indeed, averaged over the crystal all wells will
be populated equally.

Actually, in the tunneling approximation used here, one
cannot say the lithium ion is localized in any one of the po-
tential wells. The paraelectric entity can better be described
by a wave function made up of a linear combination of the
eight basic harmonic oscillator-type wave functions. The
basis wave functions can be represented by |j> where j ranges
from 1 to 8 corresponding to the eight dipoles of Fig. 1. In
the manner of a LCAO-MO approach, the total wave function
|Γ_k> may be written

|Γ_k> = Σ a_kj |j>

There are eight different wave functions |Γ_k> and they will
later be given the A, B, E, and T labels of group theory.
Fig. 1 The dipole positions of the 8 <111> dipole model.
The Hamiltonian describing the system can be separated into two parts; that part dealing with tunneling and that part dealing with an applied electric field.

\[ H = H(T) + H(ef) \]  

(2)

The zero point energy of the system is not of interest here and has been suppressed. What is of interest is the splitting of the energy levels caused by tunneling and external fields.

The tunneling Hamiltonian, \( H(T) \), can be expressed in matrix form using the eight individual dipole functions as a basis:

\[ H_{ij}(T) = \langle i | H(T) | j \rangle = - \]  

(3)

\[
\begin{array}{cccccccc}
|1\rangle & |2\rangle & |3\rangle & |4\rangle & |5\rangle & |6\rangle & |7\rangle & |8\rangle \\
|1\rangle & 0 & T_{71} & T_{109} & T_{71} & T_{109} & T_{180} & T_{109} \\
|2\rangle & T_{71} & 0 & T_{71} & T_{109} & T_{109} & T_{71} & T_{109} & T_{180} \\
|3\rangle & T_{109} & T_{71} & 0 & T_{71} & T_{180} & T_{109} & T_{71} & T_{109} \\
|4\rangle & T_{71} & T_{109} & T_{71} & 0 & T_{109} & T_{180} & T_{109} & T_{71} \\
|5\rangle & T_{71} & T_{109} & T_{180} & T_{109} & 0 & T_{71} & T_{109} & T_{71} \\
|6\rangle & T_{109} & T_{71} & T_{109} & T_{180} & T_{71} & 0 & T_{71} & T_{109} \\
|7\rangle & T_{180} & T_{109} & T_{71} & T_{109} & T_{71} & 0 & T_{71} & T_{71} \\
|8\rangle & T_{109} & T_{180} & T_{109} & T_{71} & T_{71} & T_{109} & T_{71} & 0 \\
\end{array}
\]

The value of the \( H_{ij}(T) \) matrix element is a function of overlap of the individual \( i \)th and \( j \)th basis functions, and is represented by the parameters \( T_{71}, T_{109}, \) or \( T_{180} \) instead of
by theoretically calculated values. The significance of the parameter subscripts is that they refer to the angles between the basis states dipole directions. As can be seen from Fig. 1, the potential wells occur at the eight corners of a cube, thus $T_{71}$ corresponds to "cube edge" tunneling, $T_{109}$ to "cube face" tunneling, and $T_{180}$ to "cube diagonal" tunneling.

The electric field Hamiltonian, $H(ef)$, can also be expressed in matrix form. $\alpha$, $\beta$, and $\gamma$ are the directional cosines of the electric field.

$$H_{ij}(ef) = \langle i | H(ef) | j \rangle = \langle i | -\hat{\mu} \cdot \hat{e} | j \rangle = -\mu \varepsilon / \sqrt{3}$$  \hspace{1cm} (4)

The Schrödinger equation can now be used to combine Equations (1), (2), (3), and (4) to obtain the homogeneous set of equations

$$\sum_{j} (H_{ij} - E_k S_{ij}) a_{kj} = 0$$  \hspace{1cm} (5)

Solution of Equation (5) for energy eigenvalues and eigenvectors
\(|r_k\rangle\) involves a set of eight simultaneous equations which can best be done numerically by a high speed computer. Since the overlap \(S\) between different basis wave functions is considered small, the \(S\) terms will not appear in the normalization factors of the wave functions or in the energy eigenvalues. With the eigenvectors determined, the intensity of the paraelectric resonance transitions between the different energy states can be calculated from

\[
I \propto \left| \langle r_j | \hat{\mu} \cdot \hat{\tau}_{ac} | r_k \rangle \right|^2
\]  

(6)

where the dipole moment operator is assumed to have the same matrix elements at the high frequency of \(\hat{\tau}_{ac}\) as for the static \(\hat{\tau}\).

The eight-\(\langle 111 \rangle\)-dipole model can be specialized by considering the relative magnitudes of the three tunneling parameters. In a physical sense, one would not expect the three parameters to be of equal value because of their exponential dependence upon the distance between potential wells arising from the overlap term and because of the position of the energy saddle point between two neighboring minima. For the \(KCl:Li^+\) system, Dienes et al. have calculated the saddle point to be along the \(\langle 100 \rangle\) directions, thus making cube edge tunneling dominant over cube face or cube diagonal tunneling. In fact, almost all investigators claim satisfactory agreement of theory and experiment by considering only cube edge tunneling for the \(KCl:Li^+\) system.
Figure 2 illustrates the energy level eigenvalues as a function of electric field applied along the three principle crystal directions. At zero applied field there is a manifold of ground states evenly spaced as a singlet ($A_{1g}$), triplet ($T_{1u}$), triplet ($T_{2g}$), and singlet ($A_{2u}$) in order of increasing energy. This manifold of states is entirely the result of the tunnel splitting, and as an electric field is applied, they become A, B, and E type states as required by symmetry. The energy levels are described by the following relations including electric field and zero field splitting.

$$\varepsilon \ // \ [100]$$

$$E_{1A1} = -2T_{71} - \left[ T_{71}^2 + \frac{1}{3} \mu^2 \varepsilon^2 \right]^{\frac{1}{2}} = -E_{2B2}$$  \hspace{1cm} (7)

$$E_{1E} = - \left[ T_{71}^2 + \frac{1}{3} \mu^2 \varepsilon^2 \right]^{\frac{1}{2}} = -E_{2E}$$  \hspace{1cm} (8)

$$E_{1B2} = 2T_{71} - \left[ T_{71}^2 + \frac{1}{3} \mu^2 \varepsilon^2 \right]^{\frac{1}{2}} = -E_{2A1}$$  \hspace{1cm} (9)

$$\varepsilon \ // \ [111]$$

$$E_{1A1} = - \left[ (3T_{71})^2 + \mu^2 \varepsilon^2 \right]^{\frac{1}{2}} = -E_{4A1}$$  \hspace{1cm} (10)

$$E_{2A1} = E_{1E} = - \left[ T_{71}^2 + \frac{1}{9} \mu^2 \varepsilon^2 \right]^{\frac{1}{2}} = -E_{3A1} = -E_{2E}$$  \hspace{1cm} (11)

$$\varepsilon \ // \ [\overline{110}]$$

$$E_{1A1} = -T_{71} - \left[ (2T_{71})^2 + \frac{2}{3} \mu^2 \varepsilon^2 \right]^{\frac{1}{2}} = -E_{3B2}$$  \hspace{1cm} (12)

$$E_{1B1} = +T_{71} - \left[ (2T_{71})^2 + \frac{2}{3} \mu^2 \varepsilon^2 \right]^{\frac{1}{2}} = -E_{3A1}$$  \hspace{1cm} (13)

$$E_{2A1} = E_{1B2} = -T_{71} = -E_{1A2} = -E_{2B2}$$  \hspace{1cm} (14)
Fig. 2 The splitting of the energy levels of the 8 <111> dipole model with cube edge tunneling.
In Figure 3 is shown the angular dependence of the iso-
frequency paraelectric resonance spectra as predicted by this
model. The curves are frequency independent provided the
\(<100>\) minimum is fixed and have the form \(1/\cos \theta\) where \(\theta\) is
the angle to a \(<100>\) direction. This angular dependence
arises from the cosine of the angle between the electric
dipole moment and the electric field. The dots with attached
error bars denote the positions of the lines observed in the
laboratory.\(^{12}\)

Several discrepancies are exhibited upon comparison of
the data with the predictions of theory, as can be seen from
Fig. 3. The following points may be made about the obser-
vations:

(1) The values of the low field transitions are in fairly
good agreement with the theoretical curve. The trans-
sitions observed along the three cubic directions are
ordered in field as expected with \(\varepsilon_{[111]} > \varepsilon_{[110]} > \varepsilon_{[100]}\).

(2) The high-field lines appearing at and near \(\varepsilon \parallel [100]\)
are not predicted.

(3) Two lines were expected for \(\varepsilon \parallel [112]\) with a field
ratio of 2:1 and an intensity ratio of 1:2, but only
one was observed.

If other investigations did not indicate that the eight-
\(<111>\>-dipole model with cube edge tunneling was correct for
KCl:Li\(^{+}\), one would tend to look for a new model on the basis
of the discrepancies listed above. However, a possible
Fig. 3 Angular dependence of isofrequency PER spectra. The solid curve represents the allowed transitions and the dots with error bars are the data points.
explanation for this apparent disagreement is the presence of internal stresses.\textsuperscript{10g,13}

The eight-\langle lll\rangle-dipole model as formulated by Gomez \textit{et al.}\textsuperscript{11i} assumes the lithium ion to be in an unstressed environment, but the real crystals on which observations are made are not ideal and so internal strains occur. Thus, the elastic moment of the defect can couple the defect to the internal stress fields and alter the paraelectric-resonance spectra from that predicted by the simpler theory. The effect of the internal strain is that it splits allowed lines and causes some formerly forbidden transitions to become observable, thereby leading in some cases to extra experimental signals and in other cases to a consolidation of two resolved lines into one broad signal.

\textbf{Acoustic Paraelectric Resonance in KCl:Li$^+$}

Acoustic paraelectric resonance has never been observed. It is, however, theoretically possible as will be discussed in the following. Simply stated, acoustic paraelectric resonance is a form of spectroscopy in which the energy levels of a paraelectric defect are split by an externally applied electric field and transitions are induced between the levels by an oscillating stress field in the form of monochromatic, coherent phonons. It has already been demonstrated that the paraelectric defect is coupled to an oscillating stress field by an experiment in which pulses of microwave energy (photons)
were absorbed by paraelectric resonance and the energy re-emitted as a heat pulse consisting of incoherent phonons.\textsuperscript{14}

The energy levels and the wave functions of the paraelectric defect are those discussed in the previous section. The first variation from regular paraelectric resonance comes with the Hamiltonian describing the interaction of the system with the phonon.

\[ H_I = -\hat{\lambda} : \hat{p} \] \hspace{1cm} (15)

The elastic tensor moment $\hat{\lambda}$ is a constant of proportionality coupling the imperfection to the stress field. It will be considered an experimental parameter in the same sense as the electric dipole moment $\hat{\mu}$ and the tunneling factor $T_{71}$. The elastic moment is a second rank tensor, but when expressed in the coordinate system of the crystal cubic axes, only the off-diagonal elements are considered because only shear stresses will split the energy levels. Furthermore, symmetry arguments require the off-diagonal elements to be equal. The interaction Hamiltonian is expressed in Equation (16) in matrix form using the eight individual dipole functions as a basis, and, as before, the overlap between different basis wave functions is considered negligible.
\[(H_I)_{ij} = \langle i| -\frac{\hbar}{\lambda} \sum_{m,n} P_{mn} \rangle_j = -\frac{\hbar}{\lambda} \sum_{m,n} \langle i| \lambda_{mn} \rangle_j P_{mn} = -\lambda \] (16)

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<td>1&gt;</td>
<td>(P_{xy} + P_{xz} + P_{yz})</td>
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<td>(P_{xy} + P_{xz} + P_{yz})</td>
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<td>8&gt;</td>
<td>(-P_{xy} - P_{xz} + P_{yz})</td>
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The interaction Hamiltonian is used to determine the intensity of the acoustic paraelectric transitions between the different energy states \(|\gamma_k\rangle\):

\[I \approx |\langle \gamma_j| H_I |\gamma_k\rangle|^2\] (17)

The externally applied electric field determines the energy level splitting and the externally introduced phonons determine the transitions, and the only limitation on the relative positions of the electric field and the direction of phonon propagation and polarization is what is physically realizable. A number of different orientations have been numerically investigated utilizing Equation (17), and the orientation with the most striking prediction is presented in Fig. 4. In this case a transverse phonon propagates along the [100] direction with its polarization along the [010]
direction, and the electric field is applied perpendicular to the phonon \( \vec{k} \) vector: in the [001] or [010] direction. As can be seen from Fig. 4, there is no field dependent transition for the field along [001], but there are such transitions for the field along [010]. This means that if the phonon had, for example, a frequency of 10 GHz, an absorption of the phonon would occur at \( \nu \epsilon / T_\gamma \) = 2 (or about 6 KV/cm) if the field were along [010], but no absorption would occur if the electric field were simply rotated by 90° to [001].

At this point one must consider the problems of a technical nature which would be encountered in an experiment. First of all, the phonon frequency must be chosen. The frequency should be high enough so that the line width is not much greater than the line position, but the frequency cannot be too high before excessive attenuation and poor transducer bonding efficiency create problems. It was decided that a phonon frequency of approximately 9 GHz was sufficiently high that a resolved, although broad, resonant absorption would be observed. Phonons could be generated in a transducer of quartz, CdS, ZnO, or thin permalloy or rare earth films and transmitted to the KCl crystal through a bond. The permalloy and rare earth transducers would be deposited directly upon the KCl thus resulting in an efficient phonon transfer, but a magnetic field would be required to tune the frequency and polarization of the phonons. The CdS and ZnO
Fig. 4. Acoustic Paraelectric Resonance. The value of electric field at which resonance occurs as a function of phonon frequency.
transducers do not require a magnetic field, but are difficult to make. Therefore, the quartz transducer was to be used and would be bonded to the KCl with a hydrocarbon or silicone grease. Unfortunately, a grease bond has been found to be very poor for transmitting transverse phonons at frequencies above about 1 GHz. A more rigid bond such as a cement or epoxy which is more efficient would break the KCl sample upon cooling because of the thermal contraction difference.

Although the case described above is perhaps the most striking test of acoustic paraelectric resonance it is not the only possibility. Figure 5 illustrates a case in which the difficulties of obtaining transverse phonons are avoided. In this case a longitudinal phonon propagates along the [111] direction and the electric field is applied along [110] or [112]. With the field along [110] and for a 10 GHz phonon, an absorption line is expected at $\frac{\mu \epsilon}{T_{71}} = 2.75$ (-8 KV/cm) with a relative intensity of about 0.5. For the field along [112] an absorption line is expected at $\frac{\mu \epsilon}{T_{71}} = 2.9$ (-9 KV/cm) with a relative intensity of about 0.3. Since the paraelectric resonance signals are quite broad, it is likely the acoustic paraelectric resonance signals would also be broad. It is conceivable the difference in signal appearance between the two field orientations would be insignificant. Thus, in this example, a comparison of data for pure KCl and Li doped KCl would be necessary for a complete test of acoustic paraelectric resonance.
Fig. 5 Acoustic Paraelectric Resonance. The value of electric field at which resonance occurs as a function of phonon frequency.
Experimental Difficulties

A 9 GHz superheterodyne spectrometer was built to test the theory of acoustic paraelectric resonance in KCl:Li$^+$. The plan was to first observe the transitions of the example illustrated in Fig. 5. The experimental technique was the standard pulse-echo type. A magnetron provided a high power microwave pulse to a reentrant coaxial cavity where a X-cut quartz transducer was located in the region of highest microwave electric field. The transducer had a 10 MHz resonant frequency and was operated at a high harmonic to produce the 9 GHz phonons. The longitudinal phonons were transmitted through a silicone grease bond to the KCl:Li$^+$ crystal which protruded through the wall of the cavity. Outside the cavity were two electrodes bracketing the sample for application of the electric field. The sample ends were polished to a flatness better than 1/10 wavelength of sodium light and to a parallelism of about 10 seconds of arc. The phonons were expected to travel down the crystal, reflect from the end, and travel back to the transducer thus providing the "echo" which would be monitored. The phonons would interact with the paraelectric defects during passage and the amount of interaction would be determined by the value of the electric field. The data would consist of a plot of echo strength versus electric field and should display an absorption type minimum at that value of electric field where the energy levels are split equal to the quantum of energy carried by the phonons.
Unfortunately, the experiment did not work. Phonons were introduced into the KCl as planned, but no echoes were observed. There was apparently a very strong acoustic attenuation at all values of electric field in both pure and doped KCl. A sample of another alkali halide, LiF, was prepared and tested. Echoes were observed and all the equipment was in perfect operating order, thus indicating the experimental technique was correct and that the problem was with the KCl. Lithium fluoride does not exhibit paraelectric resonance and so could not be used as a candidate for acoustic para-electric resonance.

A second attempt was made with KCl:Li\textsuperscript{+} at the lower frequency of 1 GHz. Another spectrometer was constructed for use at this frequency and samples prepared. The experimental technique and expectations were the same as at 9 GHz. The only difference expected would be in the shape of the resonance signal. The absorption minimum should be near zero field and very broad; in fact, the echo strength may only increase gradually with electric field as the energy levels are split apart. Again, no echoes were observed in either pure or doped KCl. It was then discovered that a heat treatment (see Chapter III) would decrease the attenuation of the phonons so that echoes could be observed. Then, an electric field dependence of the echo strength was observed. This will be discussed further in Chapter V.
Redirection

Even though an attenuation dependence upon electric field was found at 1 GHz after a special sample treatment, it was decided the project should be redirected toward obtaining a better understanding of the attenuation mechanisms of KCl. It was puzzling to find the attenuation in pure and doped KCl to be so much stronger than attenuation studies at lower frequencies would lead one to expect. Attenuation measurements as a function of frequency about 1 GHz and temperature down to 1.4°C would be taken to obtain clues to the source of the attenuation.
CHAPTER II
Theory of Acoustic Attenuation in Dielectric Crystals

The only acoustic attenuation mechanism not present in dielectric crystals is the electron-phonon interaction. All the other usual sources of phonon absorption and scattering are present, but the mechanisms considered most probably responsible for the unexpectedly large attenuation of longitudinal phonons in KCl are dislocation interactions, impurity scatterers, thermal phonon interactions, paraelectric-paraelastic defects, and mechanical effects. These attenuation mechanisms will be discussed in this chapter. The predictions of theory will be presented for later comparison with experiment.

Interaction with Dislocations

A dislocation interacts with a sound wave in three ways: it can move through the crystal with no pinning points; it can act as a damped, vibrating string between two pinning points; and, it can scatter sound waves by its own static strain field.

In an unperturbed crystal, a dislocation is sessile with its position being determined by interactions with other dislocations, the crystal potential, and various types of pinning points. A large amplitude sound wave can carry sufficient
energy to tear the dislocation from its pinning points and move it through the crystal. The resulting change in strain with the stress damps the sound wave. A typical interaction energy between a pinning point and a dislocation has been found\textsuperscript{15} to be about .05 eV. However, at any frequency above a few MHz the acoustic wave does not have the energy necessary to break the pinning points because of the very poor conversion efficiency from the microwave pulse generator to the phonon pulse in the sample. Hence, in the case under consideration here, this form of attenuation is of no consequence.

The vibrating string model of acoustic attenuation of Granato and Lücke\textsuperscript{16} has enjoyed widespread acclaim and acceptance. The dislocation is thought to be pinned at various points along its length, and the loops of the dislocation line between pinning points vibrate under the influence of the externally applied stress, the sound wave. The attenuation arises because the motion of the dislocation loop is damped, resulting in a phase lag between the displacement and the applied stress.

Solution of Granato and Lücke's vibrating string model involves a pair of simultaneous partial differential integral equations. If the stress due to the sound wave is of the form

\begin{equation}
\sigma = \sigma_0 \exp(-ax) \exp[i\omega(t - x/v)]
\end{equation} \hspace{1cm} (18)
then the solution yields an expression for the sound wave coefficient of attenuation $\alpha(\omega)$

$$
\alpha(\omega) = \frac{\Lambda^2 \delta}{2\pi v} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \frac{\omega^2}{\left[ (\omega_n^2 - \omega^2)^2 + (\omega \delta)^2 \right]}
$$

(19)

where $\delta$ is the ratio of the damping force/unit length, $B$, to the effective mass/unit length, $A$

$$
\omega_n = (2n+1) \frac{\pi}{L} \left( \frac{C}{A} \right)^{\frac{1}{2}},
$$

$C$ is the force/unit length due to the effective tension in a bowed-out dislocation

$$
\Lambda_0 = 8Gb^2/\pi^3 C,
$$

$G$ is the shear modulus

$$
\delta^2 = \pi^2 \frac{C}{A}
$$

$\Lambda$ is the dislocation density

$b$ is the Burgers vector, and

$L$ is the length of the dislocation loop.

Equation (19) can be expanded to give

$$
\alpha(\omega) = \frac{\Lambda^2 \delta L^2}{2\pi v} \left( \frac{\omega^2}{\omega_0^2} \right) \left( \frac{1}{\left[ 1 - \left( \frac{\omega}{\omega_0} \right)^2 \right]^2 + \omega^2 (\delta^2/\omega_0^4) \right)
$$

+ \sum_{n=1}^{\infty} \frac{1}{(2n+1)^6} \frac{1}{\left[ 1 - \left( \frac{\omega}{\omega_n} \right)^2 \right]^2 + \omega^2 (\delta^2/\omega_n^4) \right]}

(20)

From this one can see the zeroth term of the expansion is the most important term so that the expression for the coefficient of attenuation becomes

$$
\alpha(\omega) = \frac{\Lambda^2 \delta L^2}{2\pi v} \frac{\omega^2}{\left[ 1 - \left( \frac{\omega}{\omega_0} \right)^2 \right]^2 + \omega^2 \tau^2}
$$

(21)

where $\tau = \delta/\omega_0^2 = \frac{L^2}{\pi^2} \frac{B}{C}$. 
Note that a factor of $\Omega$ has been included in Equation (21) which does not appear in Equation (19). This is because the initial equations of motion considered the complete stress to be acting upon the dislocation. In an actual crystal the dislocations are found only along certain directions and movable only in certain planes. Thus, $\Omega$ is an orientation factor which takes into account that the resolved stress on the glide plane is less than the applied stress. Einspruch\textsuperscript{17} derived a general formula for $\Omega$, but Hirth\textsuperscript{18} presents a much simpler formula. The values of $\Omega$ for KCl according to Hirth's formula are 1/3 for longitudinal [100] phonons, 1/6 for longitudinal [110] phonons, and 0 for longitudinal [111] phonons.

There are three general ranges of frequency for Equation (21). For low frequencies such that $(\omega/\omega_0)^2 \ll 1$, $\alpha(\omega)$ becomes

$$\alpha(\omega) = \frac{\Omega\Delta_{\omega}^{\Delta L}}{2\pi V} \frac{\omega \tau}{1 + \omega^2 \tau^2}$$

which when written as $\alpha(\omega)/\omega$ has a relaxation type form with a maximum when the frequency is $\omega_m$

$$\frac{\alpha_m(\omega)}{\omega_m} = \frac{\Omega\Delta_{\omega}^{\Delta L}}{4\pi V}$$

$$\omega_m = \frac{\omega_0^2}{\dot{\alpha}} = \omega_0^2 \frac{\rho b^2}{B} = \tau^{-1}$$

Equations (23) and (24) can be true only for crystals in which the dislocation is strongly damped because only then
will \( \omega_m << \omega_o \). The measure of damping is given by \( d/\omega_o \) and overdamping occurs when \( d/\omega_o > 1 \). In the case of KCl, it has been found that the damping force per unit length, \( B \), is about \( 4 \times 10^{-4} \) dyne sec/cm\(^2\). Simple calculation then shows \( d = 500 \) GHz. A value for \( \omega_o \) is not known with certainty, but can be estimated

\[
\omega_o = \frac{\pi}{L} \left( \frac{C}{A} \right)^{1/2} = \frac{\pi}{L} \left[ \frac{2Gb^2}{b} (1 - v) \right]^{1/2} = \frac{\pi}{L} \left( \frac{G}{\rho} \right)^{1/2} \]

\[
= \frac{\pi}{10^{-4}} \left( \frac{4 \times 10^{11} \text{ dynes/cm}^2}{2 \text{ grams/cm}^3} \right)^{1/2} = 2 \text{ GHz}
\]

This shows \( d/\omega_o \gg 1 \) so that \( \omega_m << \omega_o \). In fact, Khalilob\(^1\) found a broad attenuation peak in \( \alpha(\omega)/\omega \) in KCl at approximately 100 MHz which would correspond to \( \omega_m \). For frequencies above \( \omega_m \), but still in the range \( (\omega/\omega_o)^2 << 1 \), the attenuation coefficient takes on the form

\[
\alpha(\omega) = \frac{\Omega \Delta_o \Lambda L^2}{2\pi\nu} \frac{\omega_m}{\omega_o} \left[ 1 - \left( \frac{\omega_m}{\omega_o} \right)^2 \right] \quad (25)
\]

For the other two ranges of frequency, \( \omega = \omega_o \) and \( (\omega/\omega_o)^2 \gg 1 \), the coefficient of attenuation, Equation (21), may be rewritten

\[
\alpha(\omega) = \frac{\Omega \Delta_o \Lambda L^2}{2\pi\nu} \frac{\omega_m}{\omega_o} \left[ 1 + \left( \frac{\omega_m}{\omega_o} \right)^2 \left( \frac{\omega}{\omega_o} \right)^2 \left[ 1 - \left( \frac{\omega}{\omega_o} \right)^2 \right] \right] \quad (26)
\]

In the range of \( \omega = \omega_o \), which in the case of KCl seems to stretch from 500 MHz to 10 GHz, Equation (27) becomes

\[
\alpha(\omega) = \frac{\Omega \Delta_o \Lambda L^2}{2\pi\nu} \omega_m \left[ 1 - \left( \frac{\omega_m}{\omega_o} \right)^2 \left( \frac{\omega}{\omega_o} \right)^2 + 2 \left( \frac{\omega_m}{\omega_o} \right)^2 - \left( \frac{\omega_m}{\omega_o} \right)^4 \right] \quad (27)
\]
which is to say the attenuation is practically constant. In the range of \((\omega/\omega_0)^2 >> 1\),

\[
a(\omega) = \frac{\Omega \Delta_0 L^2}{2\pi V} \frac{\omega_m}{1 + \left(\frac{\omega_m}{\omega_0}\right)^2 \left(\frac{\omega}{\omega_0}\right)^2}
\]  

(28)

The simple string model for dislocation movement is highly idealized. For example, the concept of a line energy and a dislocation mass is utilized whereas actually the energy and mass of a dislocation are not localized. The concept of a line energy leads immediately to a line tension, and nowhere has consideration been given to the difference in the line tension of an edge or screw dislocation. Nor has a distribution in dislocation loop lengths been considered. All of these assumptions and approximations have been treated by various investigators\(^{20}\), but with the exception of a few multiplicative constants the expressions for the attenuation are as outlined above.

The third way in which a dislocation produces acoustic attenuation is by scattering the sound wave with its associated strain field. The elastic strain field of the dislocation alters the crystal properties, e.g., the lattice spacing, the elastic constants, the density, in its vicinity, and these anharmonic terms lead to the interaction with the sound wave. Ziman\(^{21}\) presents a calculation in which he does a Born approximation to obtain a differential scattering cross section. He assumes a perturbation energy due to a strain
in an isotropic, continuous medium and plane wave phonon states. Although his calculation does not distinguish between longitudinal and transverse phonons and edge and screw dislocations, it should still lead to an understanding of the relative importance of this type of attenuation. He found the effective total scattering cross section of a dislocation to be \( \pi \gamma^2 b^2 / \lambda \) where \( \gamma \) is the Gruneisen constant, \( b \) the Burger's vector, and \( \lambda \) the phonon wavelength. The attenuation coefficient is related to this by

\[
\alpha = \lambda \pi \gamma^2 b^2 / \lambda
\]  

(29)

If \( \lambda = 10^6 / \text{cm}^2 \), \( \gamma = 1.6 \), \( b = 4 \times 10^{-8} \text{ cm} \), \( \lambda (1 \text{ GHz}) = 4 \times 10^{-4} \text{ cm} \), then

\[
\alpha = \pi \times 10^{-5} \text{ neper/cm} = 2.7 \times 10^{-4} \text{ dB/cm}
\]

Compare this with the value of \( \alpha \) from Equation (27) where \( \Delta_o = .4 \), \( L^2 = 10^{-8} \text{ cm}^2 \), \( v_m = 10^8 \text{ sec}^{-1} \), \( v_o = 2 \times 10^9 \text{ sec}^{-1} \), \( v = 10^9 \text{ sec}^{-1} \), and \( v = 4 \times 10^5 \text{ cm/sec} \)

\[
\alpha = 1 \text{ neper/cm} = 8.7 \text{ dB/cm}
\]

This comparison shows that in the range of concern here, 1 GHz to 10 GHz, scattering from the strain field is completely negligible. Only at very high frequencies would this elastic scattering be of interest.

Predictions

1. Equation (27) indicates the attenuation of .8 to
1.6 GHz phonons in KCl should be practically independent of frequency. \(\alpha(\omega)\) should decrease by .1% over this range which will not be detectable. Even at X-band, \(\alpha(\omega)\) should be only 6% less than at .8 GHz.

2. Because of the orientation factor, \(\Omega\), the attenuation of longitudinal phonons should have the ratio [100]:[110]:[111]:2.0:1.0:0.

3. In this frequency range, \(\alpha(\omega)\) is independent of dislocation loop length because \(\omega_m\) is proportional to \(1/L^2\). Thus, the attenuation should be the same in lithium doped KCl as in pure even though more dislocation pinning points are present.

4. The only temperature dependence enters indirectly through the damping constant, \(B\), which is constant below room temperature so that in this region \(\alpha(\omega)\) should be temperature independent.

5. The dislocation density, \(\lambda\), can be lowered by annealing at high temperature and raised by deformation or rough handling. Thus, the attenuation will be a function of sample treatment.

**Impurity Scatterers**

A point-type imperfection produces attenuation of a sound wave by elastically scattering the wave away from its initial direction of propagation. The imperfection can be an isotope, substitutional ion, interstitial, or vacancy or a conglomerate of these. The imperfection scatters sound
waves because it is a region in which the crystal properties are altered. The imperfection is to be considered a small sphere with a density and shear modulus different from the host crystal and with no internal modes to interact with the phonons. Its size may range from one Angstrom for a single ion or vacancy up to several hundred Angstroms in the case of a precipitate. Even so, its size will be small in comparison to the wavelength ($\lambda = 4000 \text{Å}$) up of the sound waves being scattered.

Scattering of this type is known as Rayleigh scattering. The scattering cross section, $S_{\text{cs}}$, as applied to a homogeneous, isotropic, continuous solid is

$$S_{\text{cs}} = \frac{3}{2\pi} \frac{\omega^4}{v^4} \left[ \frac{1}{6} \left( \frac{\delta M}{\rho} \right)^2 + \left( \frac{4}{3\pi a^3} \right)^2 \left( \frac{\delta v}{v} \right)^2 \right]$$

(30)

where $\omega$ is $2\pi$ times the phonon frequency,

$v$ is the phonon velocity in the host crystal,

$\rho$ is the density of the host crystal which is replaced,

$a$ is the radius of the scattering impurity,

$\delta M$ is the difference in mass between the impurity and the region of host crystal which it replaces, and

$\delta v$ is the change in the velocity of sound caused by the impurity.

The first term of Equation (30) results from the change in crystal density within the imperfection, and the second term results from the change in the elastic modulus of the crystal which leads to a change in the sound wave velocity.
Equation (30) is derived by Klemens\textsuperscript{22} and discussed by Ziman.\textsuperscript{21} They considered a perturbation Hamiltonian to describe the change in the crystal properties due to the defect, and with first order perturbation theory obtained a matrix element, or scattering amplitude, between the incident phonon state and the scattered phonon state. The product of the scattering amplitude squared and the density of final phonon states leads to an expression for the scattering probability which then leads to Equation (30).

The coefficient of attenuation, \(a(\omega)\), is of the form

\[
a(\omega) = \sum_i \eta_i S_{ii}^i
\]

\(\eta_i\) = density of impurity scatterers of type \(i\) because several different types of impurity scatterers can coexist within the crystal.

To obtain some idea of the relative importance of impurity scattering consider the following example of a KC\(_i\) crystal with lithium inclusions. Assume the following values which are typical:

\[v = 4 \times 10^5 \text{ cm/sec}; \quad \delta v = 25\% v\]

\[\rho = 2 \text{ grams/cm}^3; \quad \delta \rho = 1.5 \text{ grams/cm}^3\]

\[a = 50 \text{ Å} = 5 \times 10^{-7} \text{ cm}; \quad \frac{4}{3} \pi a^3 = 5 \times 10^{-19} \text{ cm}^3\]

\[\delta M = \frac{4}{3} \pi a^3 \delta \rho = 7.5 \times 10^{-19} \text{ grams/cm}^3\]

Thus,

\[a = \eta \omega^4 x 4.6 \times 10^{-61}\]

The density of inclusions is open to question, but if all
the lithium in a crystal of 100 ppm doped KCl were to precipitate into these 100 Å diameter inclusions, then there would be approximately $10^{13}$/cm$^3$. In this situation

$$\alpha = 10^{-8} \text{ nepers/cm} = 10^{-7} \text{ dB/cm for } \nu = 1 \text{ GHz}$$

$$\alpha = 10^{-4} \text{ nepers/cm} = 10^{-3} \text{ dB/cm for } \nu = 10 \text{ GHz}.$$  

Predictions

1. Attenuation due to impurity scatterers is completely negligible in the frequency range of 0.5 GHz to 10 GHz. Even though the attenuation has a fourth power dependence upon frequency, it is still below the detectable limits.

**Thermal Phonon Interactions**

Acoustic attenuation due to interactions with thermal phonons has to be considered differently at low and high temperatures. At low temperatures, up to about 0.1 $\theta_D$, there are few thermal phonons and interactions among them are neglected. The attenuation of a sound wave may be pictured as an inelastic three particle collision process in which a sound wave phonon collides with a thermal phonon resulting in a final thermal phonon. At high temperatures, above about 1/2 $\theta_D$, there are many thermal phonons and they interact with each other so frequently that their lifetime is shortened to the point that they do not exist sufficiently long to "see" a sound wave. Hence, the simple three phonon collision picture is no longer applicable, and one must consider the interaction
of a sound wave with an ensemble of thermal phonons.

The low temperature acoustic attenuation was first investigated by Landau and Rumer.\textsuperscript{23} They calculated the matrix elements between acoustic and thermal phonons by considering the coupling between modes due to the anharmonic terms in the elastic lattice energy. Their calculations have been checked and embellished by several other investigators\textsuperscript{24}, all of whom agree on a \( \omega T^4 \) dependence and on a similar, but not identical, set of accompanying numerical constants.

The calculation of Landau and Rumer does not apply to a real crystal (with dispersion) in as straightforward a manner as could be desired, because although a transverse acoustic phonon could interact with any mode thermal phonon, a longitudinal acoustic phonon could not due to energy and momentum conservation requirements. This would lead to a prediction that the coefficient of attenuation of longitudinal acoustic waves would not be a function of temperature, but this is not the case as found experimentally. To cure this problem, the other investigators\textsuperscript{24} considered the thermal phonon to have a finite lifetime, and, thus, through the Heisenberg uncertainty principle, the phonon would have a somewhat undefined energy and momentum. The selection rules for mode interaction were thereby relaxed and longitudinal acoustic phonons could collide with the thermal phonons.

The expression for the coefficient of attenuation of a longitudinal phonon derived by Maris\textsuperscript{24a} is given in Equation
(32) for a numerical example:

\[
\alpha (\omega, T) = \frac{2 \pi F^2 k^4}{60 \rho \nu_l \hbar \frac{3}{2}} \omega T^4 \left[ \frac{\pi}{2} - \tan^{-1} \frac{32 \omega k^2 T^2 a^2}{\hbar^2 \nu_l^2} \right] 
\]

where \( F \) is an average of the third order elastic constants,
\( \tau \) is the thermal phonon lifetime,
\( a \) is the lattice constant,
\( \nu_l \) is the velocity of propagation, and the other symbols are as usual.

In the case of KCl, \( \rho = 2 \) grams/cm\(^3\), \( F = 3 \times 10^{12} \) dynes/cm\(^2\),
\( \tau = 2 \times 10^{-10} \) sec, \( a = 4 \times 10^{-8} \) cm, and \( \nu_l = 4.5 \times 10^5 \) cm/sec,
3.9 \( \times 10^5 \) cm/sec, and 3.6 \( \times 10^5 \) cm/sec for the [100], [110],
and [111] directions respectively. The value of \( F \) is admittedly only an estimate but it is based upon experimental values\(^{25} \) of the third order elastic constants of KCl and
is of the same order of magnitude as values found for single crystal quartz by Maris. \( F \) is treated as a constant, independent of the direction of propagation of the sound wave, but actually it will vary somewhat like the velocity from one direction to another. Since \( \alpha \) depends so very strongly upon the velocity, any orientational change in \( F \) will most likely be swamped. The value of the thermal phonon lifetime was obtained from the relation \( \kappa = C_v \nu^2 \tau / 3 \) where the thermal conductivity, \( \kappa \), was taken from Ref. (1e) and the specific heat, \( C_v \), was taken from Ref. (8b). Using the above values in Equation (32) one obtains
\[ \alpha_{[100]} = 0.3 \times 10^{-15} \omega T^4 \]
\[ \alpha_{[110]} = 1.2 \times 10^{-15} \omega T^4 \]
\[ \alpha_{[111]} = 2.5 \times 10^{-15} \omega T^4 \]  
(33)

For \( \omega = 2\pi \times 10^9 \) cyc/sec, and \( T = 20^\circ \text{K} \), an order of magnitude value for the acoustic attenuation is

\[ \alpha_{[100]} = 0.29 \text{ nepers/cm} = 2.5 \text{ dB/cm} \]
\[ \alpha_{[110]} = 1.23 \text{ nepers/cm} = 11 \text{ dB/cm} \]
\[ \alpha_{[111]} = 2.56 \text{ nepers/cm} = 22 \text{ dB/cm} \]

It should be realized that the \( \omega T^4 \) dependence of the attenuation is valid only over a limited range. At very low temperatures, \( \tau \) is very long and, accordingly, the thermal phonon energy is better defined which results in a smaller coupling with the sound wave and a smaller attenuation. This is exhibited by Equation (32) when the argument of the arctan term becomes sufficiently large that the expansion, arctan \( x \rightarrow \pi/2 - 1/x \), may be made. Equation (32) becomes

\[ \alpha(T) = \frac{\pi^2 F^2 k^2}{20 \rho^3 v^8 \hbar^2} \frac{T^2}{\tau} \]  
(34)

Equation (34) explains why, in some crystals\(^{26} \), a dependence of \( \alpha \) upon temperature is greater than the fourth power since the thermal phonon lifetime has a variable power dependence. A crystal with a large impurity or defect concentration may never alter its \( \omega T^4 \) dependence in this low temperature range because the impurity scattering and not thermal phonon-thermal phonon interactions will determine
the thermal phonon lifetime.

In the high temperature regime above $1/2 \theta_D$, the acousti-
castic attenuation is calculated from a thermodynamic approach. The sound wave is treated as an externally applied stress which is only slowly changing. The accompanying strain within the crystal modulates the elastic properties of the crystal, and through the anharmonic terms modulates the population and energies of the thermal phonons. Thus, an effective temperature difference is created between groups of phonons at different points along the wavelength of the sound wave. The groups of phonons then interact with each other in order to approach a new equilibrium. The Boltzmann equation is used to calculate the rate at which the sound wave loses energy to the thermal phonon ensemble.

This is an outline of the rigorous calculations performed by several investigators. Most of this theory has been limited to the temperature range such that the thermal phonon lifetime is very much shorter than the sound wave period. A more general calculation, utilizing thermodynamic Green's functions and complete with Feynman diagrams, has been carried out by Maris. His solution can be generalized to either the high or low temperature limit. The expression for the attenuation coefficient in the high temperature limit is

$$\alpha(\omega, T) = \frac{3\pi}{4} \frac{\frac{2}{\kappa}}{\rho \frac{3}{V}} \omega^2 \frac{T}{\theta_D}$$

where all the symbols are as defined previously. Equation (35) takes on a temperature independent form when $T \geq \theta_D$
because then the thermal conductivity, $\kappa$, is inversely proportional to temperature since the specific heat, $C_V$, is constant and the thermal phonon lifetime, $\tau$, goes as $1/T$.

For the specific case of KC$_l$ at 1 GHz and 100$^\circ$K with $\kappa = 1.9 \times 10^5$ ergs/cm sec degree (from Lange's Handbook of Chemistry, 1956), and $F$, $\rho$, and $v$ as before, Equation (35) gives:

$$\alpha = 8.4 \text{ nepers/cm} = 73 \text{ dB/cm}$$

Predictions

1. Equation (32) indicates an $\omega T^4$ dependence of the acoustic attenuation up to about $0.1 \theta_D$ ($-25^\circ$K). The arctan term in Equation (32) should never become large enough for Equation (32) to approach Equation (34) for KC$_l$. Only at about 5$^\circ$K where $\tau$ is largest might the temperature dependence be somewhat greater than the fourth power, but the size of this deviation would be inversely proportional to the impurity concentration in the crystal.

2. In the $\omega T^4$ region, the attenuation should have an orientational dependence ratio of


3. In the high temperature region above $1/2 \theta_D$ ($-100^\circ$K), the attenuation should have an $\omega^2 T^n$ dependence where $n$ decreases gradually from one at 100$^\circ$K to zero above $\theta_D$. Equation (35) predicts such a high attenuation at room temperature that only in thin films will it be possible to measure it except at low MHz frequencies.
Paraelectric-Paraelastic Scattering Centers

The paraelectric-paraelastic defect, Li\textsuperscript{+} in KCl, can interact with a sound wave in two ways (not counting Rayleigh scattering which has already been considered). The phonons of the sound wave can be absorbed by a resonant process and by a relaxation process. However, in the absence of an externally applied field, the levels between which an allowed resonant absorption could occur are separated by approximately 40 GHz. Since this energy is far above that of the 1 GHz phonons whose attenuation is being observed, there will be no loss of a resonant nature.

Nor will there be a relaxation type loss at zero field because of the following argument. In this sense the term "relaxation loss" refers to the energy absorbed from the phonon by the defect as it tries to reorient in phase with the sound wave but cannot because of a finite reorientation or "relaxation" time. The loss is proportional to the imaginary component of the elastic susceptibility which is due to the phase lag of the defect dipole behind the oscillating field. The elastic susceptibility, $\chi$, is given by the expression

$$\chi = N \frac{d}{dp} \langle \lambda \rangle$$  \hspace{1cm} (36)

where $N$ is the concentration of defects, $P$ is the oscillating stress of the sound wave, and $\langle \lambda \rangle$ is the thermal average of the elastic tensor moment of an individual defect.
This expression can be expanded in terms of the \( N \) individual defects

\[
\chi = N \frac{d}{dP} \sum_{i=1}^{8} f_i(\varepsilon, P, T) \langle \lambda \rangle_i
\]  

(37)

where the summation is over the eight possible states of the defect, \( f_i(\varepsilon, P, T) \) is the population distribution function for the \( i \)th state as a function of temperature and externally applied electric field and stress, and \( \langle \lambda \rangle_i \) is the expectation value of the elastic tensor moment of the \( i \)th state. Equation (37) can be rewritten

\[
\chi = N \sum_{i=1}^{8} \left\{ \frac{d}{dP} f_i(\varepsilon, P, T) \right\} \langle \lambda \rangle_i + f_i(\varepsilon, P, T) \frac{d}{dP} \langle \lambda \rangle_i
\]  

(38)

In the absence of fields, the first term in Equation (38) disappears because the probability of any state being occupied is determined only by a Boltzmann distribution which contains energy differences due just to tunnel splitting in the first approximation. This then leaves

\[
\chi = N \sum_{i=1}^{8} f_i(\varepsilon=0, P, T) \frac{d}{dP} \langle \lambda \rangle_i
\]  

(39)

which can be evaluated by taking the derivative of the matrix elements of the operator \( \lambda \) utilizing the zero field states perturbed by a very small stress. When this is done, one finds the expression for \( \chi \) is completely real. This means there is no out of phase component and the power absorbed is thus zero.

Dispersive effects, i.e., changes in the velocity of
propagation, should be expected because of the real $\chi$. This has in fact been observed for OH$^-$ in KCl by Brugger et al.$^{2b}$ and for the Li$^+$ in KCl by Byer and Sack.$^9$ Their observations indicate that the maximum $\delta v/v$ for either defect in concentrations of about 100 ppm is on the order of 0.1% at 4°K. Although their measurements were made at low megacycle frequencies, their values of $\delta v/v$ should be approximately the same at 1 GHz because the dispersion is independent of frequency when far away from the resonance condition.

As expected from Equation (39), the magnitude of the dispersive effect should be related to the orientation of the sound wave. The measured values of $\delta v/v$ from the two experiments just mentioned are in complete agreement with theory in that the Li$^+$ defect has the greatest change along [111] and the least along [100] while the OH$^-$ defect has exactly the opposite.

The preceding discussion has considered only the ideal case in which the paraelectric-paraelastic defect exists in a stress-free, field-free environment. However, as mentioned in Chapter I, it has been necessary to assume internal stresses in order to explain the observations of paraelectric resonance. Therefore, to be consistent, consideration should also be given here to the effects of internal stresses.

The internal stresses will split the energy levels apart just as an externally applied stress would, but there will be a distribution of magnitudes and directions throughout
the crystal. Because of this distribution in their environment, all the defects will never interact at the same time in the same manner with any sound wave. The splitting of the energy levels by the internal stresses will allow absorption as well as extra dispersion of the sound wave.

The calculation of the transitions causing a resonant type absorption of the sound wave will be discussed in Chapter V. It will be found that the attenuation has a cubic frequency dependence and an inverse temperature dependence. As already seen in Chapter I there is an orientation dependence also. For example, a sound wave propagating along [100] will not interact with a Li\(^+\) defect whether there is an external or internal stress or electric field. And, of course, the attenuation will be directly proportional to the concentration of the paraelectric-paraelastic defect.

The internal stresses will also cause a nonresonant type absorption because the first term in Equation (38) will no longer vanish, but instead will have real and imaginary parts. The imaginary component which will be discussed further in Chapter V will attenuate the sound wave with a linear dependence upon frequency and an inverse dependence upon temperature. Again, there should be no attenuation for the [100] orientation and there should be a direct proportionality to the concentration of the defect.

The dispersion, observable as \(\delta v/v\), will be greater with internal stress fields because both terms of Equation (38)
will contribute as well as the resonant type transitions. The orientation and concentration dependencies will be the same as discussed above.

Predictions

1. In the absence of internal stresses there should be no attenuation of the sound wave. There should be a change in the velocity of propagation of about 0.1% if the sound wave travels along [111] or [110] and no change along [100] if the defect is Li⁺ in KCI.

2. In the presence of internal stresses there should be attenuation of sound waves propagating along [111] and [110] in KCi:Li⁺ due to both resonant (ω³ dependence) and nonresonant (ω dependence) absorption. There should be a 1/T temperature dependence. There should also be a change in δv/v of an unknown amount. The [100] orientation should be unaffected.

Mechanical Attenuation

The acoustic attenuation mechanisms discussed in the previous sections have all resulted from intrinsic characteristics of the crystal and its defects. In order to properly explain experimental observations, one must recognize of equal importance the extrinsic properties of the crystal, i.e., the surface roughness, parallelism of the ends, the transducer-crystal bond, etc. All of these factors will affect the observed attenuation as a function of temperature
and frequency.

The measurement of acoustic attenuation in the megacycle and higher frequency range is invariably made with the pulse-echo technique. A transducer is bonded to one end of the sample to introduce the sound wave. The wave travels the length of the crystal, reflects from the opposite end, and returns to the transducer to produce an echo. The sound wave will also reflect from the transducer end and so start another round trip, and in this way, one pulse may produce many echoes if the attenuation is sufficiently low.

In the ideal sense, the sound wave is a plane wave which moves between two perfectly flat and parallel ends of the crystal. However, if the ends are not flat, then the plane wave is distorted upon reflection and so the phase will be different along what was the wave front. When the distorted wave front returns to the transducer, a signal will be generated which is no longer sharp and well-defined. A contribution to the attenuation will result because some of the sound wave energy will be scattered and lost upon reflection and some will be lost from phase cancellation at the transducer.

In order that the degree of flatness not be a problem it is necessary that any deviation from flatness be very small in comparison to the sound wavelength. For example, if one half the end were $\lambda/4$ raised from the other half, the reflected wave would consist of two parts $\lambda/2$ out of phase.
The transducer could not produce an echo signal because the total average intensity of the sound wave striking it would be zero. A second example in which the raised half is only \( \lambda/40 \) above the other half shows the echo intensity to still be about 20% less than for a perfectly flat end.

These requirements for flatness appear rather stringent, and they are for very high frequency phonons. However, for the case of KC\( \ddot{A} \) at 1 GHz, \( \lambda = 40,000 \) A, and polishing to a flatness of \( \lambda/40 \) or 1000 A which is about one-fifth the wavelength of the sodium D lines is quite possible.

If the sample ends are flat, but not exactly parallel, an extra attenuation will be observed. In this case, the echo pattern will appear modulated, and the true attenuation will be somewhat confused. This can be seen from a typical echo pattern in Fig. 6. The intensity of the \( n^{\text{th}} \) echo will be given by

\[
I_n = I_0 f(t_n) e^{-\alpha t_n}
\]  

(40)

where the true attenuation coefficient, \( \alpha \), is only part of the experimental attenuation coefficient, \( \alpha_{\exp} \)

\[
\alpha_{\exp} = \frac{1}{t_n} \ln \frac{I_0}{I_n} = \alpha - \frac{1}{t_n} \ln f(t_n)
\]  

(41)

The modulating function is a sinusoidal function with a period \( T \)

\[
f(t_n) = |\cos 2\pi \frac{t_n}{T}|
\]

This can be rewritten in terms of the number of the echo
Fig. 6 Modulation of the echo pattern due to nonparallel ends.

Fig. 7 The sound wave is reflected from the sample end at twice the angle of nonparallelism and thus returns to the transducer at an angle.
being measured, \( n \), and the number of echoes in one period of modulation, \( N \),
\[
\cos 2\pi \frac{t_n}{T} = \cos 2\pi \frac{n}{N}
\]
so that Equation (41) becomes
\[
a_{\text{exp}} = \frac{v}{x_n} \ln \frac{I_0}{I_n} = a - \frac{v}{x_n} \ln |\cos 2\pi \frac{n}{N}| \tag{42}
\]
where \( x_n \) is the round trip distance the sound wave must travel to produce the \( n \)th echo.

Since no modulation, or at best, only a small modulation is desired, then \( N \) must be large. This requires the angle of nonparallelism to be small. Figure 7 is a vastly exaggerated sketch which aids in relating \( N \) to the deviation from parallelism. As can be seen from the figure
\[
\eta \lambda = d \sin 2\theta
\]
where \( d \) is the diameter of the transducer and \( \eta \) is the fraction of a wavelength phase difference due to the nonparallelism angle, \( \theta \). The number of echoes in a period of modulation, \( N \), is \( 1/\eta \). Thus
\[
\frac{\lambda}{N} = d2\theta \quad \text{or} \quad N = \frac{\lambda}{2d\theta} = \frac{v\pi}{d\omega \theta}
\]
The effect of nonparallelism upon the attenuation can now be written
\[
a_{\text{exp}} = a - \frac{v}{x_n} \ln |\cos 2\omega d \frac{n}{v}| \tag{43}
\]
A numerical analysis indicates that for KCl at 1 GHz, an angle of nonparallelism of 10 seconds of arc \( (0.50 \times 10^{-4} \)
radian), and a 0.1" diameter transducer, the echo pattern would have a modulation wavelength of 16 echoes with a minimum every eighth echo. It can be seen that a near-modulation free echo pattern would require a very high degree of polishing.

The bond between the transducer and the crystal can be a source of additional attenuation. The most efficient bonds are those in which the transducer is in intimate contact with the crystal as is the case with a vapor-deposited transducer. However, the grease bond between a small quartz transducer and the crystal is of concern here. The grease layer must be as thin as possible so that the attenuation due to the grease is minimal. The is a frequency dependent factor although little about it is known except that the attenuation is higher at higher frequencies.

If the transducer is not parallel to the crystal, i.e., the grease forms a ramp between the two, then the effect will be a loss of energy from phase cancellation along the transducer. This will not lead to a modulation of the echo pattern, but only to a constant extra loss of intensity for each echo. The effect is the same as if the initial intensity, $I_0$, were reduced. An extra multiplicative term of $\cos^2 \frac{\phi}{2}$ must be included in Equation (40) where $\phi$ is the phase angle difference across the transducer face generated by the grease ramp angle $\beta$.

$$\phi = \frac{\omega d \sin 2\beta}{V_{gr}} = \frac{2\omega \beta d}{V_{gr}}$$
Thus,
\[ \cos^2 \frac{\phi}{2} = \cos^2 \frac{\omega \beta d}{v_{gr}} \]  \hspace{1cm} (44)

where \( v_{gr} \) is the velocity of propagation of the sound wave in the grease. Thus, the intensity of each echo will be reduced approximately 25% if the bond angle is only 10 sec of arc. With this corrective term, Equation (40) now becomes
\[ I_n = I_0 (\cos^2 \frac{\phi}{2}) f(t_n) e^{-\alpha t_n} \]  \hspace{1cm} (45)

but the measured attenuation remains as given by Equation (43).

It is not expected that this factor will reduce the strength of the echo pattern too much simply because it should not be too difficult to insure that the transducer is flat against the crystal before starting to take attenuation data. One can use a monochromatic light source to provide a means of looking for interference fringes which would be indicative of a grease ramp or Newton's rings which would be indicative of a high or low grease point.

Another factor to consider is that a crystal with flat, parallel ends and a good transducer bond may be positioned in the cavity in such a way that the electric field is at an angle with the transducer face. This would be identical to the case just discussed and the additional term is
\[ \cos^2 \frac{\phi}{2} = \cos^2 \frac{\omega \gamma d}{v_o} \]

where \( v_o \) is the free space velocity of the sound wave and \( \gamma \)
is the angle between the electric field and the transducer. However, it can be seen that at 1 GHz, the angle $\gamma$ can be on the order of several degrees and the effect upon the echo pattern will be completely negligible.

Predictions

1. The crystal surfaces should be polished to a flatness such that the deviation is only about $\lambda/40$, otherwise a considerable loss of signal strength will result and few echoes will be observed. This loss increases with frequency because of the polishing limitations.

2. A lack of parallelism, bond quality, and poor crystal positioning leads to a signal pattern described by

$$I_n = I_o \cos^2 \frac{\omega d}{V_{GR}} \cos^2 \frac{\omega y d}{V_o} \cos \frac{2 \omega d}{V} n e^{-\alpha n}$$  \hspace{1cm} (47)

Thus the measured attenuation differs from the true attenuation by a factor involving the frequency as indicated by Equation (43).

3. The temperature does not enter in any way which is strictly accountable. Such qualities as the bond probably do vary in some unknown way with the temperature.
CHAPTER III
Apparatus and Experimental Procedure

The purpose of this investigation was to obtain a better understanding of the acoustic attenuation in the gigahertz range in KCl. To accomplish this, the attenuation was studied as a function of frequency, temperature, sample orientation, and sample purity. A study was also made of the effects of sample treatment upon the attenuation and the dislocation density. The experimental techniques and equipment utilized will be discussed in the following.

Attenuation Measurements

The pulse-echo technique was used to obtain a measure of the attenuation. In this technique a pulse of coherent phonons is introduced to the sample by a transducer. The phonons propagate through the sample to the opposite end from which they reflect and return to the transducer end. Upon reaching the transducer end a small portion is reconverted to photons which form the echo and the remainder start another round trip. In this way a series of many echoes may be produced by one initial pulse. A measurement of the relative intensities of the echoes will yield a value for the acoustic attenuation.

A schematic of the microwave spectrometer is presented in Fig. 8. The power oscillator (Airborne Instruments
Fig. 8 The microwave pulse-echo spectrometer
Laboratory Type 124) provides the pulsed microwave source. Each pulse is about ten microseconds in length and the repetition rate is about 1000 pulses per second although the pulse width and repetition rate are adjustable over a wide range. The pulses of microwave energy are channeled to a microwave resonant cavity in a variable temperature cryostat by a pair of diode switches. The diode switches (Microwave Associates) and the power oscillator are synchronized by a pair of pulse generators (E-H Research Laboratory Model 131) such that Switch 1 opens for a brief period during the power oscillator pulse while Switch 2 remains closed providing 20 dB isolation for the spectrometer. After the initial pulse terminates Switch 2 opens and allows the microwave echoes to travel through a precision attenuator (Arra TT Line Attenuator) to the superheterodyne mixer (Sage Laboratory Model 2523). The main purposes of the switches are to protect the spectrometer from the high power pulses (~10 watts) and to provide a well shaped pulse for the transducer. The pulse from the power oscillator has a relatively slow rise and fall time, and the switch, being rather fast, can clip a much sharper pulse of about 2 microseconds width from the center of the initial pulse and allow it to pass to the cavity. Switch 3 (Arra Model 7752B) is synchronized with Switch 2 to provide an extra 50 dB isolation from the initial pulse.

The variable precision attenuator is a very necessary item because it allows the measurement of the difference
in intensity of the echoes. The attenuator was carefully calibrated over the range of frequencies that measurements were taken.

The detection system had to be a superheterodyne type receiver because of the very low signal strength. The local oscillator (General Radio Type 1218A) provided a continuous source of microwaves 60 MHz different from the pulsed source. The 60 MHz output of the mixer was amplified by an i.f. strip amplifier (government surplus) and displayed on an oscilloscope (Hewlett Packard 175A) which was synchronized with the initial power pulse.

The echo pattern on the oscilloscope display was not linear in amplitude hence attenuation measurements obtained from a direct reading of echoes of different size were incorrect. Attenuation measurements were made by reducing the signal strength with the precision variable attenuator until the \((n-1)^{th}\) echo was the size on the oscilloscope that the \(n^{th}\) echo had been. The amount of attenuation inserted could then be read and a value in dB/cm was obtained from a knowledge of the sample length. The temporal spacing of the echoes was equal to twice the length of the crystal divided by the velocity of propagation. From a measure of this spacing and a knowledge of the length of the crystal, a value of the velocity could thus be obtained. The value of the velocity measured by this technique is only relative unless the change in crystal length as a function of temperature is known, and
in any case, the accuracy is limited to several percent be-
cause of the pulse width.

A dual trace vertical amplifier (HP 1750A) was used with
the oscilloscope to allow simultaneous display of the echo
pattern and a small portion of the initial pulse reflected
from the cavity. Straight detection of the reflected initial
pulse was accomplished with a 20 dB directional coupler (Narda
Coaxial Directional Coupler) and a coax detector. Simple
monitoring of the reflected initial pulse was very useful
in adjusting the power oscillator and cavity to the resonant
frequency of the transducer. Once this was done the super-
heterodyne receiver system could be adjusted for optimum
echo pattern display.

A display scanner (HP 1782A) was used in conjunction
with the oscilloscope to record the echo pattern on a X-Y
recorder (HP/Moseley 7005B). The echo pattern could be re-
corded just as it appeared on the oscilloscope or, alternative-
ly, the amplitude of any one point, e.g., the peak of an echo,
could be recorded versus the electric field applied across
the sample.

The electric field across the sample could be continu-
ously varied from zero to 75 KV/cm by a 0 - 25 KV power
supply (Spellmann Model Lab 20) which was driven by a vari-
able speed control (Ratiotrol Motor Speed Control Model R12).
The sample with a typical thickness of 1/3 cm was bracketed
by the electrodes between which the potential was applied.
Two different re-entrant type coaxial cavities were used in this experiment. One was a variable frequency cavity used to take data as a function of frequency and temperature and the other was of a fixed frequency to take data as a function of electric field. Ordinarily when one designs a microwave cavity, an attempt is made to obtain as high a cavity Q as possible because the high Q enhances the change in the sample susceptibility which is the signal. However, this is not the case here. A high Q is desirable in order to have a high electric field at the piezoelectric transducer, but to have a very sharp phonon pulse, the electric field must have a rapid rise and decay. This means a low Q. Thus a compromise between the two considerations must be made. A pulse of approximately 2 μsec duration with a ¼ μsec rise and fall time is desired. This rise time corresponds to an effective band width of 2 MHz so that at 1 GHz this calls for a Q of about 500. From a practical standpoint this Q is very easy to achieve for a coax cavity by using a low grade of unpolished brass.

The variable frequency cavity is sketched in Fig. 9. It was designed for the microwave range of .8 to 1.8 GHz. In addition to the desired frequency range, the main design consideration was that it must fit inside the variable temperature dewar system. This required the outer dimension to be less than 1.2". The formula for the resonant wavelength in terms of the cavity dimensions is\(^\text{29}\)
Fig. 9
Variable Frequency Cavity

rigid coax  ->  cavity support

coupling loop

movable end wall

Ge thermometer

transducer

sample
\[ \lambda = 2\pi \left[ z_o \frac{\rho_2^2}{\delta^2} \ln \frac{\rho_2}{\rho_1} \right]^{\frac{1}{2}} \]  

(48)

where \( z_o \) is the inner length of the cavity,
\( \delta \) is the spacing between the end of the center conductor and the end of the cavity,
\( \rho_1 \) is the radius of the center conductor, and
\( \rho_2 \) is the inner radius of the outer conductor.

There exists an infinity of solutions to Equation (48), but the outer size limitation and the decision to fix \( \delta \) to the thickness of the quartz transducer made the choice of dimensions easier. The dimensions decided upon are

\[ \delta = .010" \]
\[ \rho_1 = .125" \]
\[ \rho_2 = .500" \]
\[ z_o = 1" \text{ to } 5" \text{ depending upon frequency} \]

The cavity outer conductor was made from a piece of 1" I.D. brass tubing with 1/16" walls. The ends were trenched so that end pieces could be screwed on, thus producing an easy disassembly. The center conductor was soldered to the top end plate and was of the proper length that \( \delta \) was maintained.

The cavity length, \( z_o \), was altered by the sliding cavity end wall which maintained electrical contact with inner and outer conductors by phosphor-bronze "fingers". The stainless steel rigid coax line which coupled the microwave spectrometer with the cavity served the double purpose of moving the sliding cavity end wall. When the sliding end wall was full forward,
$Z_0 = 1''$, and $\nu = 1.6$ GHz, $Q = 40$; when the wall was to the rear, $Z_0 = 5''$, and $\nu = 0.7$ GHz, $Q = 500$.

One can see that the frequency range, $0.7$ to $1.6$ GHz, was somewhat different than desired, but still acceptable. The reason is that Equation (48) does not account for perturbations such as the holes in the end plates for transducer insertion and microwave coupling or for the sliding electrical contact. One also notices the very low $Q$ at the high frequency end. This turned out to be a serious problem because the electric field at the transducer was too low to produce a large amplitude sound wave. Thus, at the higher frequencies in this cavity, the echo pattern was quite weak.

A fixed frequency cavity designed by Goodell$^{30}$ was used for the electric field measurements. These measurements were conducted at $1.4^\circ$K and $4.2^\circ$K in a different and larger dewar system than the variable frequency measurements. The samples used were longer and the net attenuation of the echoes thereby greater, hence a stronger sound wave was needed. The fixed frequency cavity had a $Q$ of about 1000 which would solve this problem and only require a wider pulse. The fixed frequency cavity had a resonant frequency at $1.1$ GHz which was tunable over a $100$ MHz range. For details of dimensions, see Reference 30.

The variable temperature dewar system was the Andonian Associates Modular Helium Dewar MHD-3L-40N with variable temperature tail section 0-25/7M-200. This system provides
a continuously adjustable temperature from pumped liquid helium to above room temperature with a few hundredths of a degree accuracy. The temperature was measured in the range of interest, 1.4°K to -50°K by a sealed, gas-filled, germanium thermometer purchased also from Andonian. The thermometer was calibrated at 77°K, 4.2°K, 2.1°K (He\textsubscript{\lambda}), and 1.4°K and a standard Ge thermometer response curve fitted to these points. The calibration is probably only accurate to ±1°K, but closer accuracy is not critical in this case. The output of the thermometer was included in a bridge circuit consisting of a potentiometer (Leeds & Northrup Type K-3), a standard cell, and a galvanometer (Fluke Model 840A). An indication from the thermometer that the temperature was dropping below its set-point would cause the bridge circuit to activate a power supply (Kepco Model CK-36) which would provide a measured current to the heater in the Andonian variable temperature tail section, and this would return the temperature to its set-point.

The dewar system used in the electric field measurements consisted of a set of double glass dewars (Mueller Scientific Glass) and a large vacuum pump (NRC 30 cfm rotary). Liquid helium provided the 4.2°K operating temperature and pumped liquid helium, the 1.4°K.

Sample Preparations

Two types of KCl were purchased from Harshaw Chemical
Company for this experiment. They were KC\textsubscript{1} doped with 100 ppm Li and KC\textsubscript{1} of optical grade purity. "Optical grade purity" means that impurity concentrations are sufficiently low so that no absorption spectra was observed from the ultraviolet to the infrared. Paraelectric resonance spectra taken on both types of KC\textsubscript{1} showed the lithium concentration in pure KC\textsubscript{1} to be more than three orders of magnitude lower than in the doped KC\textsubscript{1}.

The samples used for the frequency and temperature measurements were approximately 1/3 cm x 1/3 cm x 1 cm in size. The samples used in the electric field measurements were about 1/3 cm x 1/3 cm x 2\hspace{0.17em}\text{2}/\hspace{0.17em}2 cm. The orientations used were with the length along [100] and sides along [001] and [010]; length along [110] and sides along [001] and [\overline{1}10]; and length along [111] and sides along [\overline{1}0] and [\overline{1}22]. At least two samples were prepared and measured for each orientation, each type KC\textsubscript{1}, and each of the two parts of the experiment.

The KC\textsubscript{1} was received in boule form and had to be shaped to the desired dimensions. Since KC\textsubscript{1} cleaves very easily along the \{100\} planes, the [100] samples were simply obtained by cleavage. The other orientations were cut on a diamond saw, and the various directions were determined geometrically from the cleavage planes. This method was accurate in determining the orientations to within a half degree.
As discussed in Chapter II, the flatness and parallelism of the sample ends are very important. In most experiments such as this, the samples are polished by one of several companies who specialize in polishing crystals to laser tolerance. However, no one would agree to attempt this with KCl because of its softness, hygroscopic nature, and tendency for easy cleavage. Hence, each sample was polished in the laboratory.

A polishing jig was constructed and is shown in Fig. 10. The jig body was of aluminum and supported by three precision, carbide tipped micrometer heads equally spaced on a 2" radius. The KCl sample was held by two teflon set screws in a reversible brass mounting plate which was securely screwed to a center sliding brass piston. The sliding piston was hand-lapped for a very close tolerance fit in the jig body. A thin coating of Lubriplate grease reduced any "play" to practically zero. The sliding piston was free to move under gravity feed within limits defined by a lock-ring. This insured a constant pressure of the sample upon the polishing surface.

To polish a sample, the jig with the sample in position was placed upon the polishing surface. The micrometers were adjusted to polish the crystal end to the desired angle with the axis. For this experiment the ends were polished to be perpendicular to the axis. The three micrometer heads and the sample were all in contact with the polishing surface,
and the carbide tips of the micrometers were worn away just as was the sample surface, but only very slowly because of their greater hardness. When the sample end was sufficiently flat, the mounting plate holding the sample was turned over in the sliding piston and the other end polished flat. The mounting plate consisted of a 3/8" thick brass disc with a small "V-block" soldered into a round hold in the center. Two sides of the sample were held against the V-block by two teflon screws with footpads against the opposite sides.

After the second surface was polished flat, the ends were checked for parallelism with an autocollimator. The autocollimator used was a high precision Nikon Model 6D. It utilized dark field illumination which was especially suited for measuring small diameter, poor light reflectors. The maximum sensitivity of the autocollimator for a large, good reflector was 1/2 second of arc, but on the small, 1/3 cm x 1/3 cm, KCl samples, the maximum measurable sensitivity was approximately 10 seconds of arc. With the angle of nonparallelism determined, the micrometers on the polishing jig were adjusted so that the sample end could be repolished to the new angle. A change of .0001" on the micrometer changed the polishing angle by 7 seconds of arc. Thus, the limitation of the polishing technique was in the ability to measure the deviation from parallelism. Usually, only three adjustments were necessary to obtain a KCl sample polished to within 10 seconds of arc.
The polishing surface which gave the greatest degree of success was a special polishing pad of 3 mil thick polyester impregnated with 3 micron grade aluminum oxide (made by 3M Company). This pad was pressed flat against a 1/2" thick pane of PPG plate glass especially selected for flatness. The polishing jig was moved by hand in a circular motion across the dry polishing pad with frequent pauses necessary to flush the pad clean with an isopropyl alcohol-water solution. A rotating polisher was initially used, but this did not result in scratch-free sample surfaces.

The flatness of the polished surface was measured by placing the surface against an optical flat (DoAll) and observing interference fringes under monochromatic sodium light. A typically polished sample would have zero interference fringes across its end when pressed against the flat so it was necessary to introduce a small wedge angle by slightly tilting the sample with respect to the flat. Then a fringe would appear each time the spacing between the two surfaces was a multiple of λ/2. Any deviation by the fringe from straightness was due to an irregularity in the KCl surface. The degree of flatness could be measured in this manner to at least λ/10, or approximately 500 Å.

The finishing touches to the KCl crystal could be done successfully only by wearing a surgical face mask. Otherwise, the crystal surface would become cloudy due to water absorbed from one's breath. Surgical gloves were necessary
for handling the finished sample to avoid contamination from skin oils. It was also necessary to store the finished sample in a dry box to avoid water and dust contamination of the polished surfaces.

This technique of polishing crystals has been successfully used on KCl, NaCl, LiF, and quartz. There appears to be no reason that any crystal could not be polished in this manner.

The polished KCl samples were annealed at various temperatures for different lengths of time in vacuum in order to understand why annealed samples had lower attenuation than unannealed. The samples were encapsulated in individual pyrex tubes which had been carefully purged with dry nitrogen before use.

After the annealing process the transducer was bonded to the sample. The transducer was a small disc of quartz about .1" in diameter and .01" thick. It was oriented such that the x-axis was perpendicular to the disc. In this way a microwave electric field perpendicular to the disc would produce via the piezoelectric effect a longitudinal acoustic wave along the x-axis within the quartz. The most successful bonds were made with Dow Corning 200 "grease". This grease was actually a very high viscosity silicone oil -- $10^6$ centistokes at room temperature. The best procedure for making a bond was to place a very small "dab" of the grease on the crystal surface which had just been blown clean with
compressed nitrogen. The transducer was taken from a deca-
ydronaphthalene bath, blown dry, and placed on top of the
grease spot. The transducer was then "wrung" onto the sam-
ple surface forcing any excess grease out along the edge.
A sodium lamp was used to illuminate the surface during the
last step in order that interference fringes could indicate
when the transducer was not flat against the sample.

The procedure just described is certainly not the only
way to make this bond. It is really just a technique that
worked with a fair degree of success. No one has yet been
able to refine this past the "cut-and-try" method. However,
there are certain points where some care is very beneficial.
First of all, the sample surface and transducer must be very
clean -- no dust particles. This is the reason for blowing
the sample and transducer clean with compressed nitrogen.
The building compressed air could not be used because of
moisture and oil. The transducer was cleaned of grease and
dust from past bonds by a decahydronaphthalene bath just
prior to bonding. Surgical gloves and face mask were worn
throughout the bonding procedure to protect the surfaces from
moisture and oils.

Other bonding materials were also tested. Various
greases, such as Dow Corning 33, Dow Corning silicone vac-
uum grease, Cello vacuum grease, and Nonaq grease, were tried
and the bonds were occasionally equal to, but never better
than those obtained with the DC 200 fluid. Bonds were made
with Armstrong C-7 epoxy and Devcon 5-Minute epoxy but upon cooling the sample underwent cleavage due to the stresses arising from different amounts of thermal contraction and the unyieldingness of the epoxy. Indium bonds were also tried but only with limited success. The main problem was that the indium did not adhere well to the KCl.

**Dislocation Density Determination**

The density of dislocations in the KCl samples was studied to see if there was any correlation between the polishing, the annealing, and the observed attenuation. The dislocation density was determined with the etch pit technique and by direct observation with the electron microscope.

Etch pits are small holes formed in the crystal and are very localized about the point that a dislocation intersects the surface. A simple, but correct, understanding of how an etch pit is formed requires the realization that the stress field associated with a dislocation alters slightly the chemical properties of the crystal in the vicinity of the dislocation. Hence, the proper etching solution will dissolve away some of the crystal thereby decorating the dislocation with a hole. The etch pit technique is a surface effect, i.e., it only defines dislocations penetrating the surface. It has also been shown that there is a one to one correspondence between etch pits and dislocations.³¹ Figure 11 shows a typical KCl surface with etch pits.
Fig. 11 Etch pits in a (100) KCl surface.

(approximately $10^6$ pits/cm$^2$)
Etching solutions resemble recipes more than chemical solutions. Several solutions\textsuperscript{31,32} have been discussed in the literature but the one used here was first introduced by Cook.\textsuperscript{33} A solution of propionic acid (CH$_3$CH$_2$COOH) mixed with enough BaCO$_3$ to give 1.75\% Ba by weight was the etchant. A 20 second etch time was found most satisfactory followed by a rinse in petroleum ether. The resulting etch pits in the KC$_2$ (100) plane were square and in the (111) plane were triangular thus displaying the crystal symmetry elements. The propionic acid did the actual etching, but used alone was much too rapid. The barium acted as an inhibitor. A rinse was always necessary to stop the etching action and to give well defined pits. Ethyl alcohol is often used as a rinse, but petroleum ether is better because it is not as hygroscopic. Any dissolved water in the rinse will blur the pits. Part of the study was conducted using compressed nitrogen to quickly dry the sample after the etching, thus skipping the rinse, but the resulting etch pits were not as distinct as with the fresh petroleum ether rinse. The etching solution had to be stored in clean glass containers because any impurities would result in poorly defined pits. Clean plastic tweezers were necessary to lower the sample into the solution since metal tweezers would have contaminated the solution with metal ions. After etching, the samples had to be stored in a dry box because the pits would quickly degrade from the moisture in the air.
A typical KC1 sample would be etched following carefully the procedure discussed above and the etch pits would then be observed through an optical microscope at 500 power. Some areas of the samples had more etch pits than others, hence a somewhat arbitrary decision was made as to an area representing a fair average. A picture of this area was then taken, and the number of etch pits appearing gave a dislocation density since the area covered by the picture was known. Some uncertainty also resulted from not being able to resolve and count the smallest pits or the very closely packed ones. The total certainty associated with the dislocation densities thus obtained is estimated only as an order of magnitude.

Dislocations can be observed directly with the electron microscope. The interruption to the crystal continuity caused by these defects gives rise to scattering of the incident electron beam which results in an image contrast between the disturbed area and the perfect crystal area. A dislocation, being a linear defect, will appear on a bright-field image as a dark line. The dark line does not mark the center of the dislocation, but rather will be slightly to one side. Rotation of the sample back and forth a few degrees about the diffraction angle which gives rise to the image will cause the dark line to alternate from one side to the other of the dislocation. This is a possible test of whether the dark line observed is indeed due to a dislocation. To view dislocations with the electron microscope it is
necessary that the sample be not more than several extinction distances thick. A KCl crystal of about 400 Å thickness is desirable and one about 1000 Å thick is useless.35

The following procedure was followed to prepare a sample for the electron microscope. The sample was first polished with water on a flat glass surface until it was about .002 inches thick. It was then held upright and a stream of water-ethyl alcohol (50-50) solution directed onto its flat surface from a #27 hypodermic needle. The KCl was dissolved away by the water with the alcohol acting as an inhibitor. As soon as a hole appeared in the KCl, the crystal was placed flat upon a glass slide under a low power optical microscope and the thinning was continued drop by drop of a 10% water - 90% ethyl alcohol solution. When the crystal appeared sufficiently thin, it was rinsed in pure ethyl alcohol and mounted between #150 mesh grid wires in the microscope mount. Great care had to be taken when moving the thin sample because of its softness. Even so, plastic deformation was always observed to some extent since the crystal of about 500 Å thickness cannot support itself over a gap of more than about 2 mm. This problem was most serious because any plastic deformation tended to completely alter the dislocation density.
CHAPTER IV
Experimental Data and Analysis

The Effects of Sample Treatment

The first efforts at studying interactions between phonons and defects in KCl at 1 GHz utilizing the pulse-echo technique were thwarted simply because the acoustic attenuation was too great. Only after it was discovered that annealing lowered the attenuation was the pulse-echo technique feasible. A brief study was then made to determine the optimum annealing conditions.

A number of samples were cleaved to a [100] orientation from 100 ppm lithium doped KCl, and the ends were polished flat and parallel. The samples were divided into three groups which were annealed at 200°C, 300°C, and 500°C. Each group was subdivided into five smaller subgroups which were annealed at their respective temperatures for 10, 24, 48, 72, and 96 hours. Each subgroup contained at least two samples so that there would be some indication of reproducibility. After treatment each sample was bonded one at a time to the same transducer and the acoustic attenuation tested in the fixed frequency cavity.

The lowest attenuation was found in those crystals which were annealed for 48 and 72 hours at 300°C. The 10 and 24 hour anneals showed an echo pattern with fewer echoes, i.e., more attenuation, whereas the 96 hour anneal produced no
less attenuation than the 72 hour. The attenuation in those samples which were annealed at 200°C was still high after 72 hours, but after 96 hours, it was about equivalent to the samples in the 300°C, 48 hour subgroup. No echoes were observed from the 500°C annealed samples. Closer inspection showed the polished ends of the samples to be "frosted" after treatment, even for only 10 hours. This "frosted" appearance was due to a thermal etching action. Although 500°C is still short of the KCl melting point of 770°C, the vapor pressure is apparently sufficiently high that enough sublimation occurs to ruin a highly polished surface.

The remaining 24, 48, 72, and 96 hour subgroups intended for the 500°C were rescheduled on the basis of the above to a 275°C anneal. The attenuation for these samples was found to be much the same as for the corresponding subgroups of the 300°C anneal.

These observations led to the conclusion that the lowest attenuation resulted from an annealing temperature of 275°C to 325°C for a period of 48 to 72 hours.

As stated above, these tests were initially made on [100] samples of KCl doped with 100 ppm lithium. The findings from these samples were spot-checked with [100] pure KCl, and there was complete agreement on the effects of annealing. Samples of both pure and doped KCl of the [111] orientation were also spot-checked and they were found to behave just as the [100]. However, it was found that the
attenuation in [110] pure and doped samples was apparently unaffected by the annealing and about the same as for the annealed samples of other orientations.

During the course of checking the attenuation of the samples, it was found that the moisture which condensed on the sample upon warming to room temperature severely degraded the surfaces. It was necessary to repolish each surface before using again, and then it was found that the attenuation was as high as before annealing. Further checks showed that any rough handling, including polishing, after annealing greatly reduced the benefits gained from annealing. This increase in attenuation due to handling has been observed in quartz and has been attributed to an increase in dislocations.

The Dislocation Density

The etch pit technique was used to determine the dislocation density of KCl crystals as a function of purity and treatment. Since the dislocation density is usually expressed in terms of the number of dislocations penetrating a unit area, any surface area may be selected as the reference plane. Hence, all samples were [100] orientations.

Samples were taken from pure and 100 ppm lithium doped KCl and etched. The subsequent pit counts indicated that within the degree of uncertainty accompanying this technique, there was no difference in the dislocation density as a function
of lithium concentration.

Samples were prepared and divided into groups which were then treated in several ways as is summarized in the following:

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Dislocation Density ((\text{dislocations/cm}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>on the surface</td>
</tr>
<tr>
<td>Cleaved</td>
<td>(10^6)</td>
</tr>
<tr>
<td>Cleaved, 300°C anneal for 72 hours</td>
<td>(10^6)</td>
</tr>
<tr>
<td>Cleaved, polished</td>
<td>very disturbed</td>
</tr>
<tr>
<td>Cleaved, polished, and 300°C anneal for 72 hours</td>
<td>very disturbed</td>
</tr>
<tr>
<td>Cut</td>
<td>very disturbed</td>
</tr>
</tbody>
</table>

In the first column the treatment given the samples is described. In the second column the dislocation density of the surface after treatment is listed, and in the third column the dislocation density of a surface at some depth is given. This was obtained by dissolving away the outer surfaces with water, thereby revealing a surface descriptive of the interior of the crystal. The dislocation densities are only given as order of magnitude quantities because these are the averages of several samples, each of which differed one from another by a factor of 4 or 5.

It was immediately noticed that cleavage produced about \(10^6\) dislocations/cm\(^2\). This was surprising since it is commonly thought cleavage does not produce many dislocations.
However, the surfaces which were polished or cut with the diamond saw were very disturbed. The surfaces were of such poor quality that individual etch pits were indistinguishable from general erosion around scratches and gouges. Even what initially appeared to be the best polished surfaces to the naked eye were quite badly scratched and eroded after etching. The polished and cut surfaces were also decorated with what appeared to be vertical cleavage planes which were initiated by the polishing or cutting. These markings had a density of approximately $5 \times 10^6$/cm$^2$, and by slow dissolution and frequent re-etching, it was determined that they extended no deeper than about .05 cm into the crystal. The dislocation from cleavage and the other disturbed areas from cutting and polishing did not extend more than .02 cm into the crystal. Thus, it can be seen that the sample treatment affects only the outer layers of a crystal and has little effect internally.

However, it was observed that dislocations did move about during the annealing period even though they did not decrease in number. This movement was quite noticeable because in a cleaved but unannealed sample, there were no etch pits within about .005 cm from the edge, possibly because dislocations closer to the edge tended to "relax" out. In the freshly annealed samples the etch pits were up to 25% closer to the edge in general, and in some cases, right up to the edge. One should expect the dislocations to move at 300°C. In
Chapter II, the interaction energy between a dislocation and a pinning point was stated as about .05 eV. In this case 300°C also corresponds to a thermal energy of .05 eV and should break simple pinnings due to point defects.

Dislocations in KCl were also studied with the electron microscope. There was some trouble in obtaining samples sufficiently thin. On most samples only the area near the edge was thin enough and even that was somewhat obscured by "clouds" or "fog" which may have been due to a surface contamination. Immediately noticed was the necessity of using a very low intensity electron beam to avoid disturbing the sample. Too intense a beam first caused a movement of the "clouds" and finally complete vaporization of that sample area. This was a result of localized heating which could not be conducted away quickly enough.

When an intermediate beam intensity was used, many hundreds of hair-like dark lines could be seen "wiggling" away from the hottest area. The average length of the lines was about 100 Å. These lines may have been caused by dislocations which were motivated by the high temperature to move on the \{110\} glide planes.

All the samples looked very much alike regardless of their various treatment. No dislocation counts could be obtained because of the movement every time the beam intensity was high enough to allow observation.
The Attenuation as a Function of Frequency

The attenuation of acoustic phonons in KCl was studied as a function of frequency between .83 GHz and 1.55 GHz. These measurements were made at 1.4°K and at 5°K with identical results. The measurements were also made on pure samples and samples doped with 100 ppm lithium, and the attenuation was found to be independent of lithium doping. The variation of transducer bond quality from one sample to another precludes any firm statements as to the absolute magnitudes of the attenuation as a function of orientation. However, in a relative sense, it appeared that a sound wave propagating along [100] suffered about twice the attenuation as a sound wave propagating along [110] or [111]. All [100] and [111] samples in which the attenuation was measured were annealed at 300°C for 72 hours. Some [110] samples were annealed and some were not, but the attenuation was the same in either case.

There was a considerable spread in the measured values of attenuation as a function of frequency in each sample. This variation is apparent in Fig. 12. Each of the three panels of Fig. 12 contains measured values of the attenuation in a sample of the designated orientation. For no sample were the measured values closely enough gathered to warrant drawing with certainty a single line representing the attenuation as a function of frequency. A solid line has been drawn through the values in Fig. 12 which
Fig. 12 The acoustic attenuation as a function of frequency
only indicates a general trend. The general slope of the line could easily be argued, but the point of importance is that there appears to be an increase of the attenuation with frequency.

The dashed lines are almost independent of frequency, and they represent an average of the triangular marks which are the measured values of attenuation corrected for non-parallelism of the sample ends. In Chapter II the effects of nonparallelism of the sample ends were discussed with the derivation of Equation (43):

\[ a_{\text{true}} = a_{\text{exp}} + \frac{8.686}{x_n} \ln|\cos \frac{2dn\theta}{v} \omega| \text{(dB/cm)} \]  

(43)

In Chapter III the sample polishing technique was discussed and the limitation on obtaining parallelism was stated to be 10" of arc. Hence, this value of \( \theta \) was placed in Equation (43) and the true attenuation calculated. The result is the dashed line in each panel of Fig. 12 which shows the attenuation to be essentially independent of frequency from .8 to 1.6 GHz.

The Attenuation as a Function of Temperature

The attenuation of acoustic phonons in KCl was studied as a function of temperature between 1.4°C and 40°C. These measurements were made at 1.11 GHz on both pure and lithium doped samples. The attenuation over this temperature range was found to be independent of lithium concentration. Only
samples of the [110] orientation could be used without annealing and the attenuation as a function of temperature was much the same in either the annealed or unannealed samples. The attenuation values were obtained by monitoring the difference in intensity of the first and second echoes over the temperature range. No attempt was made to correct for nonparallelism in this case because only the relative change with temperature was of interest.

The attenuation of a sound wave propagating along [110] and [111] was identical. It was temperature independent from 1.4°K to about 10°K and proportional to $T^{4.3\pm0.5}$ from about 15°K up to 27°K. Above 27°K the attenuation began to level off at a very high value. Data from a typical sample is presented in Fig. 13.

The attenuation along [100] was somewhat different in that it changed from the temperature independent region to the $T^4$ realm somewhat more gradually. An example of this is shown in Fig. 14.

Discussion of the Data and Conclusions

The acoustic attenuation as a function of temperature is in rather good agreement with the theory of thermal phonon interactions. The dependence upon temperature is within the experimental uncertainty and the measured values are in general agreement with the theoretically calculated values. As observed in Figs. 13 and 14, the attenuation appears to change
Fig. 13 The acoustic attenuation as a function of temperature

$k// [111], [110]$
Fig. 14 The acoustic attenuation as a function of temperature
from a $T^4$ dependence to a temperature independence below about $15^\circ K$, but what actually occurs is that the $T^4$ component of the attenuation becomes smaller than the general background attenuation and is lost. There is no evidence of a rise in the attenuation as the temperature drops below $10^\circ K$ as predicted for the paraelectric-paraelastic scattering centers with internal stresses. Again, it may be that this contribution to the attenuation is very small and lost under the general background.

The importance of the more gradual increase of attenuation with temperature along [100] than along [110] or [111] as seen in Fig. 14 is not understood. It can not be due to a variation from the $T^4$ dependence as is allowed in the theory due to impurities because the effect has been observed to be independent of lithium concentration and characteristic only of the one orientation.

The variation of transducer bond quality was such that a determination could not be made of any orientational dependence of the attenuation in the $T^4$ range.

The attenuation was found to be a function of frequency over the range investigated for all orientations. However, it was demonstrated that the frequency variation could be entirely accounted for by the nonparallelism of the sample ends. The resulting independence of frequency is what would be expected in this range from dislocations. The indication that the attenuation was somewhat larger along [100] also is
expected from dislocation interaction theory. The attenuation was not found to be lower in doped KCl than in pure which is according to expectations. This is explainable in terms that the dislocation is so heavily damped at high frequencies that it moves more as a rigid rod rather than a vibrating line. Thus, the addition of lithium to act as pinning points does not appreciably change the slight movement of the "rigid" dislocation. In general, the background attenuation measured at 1.4°K and 5°K was in good agreement with that expected from dislocations.

There was no indication of a linear or cubic frequency dependence or a Li+ concentration dependence as predicted for the paraelectric-paraelastic scattering centers with internal stresses.

The much lower attenuation for the unannealed [110] samples than for other unannealed orientations is unexpected and unexplainable in terms of the theory considered. There was no suggestion obtained from the dislocation density study as to any effect the annealing process had except for rearranging the dislocations within the sample. It may be that the anneal treatment did remove shallow dislocation loops at the polished surfaces which could not be observed because of the general disturbance due to the polishing, but this would not explain the [110] case.

In the course of measuring the frequency and temperature dependencies of the attenuation, the velocity of
propagation was also noted. There was no detectable variation in the velocity as a function of frequency or temperature. However, there was a dependence upon lithium concentration and orientation:

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Relative velocity as a function of Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>11% slower in Li doped sample than pure</td>
</tr>
<tr>
<td>[110]</td>
<td>6% slower in Li doped sample than pure</td>
</tr>
<tr>
<td>[111]</td>
<td>No difference</td>
</tr>
</tbody>
</table>

A velocity dependence upon orientation can be expected due to a real component of the susceptibility as noted in Chapter II, but these observations are very strange for two reasons. First, the change is greatest for [100] in a lithium doped sample. This is in contrast to theory and other experimental observations. As can be seen from the theory outlined in Chapter I, a stress applied along [100] should not interact with an eight-<111>-defect. The measurements of Byer and Sack\(^9\) also show no interaction between a [100] sound wave and a Li\(^+\) defect. The velocity change reported here would be compatible with a six-<100>-defect such as OH\(^-\), but these samples show no evidence of a paraelectric resonance signal due to OH\(^-\). Secondly, the velocity changes observed are about two orders of magnitude larger than previously reported for either the Li\(^+\) or OH\(^-\) defects. Hence, the variation of velocity as a function of lithium concentration and orientation can not be explained.
This study has suggested several explanations of why the pulse-echo technique can be used at 1 GHz, but not at 10 GHz. It does not appear the large attenuation encountered at 10 GHz at liquid helium temperatures is due to dislocations or a $T^4$ thermal phonon interaction. It may possibly be that there is a very strong frequency dependence due to a Rayleigh type scattering such that it is undetectable at 1 GHz but very much in evidence at 10 GHz. However, the most probable explanation may be a combination of the cubic frequency dependence of the paraelectric-paraelastic scattering centers with internal stresses and nonparallelism effects of the sample plus a reduced transducer bond efficiency at the higher frequency.
CHAPTER V

Attenuation as a Function of Electric Field

Measurements of the acoustic attenuation as a function of electric field are not normally made in crystals because the usual attenuation mechanisms are not affected by field. However, the paraelectric defect is coupled to both the electric field and the stress field as has already been discussed. Therefore, the measurement of attenuation as a function of field is a logical extension of the usual attenuation studies, irrespective of the fact this was to have been done in the original project. Preliminary measurements were taken and will be discussed in the following.

Resonant Absorption

In resonant absorption the defect attenuates the sound wave according to

\[ P_{\text{abs}} = n_0 h\nu \frac{V}{1 + Vt} \quad (49) \]

where \( P_{\text{abs}} \) is the power absorbed by the defect from the sound wave,

\( n_0 \) is the population difference between the two energy levels when in thermal equilibrium,

\( V \) is the transition probability per unit time due to the phonon which disturbs the equilibrium condition, and
is the time the system requires to return to equilibrium.

It is through the transition probability, $V$, that the orientation dependence enters so it is instructive to look at the calculation of $V$ in a little detail. The interaction Hamiltonian has been given in Equation (15).

$$H_I = \Sigma_{ij} \lambda_{ij} P_{ij}$$  \hspace{1cm} (15)

The phonon stress tensor $P_{ij}$ can be related to the phonon strain through Hooke's law:

$$P_{ij} = \Sigma_{mn} C_{ijmn} \varepsilon_{mn}$$  \hspace{1cm} (50)

where $C_{ijmn}$ is the $ijmn$th component of the fourth rank tensorial elastic constant and is determined entirely by the host crystal independently of the paraelectric imperfection, and

$\varepsilon_{mn}$ is the $mn$th component of the phonon strain tensor.

The strain tensor is defined to be

$$\varepsilon_{mn} = \frac{1}{2} (\frac{\partial u_m}{\partial x_n} + \frac{\partial u_n}{\partial x_m})$$  \hspace{1cm} (51)

where $u_m$ is the displacement in the $m$th direction. The displacement of the lattice ions from their equilibrium position is the manifestation of the phonon as it passes through the crystal. The phonon strain may be quantized by writing the displacement in terms of phonon creation and annihilation operators.
\[ \hat{u} = \sum_{k', \ell} \sqrt{\frac{\hbar}{2MN\omega_\ell(\vec{k})}} \hat{x}_{k', \ell}(\vec{k}) [a_{k', \ell} e^{i\vec{k} \cdot \vec{r}} + a_{k', \ell}^* e^{-i\vec{k} \cdot \vec{r}}] \] (52)

where \( M \) is the mass of the ion being displaced,

\( N \) is the number of ions in the crystal,

\( \omega_\ell(\vec{k}) \) is the frequency of the phonon with wave vector \( \vec{k} \) and orientation \( \ell \),

\( a_{k', \ell} \) and \( a_{k', \ell}^* \) are, respectively, the phonon annihilation and creation operators.

With these substitutions, Equation (15) may now be written

\[ H = -\sum_{i,j,m,n} \lambda_{ij} C_{ijmn} \sum_k \frac{i}{2} (\hat{k}_n \hat{x}_m + \hat{k}_m \hat{x}_n) \sum_\ell \sqrt{\frac{\hbar}{2MN\omega_\ell(\vec{k})}} \] (53)

\[ \times (a_{k', \ell} e^{i\vec{k} \cdot \vec{r}} - a_{k', \ell}^* e^{-i\vec{k} \cdot \vec{r}}) \]

This interaction Hamiltonian used with Fermi's Golden Rule from time dependent perturbation theory gives an expression for the transition probability per unit time, \( V \),

\[ V = \frac{2\pi}{\hbar} \int \sum_\ell \rho_{\Omega \ell}(E) |H_{fi}|^2 d\Omega \] (54)

where \( \rho_{\Omega \ell}(E) \) is the density of energy states for phonons with a \( \ell \)th polarization,

\[ \rho_{\Omega \ell}(E) = \frac{V}{2\pi^2} \frac{\omega^2}{\hbar v_\ell(\vec{k})^3} \] (55)

and \( v_\ell(\vec{k}) \) is the velocity of propagation of the phonon. This form of \( \rho(E) \) assumes a Debye crystal which is reasonable if the phonon energy is not too large. \( H_{fi} \) is the matrix element of Equation (53) with the initial and final states.
Since what is of interest here is the absorption of a longitudinal sound wave passing through KCl:Li\(^+\), Equation (54) can be simplified to

\[
V = \frac{\bar{n}}{8\pi \rho v^3} \sum_{ij} |\Gamma_{\text{final}} \langle \lambda_{ij} | \Gamma_{\text{initial}} | C_{ijmn} k_{m} x_{n} | \|^2 \]  
\tag{56}
\]

where \(\bar{n}\) is the average number of phonons from the sound wave undergoing absorption by the defect and \(\rho\) is the density of the crystal. \(\bar{n}\) could also be considered as proportional to the amplitude of the sound wave. The initial and final states, \(\Gamma\), are those defined by Equation (1) and obtained by solving Equation (5).

When expressed in the coordinate system of the crystal axes, only the off-diagonal elements of the elastic tensor moment, \(\lambda_{ij}\), contribute to the energy level splitting. For this reason the diagonal elements may be suppressed and \(\lambda_{ij}\) written as

\[
\lambda_{ij} = \begin{pmatrix}
0 & \lambda_{xy} & \lambda_{xz} \\
\lambda_{xy} & 0 & \lambda_{yz} \\
\lambda_{xz} & \lambda_{yz} & 0
\end{pmatrix}
\]  
\tag{57}
\]

where \(\lambda_{xy} = \lambda_{xz} = \lambda_{yz}\). For the case of KCl, as with all cubic crystals, there are only three independent components of \(C_{ijmn}\):

\[
C_{ijmn} = \begin{pmatrix}
C_{xxxx} & C_{xxyy} & C_{xyxy} & 0 & 0 & 0 \\
C_{xxyy} & C_{xxxx} & C_{_xxxy} & 0 & 0 & 0 \\
C_{xyxy} & C_{xyxy} & C_{xxxx} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{yzyz} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{yzyz} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{yzyz}
\end{pmatrix}
\]  
\tag{58}
\]
Equation (56) may now be expressed for specific orientations of the phonon \( \hat{k} \)-vector. For example, consider the special case illustrated in Fig. 5a in which the sound wave propagates along the [111] direction with an electric field applied along [\(1\bar{1}0\)]:

\[
\hat{k} = \frac{1}{\sqrt{3}} \frac{\omega}{v} (\hat{i} + \hat{j} + \hat{k})
\]

\[
\hat{\mathbf{z}} = \hat{i} + \hat{j} + \hat{k}
\]

\[
\mathbf{v} = \frac{1}{6\pi} \frac{\omega^3 \rho_0}{\hbar v^5} C^2 \left[ \frac{\lambda_{xy}}{\lambda_{xx}} + \lambda_{yz} + \lambda_{xz} \right]^{\text{final}} \left\langle \lambda_{xy} + \lambda_{yz} + \lambda_{xz} \right\rangle^{\text{initial}}
\]

(59)

where \( C_{ijmn} \) is written in the usual Voigt notation. This expression can be recognized as essentially the same as Equation (17) in Chapter I.

The relaxation time, \( \tau \), must also be evaluated before the attenuation due to the defect is known as a function of field. The relaxation time will not be characterized as the inverse of the transition probability per unit time between only two states. The defect can relax by going through intermediate states, hence the relaxation time is the inverse sum of the \( \tau_i \)'s between all combinations of states:

\[
\frac{1}{\tau} = \sum_{i} \frac{1}{\tau_i} = \sum_{i} W_i
\]

Only the direct relaxation process will be considered as important. This will be a good assumption below about 5°C.\(^3\) The \( W_i \)'s will be calculated from Equation (54) with the expressions of Equations (53) and (55). However, the problem
is vastly more complex since account must be taken of all the possible \( \mathbf{k} \)-vector values and polarizations of the thermal phonons and the different \( v_\mathbf{k} (\mathbf{k}) \) for each \( \mathbf{k} \)-vector.

Estle\textsuperscript{11c} has calculated total relaxation times between certain pairs of states and has found \( \tau \) to change little with electric field except at low fields where zero field selection rules become dominant. The same general behavior of \( \tau \) is expected here but further calculations will not be conducted at this time.

In the ideal sense, Equation (49) states that the defect will absorb power from the sound wave at only those values of electric field for which the energy conservation requirement that is implicit in Equation (56) is satisfied. However, in a real crystal internal fields produce an environment for the defects such that a range of values of the electric field will tune the states of different defects through the resonant condition, thus leading to a broadened absorption peak. At very low frequencies such as 1 GHz, the electric field at which resonance occurs is small. Indeed, so small that its effect upon the defect will be comparable to the internal fields, hence the width of a resonance line may be very great. At these low frequencies, \( \hbar \omega \ll kT \), so the population difference, \( \eta_o \), and therefore the power absorbed, is proportional to \( 1/T \).
Nonresonant Absorption

The nonresonant absorption or "relaxation loss" attenuates the sound wave according to

$$P_{\text{abs}} = \omega \chi'' |P|^2 \quad (60)$$

where $|P|$ is the amplitude of the phonon stress wave and $\chi''$ is the imaginary component of the elastic susceptibility.

The elastic susceptibility $\chi$ was introduced in Chapter II, and was found to consist of two terms:

$$\chi = N \sum_{i=1}^{8} \left[ \frac{d \epsilon}{dP} f_i (\epsilon, P, T) \right] \langle \lambda \rangle_i + f_i (\epsilon, P, T) \frac{d}{dP} \langle \lambda \rangle_i \quad (38)$$

If, at some nonzero value of electric field $\epsilon$, a sound wave interacts with a defect but the defect lags the sound wave in phase, then $\chi$ will have real and imaginary parts. The second term in Equation (38) will not contribute to $\chi''$ because neither $\lambda$ nor the wave functions contained in $\langle \lambda \rangle_i$ are frequency dependent. To obtain $\chi''$ from the first term consider the definition of the polarization, $q$, with a relaxation time, $\tau$,

$$\frac{dq}{dt} = \frac{1}{\tau} [q(t \gg \tau) - q(t)] .$$

If for $t \gg \tau$,

$$q(t \gg \tau) = \chi P e^{i \omega t}$$

where

$$\chi = N \sum_{i=1}^{8} \langle \lambda \rangle_i \frac{d}{dP} f_i$$

then the solution for the polarization at some time $t$ is
\[ \tau(t) = x_{\text{complex}} e^{i\omega t} \]

where

\[ x_{\text{complex}} = \frac{x}{1 + i\omega \tau}. \]

Thus, the expression for \( x'' \) is

\[ x'' = N \sum_{i=1}^{8} \langle \lambda \rangle_i \frac{d}{dP} f_i(\varepsilon, P, T) \frac{\omega \tau}{1 + \omega^2 \tau^2} \]  

(61)

The nonresonant attenuation can now be obtained by substituting Equation (61) into Equation (60). The evaluation of \( d/dP(f_i) \) and \( \langle \lambda \rangle_i \) is straightforward but tedious. The relaxation time, \( \tau \), is the inverse sum of the \( \tau_i \)'s between all combinations of states as in the previous section. The power absorbed is a complicated function of electric field because of the dependency of \( \langle \lambda \rangle_i, f_i, \) and \( \tau \) upon it. In the high temperature limit, the power absorbed will display a \( 1/T \) dependence due to \( f_i \).

**Discussion of the Data**

A variation of acoustic attenuation with electric field was observed. The variation was always quite broad; never possessing a half-width of less than 10 KV/cm. The signal obtained most often showed the attenuation to be a maximum at zero field and to gradually decrease with increasing field until at about 15 KV/cm, it leveled off at about 10% below its maximum. However, the signals were very erratic for unknown reasons. The way in which the attenuation varied with field was often different for different echoes and
occasionally varied from one part of an echo to another part of the same echo. The change in attenuation with field was quite pronounced, ranging between .1 and 1 dB/cm, but while some of the echoes in an echo pattern would increase, neighboring echoes might decrease.

One conceivable explanation of this irregular signal can be based upon the echo modulation problem discussed in Chapter II. The acoustic attenuation is expected to be a complicated function of electric field as can be seen from Equation (56) and (61). Perhaps this dependence upon field is modulating the echo pattern in much the same way that a changing angle of parallelism would. To see how this could occur, one must think of the sound wave pulse as a planer wave front moving through a region of inhomogeneity in the crystal. It is quite conceivable that a certain amount of inhomogeneity could exist due to a gradient in defect concentration or a variation in internal strains and fields. As the planer wave front moved through this region at a certain value of the externally applied electric field, one part of the wave front could undergo a different dispersive effect than another part, thus the wave front would no longer be planer in character. If this were happening it could explain in terms of phase cancellation why some echoes changed differently than others.

The variation in attenuation was approximately three times greater at 1.4°K than at 4.2°K. Since this 1/T
dependence was expected for both resonant and nonresonant absorption, no conclusion as to which is dominant can be drawn.

Some of the echoes were observed to shift to later arrival times upon application of the electric field which could possibly be attributed to a dispersive effect. However, the velocity changes were about 2% which is an order of magnitude too large, but, even so, on the very border of the detection capability. In addition, the shift in the echo pattern was not progressive; that is, the third echo did not necessarily shift more than the second, etc. Therefore, this is most likely not dispersion, but a suitable explanation is lacking.

The most difficult to understand observation was an attenuation variation in pure KCl just as in 100 ppm Li⁺ doped KCl. Signals were first recorded in the doped KCl for the phonon $\mathbf{q}$-vector parallel to [111] and the electric field parallel to [110] because the effect was expected to be greatest for this combination. A variation with field was observed. Then, Harshaw grade pure KCl was used with the phonons along [100] and the electric field along [001], and data taken. This orientation was chosen because no coupling of the stress to any Li⁺ defects present should occur. But, an attenuation variation with field was observed just as strong as in the first sample!

Paraelectric resonance measurements were made on the
two samples to determine the relative amounts of lithium present and the effect of the 300°C anneal. The results are as follows:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative PER Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>annealed KC\textsubscript{L}:Li - 100 ppm</td>
<td>1200</td>
</tr>
<tr>
<td>unannealed KC\textsubscript{L}:Li - 100 ppm</td>
<td>60</td>
</tr>
<tr>
<td>annealed KC\textsubscript{L} - pure</td>
<td>1</td>
</tr>
<tr>
<td>unannealed KC\textsubscript{L} - pure</td>
<td>0 (no signal)</td>
</tr>
</tbody>
</table>

It can be seen that although annealing did free some of the inherent lithium impurity to act as a paraelectric-paraelastic defect, the relative concentrations are still far apart so that this does not explain the large attenuation change in the pure KC\textsubscript{L}.

If the hydroxyl ion were present in the KC\textsubscript{L}, this could explain the strong attenuation variation in the [100] direction because KC\textsubscript{L}:OH\textsuperscript{-} is best described by the six-\langle 100\rangle-di-pole model which predicts the greatest interaction with stress along [100]. However, the paraelectric resonance spectra of the pure KC\textsubscript{L} was identical, but weaker, in appearance to the lithium doped KC\textsubscript{L} and did not give any hint of a sizeable OH\textsuperscript{-} concentration.

The data can be summarized as follows with respect to orientation and purity:
<table>
<thead>
<tr>
<th>Orientation</th>
<th>Purity</th>
<th>Attenuation</th>
<th>Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phonon $\vec{k}$</td>
<td>$\epsilon$-Field</td>
<td>Observed</td>
<td>Expected</td>
</tr>
<tr>
<td>[100]</td>
<td>[001]</td>
<td>pure</td>
<td>strong</td>
</tr>
<tr>
<td>[100]</td>
<td>[001]</td>
<td>100 ppm</td>
<td>strong</td>
</tr>
<tr>
<td>[110]</td>
<td>[001]</td>
<td>pure</td>
<td>none</td>
</tr>
<tr>
<td>[110]</td>
<td>[001]</td>
<td>100 ppm</td>
<td>strong</td>
</tr>
<tr>
<td>[111]</td>
<td>[1\bar{1}0]</td>
<td>pure</td>
<td>none</td>
</tr>
<tr>
<td>[111]</td>
<td>[111]</td>
<td>100 ppm</td>
<td>strong</td>
</tr>
</tbody>
</table>

Conclusions

A variation of the acoustic attenuation with electric field exists with a $1/T$ dependence. There is insufficient information at this time to define the source of the attenuation, but it does not appear to be lithium.
REFERENCES


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