THIRD-ORDER ELASTIC CONSTANT

\[ C_{111} \] IN LITHIUM FLUORIDE

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The Faculty of the Graduate Division
by
James Robert Archer, Jr.

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Approved:

Chairman

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TABLE OF CONTENTS

ACKNOWLEDGMENTS ........................................ ii
LIST OF TABLES ........................................ iv
LIST OF FIGURES ........................................ v
SUMMARY ................................................ vi

CHAPTER

I. INTRODUCTION ........................................ 1

II. REVIEW OF THE LITERATURE .......................... 3
   Elastic Theory of Infinitesimal Strains
   Elastic Theory of Finite Strains
   Lattice Dynamics
   Measurement of the Third-Order Elastic Constants

III. INSTRUMENTATION AND EQUIPMENT ................. 15

IV. EXPERIMENTAL PROCEDURE ........................... 22
   Sample Preparation
   Measurement
   Calibration
   Method of Calculation

V. DISCUSSION OF RESULTS ................................ 29

VI. CONCLUSIONS AND RECOMMENDATIONS ............... 32

APPENDICES .............................................. 33

BIBLIOGRAPHY ............................................ 41
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Crystal Classes and Numbers of Independent Coefficients</td>
<td>9</td>
</tr>
<tr>
<td>2. $C_{111}$ Elastic Constant for NaCl and KCl</td>
<td>14</td>
</tr>
<tr>
<td>3. Amplitudes and $C_{111}$ Elastic Constants for LiF</td>
<td>30</td>
</tr>
<tr>
<td>in the [100] Direction</td>
<td></td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Potential Energy vs Atomic Separation</td>
<td>6</td>
</tr>
<tr>
<td>2.</td>
<td>Schematic Diagram of Experimental Arrangement</td>
<td>16</td>
</tr>
<tr>
<td>3.</td>
<td>Capacitance Microphone Assembly</td>
<td>18</td>
</tr>
<tr>
<td>4.</td>
<td>Schematic Diagram of Detector and Preamplifier Circuit</td>
<td>20</td>
</tr>
<tr>
<td>5.</td>
<td>Equivalent Circuit of Preamplifier</td>
<td>21</td>
</tr>
<tr>
<td>6.</td>
<td>Pulse Echo Train of 30 MHz (upper trace) and 60 MHz (lower trace) Pulses</td>
<td>25</td>
</tr>
<tr>
<td>7.</td>
<td>The Second Harmonic Amplitude vs. the Square of the Fundamental Amplitude for LiF in the [100] Direction</td>
<td>28</td>
</tr>
</tbody>
</table>
SUMMARY

The third-order elastic constants characterize the anharmonic properties of crystal lattices. The anharmonic properties explain such solid state phenomena as thermal conductivity, thermal expansion, and thermal relaxation times.

The mathematical theory involving these constants has been known for some time, but only recently have measurements been made of these constants. They have been measured by such methods as determining the velocity of sound in the sample under uniaxial stress and by an ultrasonic-optical technique.

A capacitance microphone technique was developed to measure vibration amplitudes in solids, and equations have been developed to calculate the third-order elastic constants from these amplitude measurements.

In the capacitance microphone technique, sound waves, or phonons, of a single frequency are introduced into a sample by a transducer. As the sound waves travel through the sample, the fundamental wave is distorted so that the second harmonic builds up. The amplitude of these sound waves is measured by a capacitance assembly at the end of the sample. The sample rests on a copper disk with a recessed copper button. The end of the sample and the copper button form a capacitor with the copper button as the fixed plate of the capacitor. A bias voltage is placed on the copper button. As the sound waves reach the end of the sample, the end vibrates. This changes the gap spacing or distance
between the plates of the capacitor, and thus the voltage associated with this capacitance. This voltage is amplified and displayed on a dual trace oscilloscope that shows the 30 and 60 MHz traces.

The amplitudes are calculated from equations derived from the electronic equipment and the physical processes associated with this method.

The range of amplitude values measured in this work was 5.64 to 25.8 Å for the fundamental pulses and 0.041 to 0.621 Å for the second harmonic pulses. A value of $-6.9 \pm 0.6 \times 10^{12}$ dynes/cm$^2$ for the $C_{111}$ third-order elastic constant in LiF in the [100] direction was obtained.
CHAPTER I

INTRODUCTION

In the theory of elasticity, the strain energy of a solid is defined by Taylor's series expansion of the strain energy function, \( U \). Associated with the third and fourth terms of the expansion are two groups of constants, called second- and third-order elastic constants respectively. The second-order elastic constants are known as moduli of elasticity, and their values have been known for many years. However, only recently have techniques been developed that would enable one to measure the third-order elastic constants.

The third-order elastic constants characterize the anharmonic properties of crystal lattices. These anharmonic properties are related to such things as thermal conductivity, thermal expansion, and reactions between thermal and acoustical phonons.

Kaplan\(^1\) in 1931 introduced the elastic constants of higher order (third, fourth, etc.) into stress and strain equations obtained by Murnaghan. Birch\(^2\) and Hearmon\(^3,4\) applied the strain energy function to specific crystal systems.

In 1961 Bateman, Mason, and McSkimin\(^5\) made the first complete study of a material by measuring all six third-order elastic constants of Ge by determining the velocity of sound in the medium under uniaxial stress. Parker and Kelly\(^6\) measured the \( C_{111} \) third-order elastic constant of single crystal NaCl using an ultrasonic-optical method.
In 1965 Thompson, Breazeale, and Gauster\textsuperscript{7} developed a capacitance microphone technique in which one end of the specimen acts as one of the plates of a capacitor, and as it vibrates, the peak voltage generated is monitored on an oscilloscope.

The purpose of this work was to measure the $C_{111}$ third-order elastic constant of LiF using the capacitance microphone technique.
CHAPTER II

REVIEW OF THE LITERATURE

Elastic Theory of Infinitesimal Strains

In the classical definition of elasticity, Love states that for infinitesimal strains, the solid obeys Hooke's law. "Each of the six components of stress at any point of a body is a linear function of the six components of strain at the point."

The above statement is a generalized version of the work done by Robert Hooke in 1678 in which Hooke, working with the elastic restoring force of a spring, observed that the restoring force of the spring was directly proportional to the distance from its equilibrium position. The equation for the elastic restoring force is

\[ F = -kx, \]  \hspace{1cm} (1)

where \( F \) is the restoring force, \( x \) is the distance from the equilibrium position, and \( k \) is a proportionality constant.

In the generalized case the six stress components are expressed as linear functions of the strain components by equations of the form:

\[ X_x = c_{11}e_{xx} + c_{12}e_{yy} + c_{13}e_{zz} + c_{14}e_{yz} + c_{15}e_{zx} + c_{16}e_{xy} \]

\[ Y_y = c_{21}e_{xx} + c_{22}e_{yy} + c_{23}e_{zz} + c_{24}e_{yz} + c_{25}e_{zx} + c_{26}e_{xy} \]

\[ Z_z = c_{31}e_{xx} + c_{32}e_{yy} + c_{33}e_{zz} + c_{34}e_{yz} + c_{35}e_{zx} + c_{36}e_{xy} \] \hspace{1cm} (2)
\[ Y_z = c_{41}e_{xx} + c_{42}e_{yy} + c_{43}e_{zz} + c_{44}e_{yz} + c_{45}e_{zx} + c_{46}e_{xy} \]

\[ Z_x = c_{51}e_{xx} + c_{52}e_{yy} + c_{53}e_{zz} + c_{54}e_{yz} + c_{55}e_{zx} + c_{56}e_{xy} \]

\[ X_y = c_{61}e_{xx} + c_{62}e_{yy} + c_{63}e_{zz} + c_{64}e_{yz} + c_{65}e_{zx} + c_{66}e_{xy} \]

where the capital letter (X, Y, Z) indicates the direction of the force in an orthogonal coordinate system, and the subscript (x, y, z) indicates the normal to the plane to which the force is applied.

c_{ij} (i, j = 1, 2, 3, 4, 5, 6) are the elastic stiffness constants, and e_{mn} (m, n = x, y, z) are the strain components.

In the Hookian motion described above, it can be shown that if the particle is free from any damping effects, the motion of the particle can be described by a differential equation of the form:

\[ \frac{d^2x}{dt^2} + \frac{kx}{m} = 0 \]  

(3)

The equation for Newton's law is

\[ F = ma = m \frac{d^2x}{dt^2} \]  

(4)

Setting equation (1) equal to Newton's law yields

\[ -kx = m \frac{d^2x}{dt^2} \]  

(5)

By rearranging terms one obtains

\[ \frac{d^2x}{dt^2} + \frac{kx}{m} = 0 \]  

(6)
A particle whose motion can be described by equation (6) is said to execute simple harmonic motion. A graph of potential energy versus atomic separation for a one dimensional set of particles executing simple harmonic motion would be a parabola.

**Elastic Theory of Finite Strains**

The linear or simple harmonic oscillator approach to such things as transport phenomena, thermal expansion, and thermal relaxation times in which finite strains appear is insufficient. The linear approach does not account for the energy coupling between the modes of vibration in solids. For example, no thermal conductivity would occur if anharmonic terms were not included in the theoretical calculation of thermal conductivity.

The actual potential energy curve for a one dimensional array of atoms in a solid is shown in Figure 1. In Figure 1, \( V \) represents the potential energy and \( r \) represents the distance between the atoms. At \( r = d_0 \), the potential energy is at a minimum because the repulsive and attractive forces between the atoms are zero. In a simple harmonic oscillator approximation, the potential is symmetrical; however, Figure 1 shows that the actual potential is asymmetrical.

In the symmetrical or parabolic model the mean position of the atoms would remain constant no matter how great the vibration (thermal energy). If the amplitude of vibration is increased in the asymmetrical case, the mean position would be displaced to the right. This would correspond to a larger atomic separation, i.e., thermal expansion.
Hearmon\textsuperscript{3} defines the third-order elastic constants from the fourth term in the expansion of the strain energy function, $U$, of a body:

$$U = U_0 + U_1 + U_2 + U_3 + \ldots,$$

where

- $U_0 = \text{initial energy of the solid}$
- $U_1 = c_{ij}^{n_{ij}}$
- $U_2 = \frac{1}{2!} c_{ijkl}^{n_{ij}n_{jk}n_{kl}}$
- $U_3 = \frac{1}{3!} c_{ijklmn}^{n_{ij}n_{jk}n_{kl}n_{mn}}$. 

**Figure 1. Potential Energy vs Atomic Separation.**
The first two terms of the expansion, \( U_0 \) and \( U_1 \), are zero if the initial energy and dilation are zero, i.e., there is no initial internal strain present. The constants \( c_{ijkl} \) and \( C_{ijklmn} \) are the second- and third-order elastic constants respectively.

Ghate points out how the subscripts of the elastic coefficients may be contracted. The second-order elastic constants are contracted by:

\[
c_{ijkl} = c_{uv},
\]

where \( i, j, k, l = 1, 2, 3 \)

\( u, v = 1, 2, 3, 4, 5, 6 \)

\( 11 \rightarrow 1 \)
\( 22 \rightarrow 2 \)
\( 33 \rightarrow 3 \)
\( 23 \rightarrow 4 \)
\( 31 \rightarrow 5 \)
\( 12 \rightarrow 6 \).

Contraction of the third-order elastic coefficients is handled in a similar manner. From this it can be seen that the second-order elastic constants in equation (12) are the same as those in equation (2).

The concept of tensor analysis may be used in defining these elastic terms. From a brief review of tensor analysis, a point in three-dimensional space is located by a set of three numbers, or coordinates, corresponding to a particular coordinate system or frame of reference. Suppose \( N \) quantities \( A^1, A^2, \ldots, A^N \) in a coordinate system \( (x^1, x^2, \ldots, x^N) \) are related to \( N \) other quantities \( \tilde{A}^1, \tilde{A}^2, \ldots, \tilde{A}^N \) in another coordinate system \( (\tilde{x}^1, \tilde{x}^2, \ldots, \tilde{x}^N) \) by transformation equations

\[
\tilde{A}^p = \frac{\delta x^p}{x^q} A^q
\]

(13)
These equations are called contravariant (13) or covariant (14) tensors of the first order. This definition can be extended to higher order tensors. The components of a tensor can be arranged in a matrix, and the tensor is called symmetric if the components are unaltered upon interchange of indices or is called asymmetric if altered by an indicial interchange. The second-order elastic constants form a fourth-order tensor with 81 components, and the third-order elastic constants form a sixth-order tensor with 729 components. Because of the symmetry of the tensors one may reduce the number of components to 21 independent components in the case of the fourth-order tensor and 56 independent components in the sixth-order tensor. In the application of tensor analysis to the strain energy function and elastic coefficients, Hearmon and Birch showed that the number of independent constants could be reduced in crystal systems of high symmetry. Table 1 shows the number of independent elastic constants for the seven crystal systems.

Lattice Dynamics

Phonons are quantized elastic waves associated with lattice vibrations in crystals. Phonons are characterized by an energy $hv$ and a wave vector $k$. They cause displacement of ions in solids from their equilibrium positions and thus are an essential part of the theory of elasticity in solids. Because phonons are subject to anharmonic terms in the elastic
Table 1. Crystal Classes and Numbers of Independent Coefficients

<table>
<thead>
<tr>
<th>System</th>
<th>Crystal classes Hermann-Mauguin symbols</th>
<th>Numbers of Elastic coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2nd order</td>
</tr>
<tr>
<td>Triclinic</td>
<td>1, i</td>
<td>21</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>2, m, $\frac{2}{m}$</td>
<td>13</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>2mm, 222, $\frac{2}{m}$ $\frac{2}{m}$</td>
<td>9</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>a $4, \frac{4}{m}$</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>b $4mm, 4 2m, 422, \frac{4}{m} \frac{2}{m} \frac{2}{m}$</td>
<td>6</td>
</tr>
<tr>
<td>Trigonal</td>
<td>a $3, \frac{3}{m}$</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>b $3m, \frac{3}{m} \frac{2}{m}, 32$</td>
<td>6</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>a $6, \frac{6}{m}$</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>b $6mm, \frac{6m2}{m}, 622, \frac{6}{m} \frac{2}{m} \frac{2}{m}$</td>
<td>5</td>
</tr>
<tr>
<td>Cubic</td>
<td>a $23, \frac{2}{m} \frac{3}{m}$</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>b $\frac{43m, 432, \frac{4}{m} \frac{3}{m} \frac{2}{m}}$</td>
<td>3</td>
</tr>
</tbody>
</table>
theory which accounts for coupling between the modes of vibration in solids, they are responsible for such transport properties as thermal conductivity as previously mentioned.

Phonons are considered by Seitz\textsuperscript{17} to be one of six primary imperfections in crystals:

1. Phonons
2. Electrons and holes
3. Excitons
4. Vacant lattice sites and interstitial atoms
5. Foreign atoms in either interstitial or substitutional positions
6. Dislocations.

The interaction of phonons with other phonons and with the other five primary imperfections has a marked effect on energy transport in solids.

The equations of motion of non-linear wave propagation in cubic crystals as presented by Gauster\textsuperscript{18} will be developed to describe how phonons are transported through an elastic medium.

Let a point have the coordinates \( (a_1, a_2, a_3) \) in the initial or unstrained state and the coordinates \( (x_1, x_2, x_3) \) in the final or deformed state. The components of displacement are \( u_i = x_i - a_i \).

To define the strain tensor, two points very close together are considered with a radius vector \( da_1 \). The distance between the two points is \( dl = (da_1^2 + da_2^2 + da_3^2)^{1/2} \). The radius vector after deformation is \( dx_1 = da_1 + du_1 \). Squaring the distance yields...
\[ d1'^2 = dx_i^2 = (da_i + du_i)^2 = (da_i + \frac{\partial u_i}{\partial a_k} da_k)^2 \]  
\[ = d1^2 + 2 \frac{\partial u_i}{\partial a_k} da_ida_k + \frac{\partial u_i}{\partial a_k} \frac{\partial u_i}{\partial a_l} da_k da_l. \]  

By rearranging terms one obtains

\[ d1'^2 - d1^2 = 2 \frac{1}{2} \left( \frac{\partial u_i}{\partial a_k} + \frac{\partial u_i}{\partial a_l} + \frac{\partial u_i}{\partial a_k} \frac{\partial u_i}{\partial a_l} \right) da_ida_k \]

\[ = 2n_{ik} da_ida_k. \]

\( n_{ik} \) are the elements of the strain tensor. The strain tensor is symmetric by definition; and when the space derivatives of the displacements are small enough, their products and squares can be neglected. The \( n_{ik} \) strains in equation (16) are the Lagrangian strains.

The strain can also be expressed in terms of the Jacobian matrix \( J \) of the transformation from initial to final coordinates:

\[ J = \begin{bmatrix} \frac{\partial x_1}{\partial a_1} & \frac{\partial x_1}{\partial a_2} & \frac{\partial x_1}{\partial a_3} \\ \frac{\partial x_2}{\partial a_1} & \frac{\partial x_2}{\partial a_2} & \frac{\partial x_2}{\partial a_3} \\ \frac{\partial x_3}{\partial a_1} & \frac{\partial x_3}{\partial a_2} & \frac{\partial x_3}{\partial a_3} \end{bmatrix} \]

\[ \tilde{J} \] is the unit matrix \( E_3 \) for rigid displacement and is defined as

\[ [n] = \frac{1}{2} [\tilde{J} - E_3], \]
where $\tilde{J}$ is the transpose of $J$. These are the same strain elements as in equation (16).

From Lagrange's equations and from the definition of strain in terms of the Jacobian matrix, the equation of motion is

$$\rho \ddot{x}_i = \frac{d}{da_k} \left( J_{i1} \frac{\partial U}{\partial n_{kl}} \right), \quad (19)$$

where the dot indicates a time derivative and $\rho$ is the mass density in the unstrained state.

As seen in Table 1 a crystal of cubic symmetry with a four-fold axis has 3 second-order elastic constants and 6 third-order elastic constants. The general non-linear equation for wave propagation in this crystal class is obtained by rearranging equation (19) and forming derivatives of $U$ with respect to $n$. The derivatives are expressed in terms of $\frac{\partial u}{\partial a}$, and three coupled equations are obtained, one for particle displacements in the $u_1$, $u_2$, $u_3$ directions.

The equations are of the form

$$\rho \ddot{u}_1 = c_{111} \frac{\partial^2 u_1}{\partial a_1^2} + c_{12} \left( \frac{\partial^2 u_2}{\partial a_1 \partial a_2} + \frac{\partial^2 u_3}{\partial a_1 \partial a_3} \right) + \ldots \quad (20)$$

$$+ c_{111} \frac{\partial u_1 \partial^2 u_1}{\partial a_1^2 \partial a_1} + \ldots + c_{123} \left( \frac{\partial u_3}{\partial a_3} \frac{\partial^2 u_2}{\partial a_1 \partial a_2} + \frac{\partial u_1}{\partial a_2} \frac{\partial^2 u_3}{\partial a_1 \partial a_3} \right) + \ldots$$

The other two equations are obtained by cyclic permutations of the subscripts in (20).
Measurement of the Third-Order Elastic Constants

Although the theory of finite strains has been known for some time, the methods of measuring the third-order elastic constants have just recently been developed. Hearmon in 1953 states that "it appears, however, that no numerical estimates have hitherto been published, nor have methods of measuring them been suggested . . . ."

The first method developed to measure the third-order elastic constants was to subject the specimen to hydrostatic pressure or uniaxial stress. In this method a quartz transducer was used to send sound waves through the specimen under pressure, and the change in sound velocity as a function of pressure was measured. Bateman, Mason, and McSkimin made the first complete study of the third-order elastic constants by measuring all six constants for Ge. In 1965 Thurston, McSkimin, and Andreatch measured all 14 third-order elastic constants of quartz.

In 1964 Parker and Kelly measured the $C_{111}$ constant of single crystal NaCl using an ultrasonic-optical method.

Thompson, Breazeale, and Gauster developed a capacitance microphone technique in which the magnitude of the strain amplitudes was measured directly. In this method a transducer was bonded to the sample, and a capacitor assembly was placed on the opposite end. The amplitude of the second harmonic was measured by a technique described in this work.

Breazeale and Ford showed that the solution to the wave equation for longitudinal waves in cubic crystals leads to

$$A_2 = -\frac{3}{8} \frac{\omega^2}{c_L} \left(1 + \frac{C_{111}}{2c_{11}}\right) aA_1^2,$$

(21)
in which \( A_1 \) is the amplitude of the fundamental wave introduced into the medium, \( A_2 \) is the amplitude of the second harmonic at the end of the sample, \( a \) is the length of the sample, \( \omega \) is the angular frequency, \( C_L \) is the velocity of a longitudinal wave in the \([100]\) direction, \( c_{11} \) is the second-order elastic constant of the material, and \( c_{111} \) is the third-order elastic constant.

Stanford and Zehner\(^{22}\) measured the third-order elastic constant \( c_{111} \) in NaCl and KCl. Table 2 shows how their results using the capacitance microphone technique compared with others.

### Table 2. \( c_{111} \) Elastic Constant for NaCl and KCl

<table>
<thead>
<tr>
<th>Experimenter</th>
<th>Method</th>
<th>NaCl</th>
<th>KCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stanford and Zehner(^{22})</td>
<td>Capacity Microphone</td>
<td>(-8.3 \pm 0.8)</td>
<td>(-7.1 \pm 0.7)</td>
</tr>
<tr>
<td>Chang(^{19})</td>
<td>Uniaxial Compression</td>
<td>(-8.8) (est)</td>
<td>(-7.0) (est)</td>
</tr>
<tr>
<td>Parker and Kelly(^6)</td>
<td>Ultrasonic-optical</td>
<td>(-6.4)</td>
<td></td>
</tr>
<tr>
<td>Gedroits and Krasil’nikiv(^{23})</td>
<td>Harmonic</td>
<td>(-8.7)</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER III

INSTRUMENTATION AND EQUIPMENT

A schematic diagram of the equipment used in the present experiment is shown in Figure 2. The pulser is a pulsed oscillator (Arenburg Ultrasonic Laboratory, Inc.) with a variable pulse length control (1 1/2 to 20 μseconds), a frequency control, and a pulse repetition frequency control. It generates 30 MHz pulses, and, with an exchange of coils and frequency adjustment, can produce 60 MHz pulses which are used in calibrating the equipment. The oscilloscope is triggered from the pulser. The harmonic suppressor is a quarter-wavelength electrical cable which essentially grounds all of the 60 MHz or second harmonic pulses from the pulser when connected. The suppressor insures that all of the detected second harmonic pulses are generated in the sample when measurements are being made. It is removed from the circuit during the 60 MHz calibration. It was observed that it performed its function adequately as indicated by the linear relationship obtained between $A_1^2$ and $A_2$ (equation 21) in the present experiment.

The calibrated attenuators (30 and 60 MHz) were two Airborne Instruments Laboratory precision attenuators with a range of 0-100 db. They allowed a known signal from the pulsed oscillator to be attenuated and to produce a signal on the oscilloscope identical to the measured signal from the sample. Thus, the voltage at the input of the preamplifier circuit that produced the signal recorded from the sample was calculated.
Figure 2. Schematic Diagram of Experimental Arrangement.
The capacitance microphone assembly is shown in Figure 3. A quartz transducer with a fundamental frequency of 30 MHz was bonded to the sample with Fisher Nonaq Stopcock Grease. The upper assembly drove the transducer at its fundamental frequency from the output of the pulsed oscillator.

The detector assembly of Figure 3 consisted of a copper disk with a recessed copper button in the center. The button was bonded to the copper disk by epoxy resin. The copper disk had a threaded neck which screwed into the brass box which housed the preamplifier assembly. The copper button had an extension on the bottom which made an electrical connection with the preamplifier assembly. The disk was polished to an optical flat so as to give a uniform capacitor gap spacing.

The sample, onto which a conducting surface had been evaporated, was positioned as in Figure 3 and formed a parallel plate capacitor with the recessed copper button. Stanford and Zehner measured the gap spacing of the assembly with a Leitz microscope with a depth of field of one micron and a focal plane position calibrated to one micron. They showed that the results of the gap spacing determined by the microscope coincided with gap spacing obtained by measuring the capacitance with a General Radio Company impedance bridge within 5%. In the present experiments on LiF, the impedance bridge was used to determine the gap spacing.

The gap between the button and the sample may be evacuated (Figure 3) by a vacuum pump so that a larger bias voltage may be placed across the capacitor. In the present experiments a thin film of Mylar, 1.5 x 10^{-4} inches thick, was used as a dielectric instead of evacuating the gap between the sample and the button. This allowed biasing voltages (supplied by a Kepco regulated DC power supply with an output of 0-1000 volts)
of up to 1000 volts to be applied.

After the sound beam traveled down the sample, it caused the free end of the sample to vibrate. The variation of the capacitor voltage produced by this vibration was introduced into the preamplifier circuit. A schematic diagram of the detector and preamplifier circuit is shown in Figure 4. Gauster\(^1\) has shown that this circuit can be reduced to the equivalent circuit of Figure 5 and that the output impedance of the preamplifier is matched to that of the intermediate frequency amplifier strips. The intermediate frequency amplifier strips (RHG Electronics Laboratory Inc.) have center frequencies of 30 and 60 MHz with 10 MHz bandwidths. The output of these IF strips was displayed on a dual trace oscilloscope.
Figure 4. Schematic diagram of Detector and Preamplifier Circuit.
Figure 5. Equivalent Circuit of Preamplifier.
CHAPTER IV

EXPERIMENTAL PROCEDURE

Sample Preparation

A lithium fluoride single crystal was obtained from the Harshaw Chemical Company. The crystal was a cylinder one inch in diameter and two inches long with tolerances in all dimensions of ± 0.005 inches. The axis of the cylinder coincided with the [100] direction. The ends were cleaved perpendicular to the [100] direction and polished to an optical flat. A gold film, approximately 1000 Å thick, was evaporated on each end of the sample.

The LiF sample initially exhibited pronounced attenuation; no second harmonic was detected that was large enough to measure. The gold film was removed from the ends, and the sample was annealed in an attempt to relieve thermal stresses obtained when the LiF crystal was pulled from the melt. The melting point of LiF is 870°C. The sample was annealed in a horizontal Globar furnace at 585°C for one minute. The heating and cooling rates were controlled by a cam on the temperature recorder. Both the heating and cooling rates were 66°C per hour. After annealing, gold was deposited on the ends of the sample. The attenuation of sound waves was significantly reduced, and a considerable second harmonic was obtained.

Measurement

The LiF sample was positioned on the capacitance microphone
assembly as in Figure 3. A quartz transducer with a gold film on one side was bonded to the top with stopcock grease. The gold side of the transducer was the side bonded to the sample. The upper assembly was positioned on the sample and held there with rubber bands which went around the preamplifier housing to the upper assembly.

The apparatus was arranged so that 30 MHz voltage pulses from the pulser went directly into the transducer assembly. This produced 30 MHz sound wave pulses in the sample. A bias voltage was applied to the capacitor assembly, and the resulting train of echos was amplified and displayed on the oscilloscope. The time for one pulse to travel the length of the sample was recorded. The heights of the first two 30 MHz pulses through the sample were recorded so that the attenuation effect in the sample could be calculated.

The capacitor bias voltage (usually about 50 volts for the LiF sample) was applied to measure the height of the first 30 MHz peak. This voltage corresponds to the voltage \( V_0 \) in Figure 4. It was recorded with a Keithley Instruments electronic voltmeter. The bias voltage was increased to a maximum of 1000 volts to produce a measurable value of the second harmonic of 60 MHz pulses. The height of the first 60 MHz peak was measured, and the voltage \( V_0 \) that produced it was recorded with a Weston voltmeter. Several readings were taken by varying the amplitude of the output signal from the pulser. Because the Mylar dielectric was charged after a bias voltage was applied, it had to be replaced with new Mylar for each reading. The capacitance of the detector assembly with the sample in place was determined by an impedance bridge after each reading.
Calibration

In order to calculate the amplitude of the sample vibration at the capacitor end, it was necessary to determine the capacitor voltage associated with the 30 and 60 MHz components of the vibrations. With the apparatus in the calibrate position in Figure 2, a line was run directly to the oscilloscope, and a signal was generated by the pulser and measured on the oscilloscope. The attenuator (either 30 or 60 MHz) was switched into the circuit, and the attenuation value was adjusted to give the height obtained when the peak was measured. Knowing the input voltage and the attenuator reading, the output voltage at the capacitor was calculated from the equation

\[ \text{attenuation in db} = 20 \log \frac{V_{\text{input}}}{V_{\text{output}}} \]  (22)

For the 60 MHz measurements, the harmonic suppressor was removed, the pulser was adjusted to produce 60 MHz pulses, and the 30 MHz attenuator was removed and replaced by the 60 MHz attenuator. This procedure was repeated for each measurement. Several amplitude measurements of \( A_1 \) and \( A_2 \) were obtained by varying the power output of the pulser.

Method of Calculation

Appendix A is a sample calculation of the vibration amplitudes for one measurement, and Appendix B is a sample calculation of \( C_{111} \). The sound waves were attenuated as they traveled through the sample, therefore an attenuation correction for the 30 and 60 MHz amplitudes was necessary. Figure 6 shows the 30 and 60 MHz pulse trains displayed on an oscilloscope. The upper trace shows the 30 MHz pulses, and the lower
Figure 6. Pulse Echo Train of 30 MHz (upper trace) and 60 MHz (lower trace) Pulses. (The first pulse in the upper trace is the electric pulse, and the second pulse is the first 30 MHz pulse through the sample. The first pulse in the lower trace is the first 60 MHz pulse through the sample.)
trace shows the 60 MHz pulses. The attenuation effect is observed in Figure 6 as the decreasing height of the pulses as they pass through the sample. The attenuation is exponential in nature and is described by the equation

\[ A = A_0 e^{-\alpha t}, \]  

(23)

where \( A_0 \) is the initial pulse height, \( A \) is the pulse height at the end of the sample, \( \alpha \) is the attenuation coefficient, and \( t \) is the pulse transient time. By measuring the heights of two succeeding 30 MHz pulses and the pulse transient time, the attenuation coefficient was calculated by substituting these values in equation (23). The pulse transient time was 7.7 \( \mu \)sec, and the computed attenuation coefficient was 0.0544/\( \mu \)sec.

The attenuation equation (23) was used to calculate the 30 and 60 MHz vibration amplitudes, \( A_1 \) and \( A_2 \). The respective voltages generated at the capacitor were calculated from equation (22). Equation (21) requires that \( A_1 \) be the fundamental amplitude introduced into the sample and \( A_2 \) be the second harmonic amplitude detected at the end of the sample. To obtain \( A_1 \), the 30 MHz voltage at the capacitor was substituted in equation (23), which yielded the corrected voltage corresponding to the 30 MHz amplitude introduced into the sample. \( A_2 \) built up as it traveled through the sample. However, this build-up was reduced because of attenuation. The same attenuation factor was used to calculate the voltage and corresponding amplitude \( A_2 \) that must be used in equation (21). \( A_1 \) and \( A_2 \) were calculated from Gauster's equation:

\[ A_1 = \frac{V_1}{V_{01}}, \]  

(24)
where $A_1$ is the magnitude of vibration of the sound wave, $s_0$ is the capacitor gap spacing, $V_1$ is the voltage produced by the 30 or 60 MHz vibrations (corrected for attenuation), and $V_{01}$ is the bias voltage applied to the copper button.

Figure 7 is a graph of $A_1^2$ versus $A_2$. The range of amplitudes measured was 5.64 to 25.8 $\AA$ for the fundamental pulses and 0.041 to 0.621 $\AA$ for the second harmonic pulses. The straight line in Figure 7 verified the linear relationship between $A_1^2$ and $A_2$ predicted in equation (21) and demonstrated that the harmonic suppressor was effective in grounding the second harmonic signals from the pulser.

The values of $C_{111}$ were calculated (see Appendix B) from $A_1$ and $A_2$. The value of $c_{11}$ used in the calculations was $9.9 \times 10^{11}$ dynes/cm$^2$ as reported by Hoerni and Wooster. The average value of $C_{111}$ was $-6.9 \times 10^{12}$ dynes/cm$^2$. 
Figure 7. The Second Harmonic Amplitude vs the Square of the Fundamental Amplitude for LiF in the [100] Direction.
CHAPTER V

DISCUSSION OF RESULTS

The amplitudes for the 30 and 60 MHz pulses and the calculated values of $C_{111}$ are shown in Table 3. $A_1$ is the magnitude of vibration of the 30 MHz pulses introduced into the sample, and $A_2$ is the magnitude of vibration of the 60 MHz pulses detected at the end of the sample. The first point in Table 3 was deleted because it did not lie on the straight line in Figure 7. This could be attributed to several factors such as the charged Mylar dielectric or instrumental errors.

An estimate of the error involved in the calculations was made from computations using probable errors made in reading the attenuators, voltmeters, and impedance bridge. The maximum error was ± 3.5% for the capacitor measurements. The two attenuator readings and the voltage $V_{02}$ produced a possible ± 1% error each. The $V_{01}$ voltage error was estimated at ± 0.5%. Other cumulative errors such as frequency, pulse transient time, and length measurements were estimated at ± 1%. Thus, the possible errors from the above factors indicates that an error in the $C_{111}$ value of ± 8.0% is reasonable. This value is lower than the ± 10% error reported by Stanford and Zehner because calibrated attenuators, which could be read more accurately than those in Stanford and Zehner's work, were obtained and used in this experiment.

Pratt, Chang, and Newey have shown that the purity of single crystals effects the stress characteristics of alkali halides. Nadeau
Table 3. Amplitudes and $C_{111}$ Elastic Constant for LiF in the [100] Direction

<table>
<thead>
<tr>
<th>$A_1$ (angstroms)</th>
<th>$A_2$ (angstroms)</th>
<th>$C_{111} \times 10^{-12}$ dynes/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.5</td>
<td>0.215</td>
<td>-7.46</td>
</tr>
<tr>
<td>5.64</td>
<td>0.041</td>
<td>-7.87</td>
</tr>
<tr>
<td>8.19</td>
<td>0.070</td>
<td>-6.93</td>
</tr>
<tr>
<td>25.8</td>
<td>0.621</td>
<td>-6.49</td>
</tr>
<tr>
<td>23.7</td>
<td>0.523</td>
<td>-6.48</td>
</tr>
<tr>
<td>20.5</td>
<td>0.391</td>
<td>-6.49</td>
</tr>
</tbody>
</table>
and Johnston have pointed out that the Harshaw Chemical Company, from which the LiF crystal used in this experiment was purchased, until around 1960, produced relatively impure LiF crystals containing about 80 ppm magnesium. Today, however, the Company's LiF crystals do not contain any impurities that are spectroscopically detectable. Thus, the value of the $C_{111}$ constant reported in this work should be relatively free from any impurity effects. There have been no published values for any third-order elastic constants of LiF up to this time; however, the $C_{111}$ constants for the other alkali halide materials measured, NaCl and KCl, are of the same order of magnitude as the value of $C_{111}$ for LiF, as seen in Table 2.
CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. The $C_{111}$ third-order elastic constant for LiF in the [100] direction is $-6.9 \pm 0.6 \times 10^{12}$ dynes/cm$^2$.

2. The capacitance microphone technique is an excellent method for measuring small amplitude vibrations in solids.

3. Annealing is an effective process for reducing attenuation in single crystal LiF.

Recommendations

Improvements in the method of measuring gap spacing would reduce the major source of error encountered in this experiment.

It is desirable to obtain the complete set of third-order elastic constants for LiF.

It is also recommended that further theoretical work be done in the application of these constants to areas of transport phenomena so that they may be utilized in practical problems.
APPENDIX A

SAMPLE CALCULATION OF 30 and 60 MHz VIBRATION AMPLITUDES, $A_1$ AND $A_2$

The data used in this sample calculation of the 30 and 60 MHz amplitudes are:

- $t = 7.7 \mu\text{sec}$
- $C = 27 \text{ picofarads}$
- $V_{0s} = 5.0 \text{ volts}$
- $A_{t1} = 64.45 \text{ db}$
- $V_{01} = 54.5 \text{ volts}$
- $A_{t2} = 76.86 \text{ db}$
- $V_{02} = 595 \text{ volts}$
- $B = 0.859 \text{ cm}^2$

where $t$ is the pulse transient time, $V_{0s}$ is the oscillator voltage, $V_{02}$ is the 30 MHz bias voltage, $V_{02}$ is the 60 MHz bias voltage, $C$ is the capacitance, $A_{t1}$ is the 30 MHz attenuator reading, $A_{t2}$ is the 60 MHz attenuator reading, and $B$ is the area of the copper button.

To determine the attenuation coefficient, the height in arbitrary units of the first two 30 MHz sound pulses were measured. These heights were 30 and 13 respectively. The transient pulse time was measured to be $7.7 \mu\text{sec}$. The attenuation equation is

$$A = A_0 e^{-\alpha t}, \quad (23)$$

where $A_0$ is the initial pulse height, $A$ is the pulse height at the end of the sample, $\alpha$ is the attenuation coefficient, and $t$ is the pulse transient time.

Let $A_1 = 30$, $A_2 = 13$, $t_1 = 7.7 \mu\text{sec}$, and $t_2 = 23.1 \mu\text{sec}$ so that two
equations are obtained:

\[ 30 = A_0 e^{-\alpha(7.7 \, \mu\text{sec})} \]  
(25)

and

\[ 13 = A_0 e^{-\alpha(23.1 \, \mu\text{sec})} \]  
(26)

Dividing equation (25) by equation (26) yields

\[ \frac{30}{13} = e^{-\alpha(7.7 \, \mu\text{sec})} e^{\alpha(23.1 \, \mu\text{sec})} \]  
(27)

and

\[ 2.31 = e^{\alpha(15.4 \, \mu\text{sec})} \]  
(28)

By taking the logarithm of both sides of equation (28) and solving for \( \alpha \), one obtains

\[ \ln 2.31 = (15.4 \, \mu\text{sec}) \alpha \]  
(29)

and

\[ \alpha = \frac{0.837}{15.4 \, \mu\text{sec}} = 0.0544/\mu\text{sec} \]  
(30)

To calculate the voltage \( V_1 \) corresponding to the amplitude \( A_1 \) of the sound wave introduced into the sample, the oscillator or input voltage \( V_0 \) and the attenuator reading for the 30 MHz calibration are substituted in equation (22), which yields
\[
\text{Attenuation in db} = 20 \log \frac{V_{\text{os}}}{V_1}. \quad (31)
\]

Substituting the attenuator reading and oscillator voltage in equation (31) yields

\[
64.45 \text{ db} = 20 \log \frac{5 \text{ volts}}{V_1}. \quad (32)
\]

Solving equation (32) for \(V_1\) yields

\[
V_1 = \frac{5 \text{ volts}}{10^{3.22}} = 3.01 \times 10^{-3} \text{ volts}. \quad (33)
\]

This voltage is the 30 MHz voltage generated at the end of the sample. To obtain the required voltage \(V_1\) the attenuation equation is used and yields

\[
3.01 \times 10^{-3} \text{ volts} = V_1 e^{-\left(0.0544/\mu\text{sec}\right) \left(7.7 \mu\text{sec}\right)}. \quad (34)
\]

Solving equation (34) for \(V_1\) gives

\[
V_1 = \frac{3.01 \times 10^{-3} \text{ volts}}{e^{-0.418}} = 4.59 \times 10^{-3} \text{ volts.} \quad (35)
\]

To obtain the 30 MHz sound wave amplitude introduced into the sample, the equation for the capacitance of the detector was substituted in Gauster's equation for the gap spacing to obtain a formula in terms of the measured capacitance and corresponding voltages. The equation for the capacitance is
where $C$ is the capacitance, $e_0$ is the permittivity of free space, and $s_0$ is the distance between the capacitor plates. Gauster's equation from the gap spacing is

$$A_1 = \frac{s_0 V_1}{V_{01}}, \quad (24)$$

where $A_1$ is the magnitude of vibration of the sound wave, $s_0$ is the gap spacing between the end of sample and the copper button, $V_1$ is the voltage produced by the $30 \text{ MHz}$ vibrations (corrected for attenuation), and $V_{01}$ is the bias voltage applied to the copper button. Solving equation (36) for $s_0$ and substituting in equation (24) yields

$$s_0 = \frac{e_0 B}{C}, \quad (37)$$

and

$$A_1 = \frac{V_1 e_0 B}{CV_{01}}, \quad (38)$$

Substituting the values obtained for this reading into equation (38) yields

$$A_1 = \frac{(4.59 \times 10^{-3} \text{ volts}) (8.85 \times 10^{-2} \text{ pf/cm}) (0.859 \text{ cm}^2)}{(27 \text{ pf}) (54.5 \text{ volts})} \quad (39)$$

and
The same procedure is followed to obtain the 60 MHz amplitude $A_2$ of the sound wave at the end of the sample. This value is

$$A_2 = 5.23 \times 10^{-9} \text{ cm}.$$  \hspace{1cm} (41)

It should be emphasized that $A_1$ is the magnitude of the 30 MHz sound wave introduced into the sample and $A_2$ is the magnitude of the 60 MHz sound wave at the end of the sample. These are the values that are substituted in equation (21) to yield $C_{111}$. 

$$A_1 = 2.37 \times 10^{-7} \text{ cm}.$$  \hspace{1cm} (40)
APPENDIX B

SAMPLE CALCULATION OF C_{111}

The data used in this sample calculation of C_{111} is

\[ F = 30 \text{ MHz} \quad a = 5.08 \text{ cm} \]
\[ A_1 = 2.37 \times 10^{-7} \text{ cm} \quad t = 7.7 \mu\text{sec} \]
\[ A_2 = 5.23 \times 10^{-9} \text{ cm} \quad c_{11} = 9.9 \times 10^{12} \text{ dynes/cm}^2, \]

where \( F \) is the input frequency, \( a \) is the sample length, \( t \) is the pulse transient time, \( A_1 \) is the magnitude of 30 MHz vibrations introduced into the sample, \( A_2 \) is the magnitude of the 60 MHz vibrations at the end of the sample, and \( c_{11} \) is the second-order elastic constant.

The equation used in this work for the calculation of \( C_{111} \) is

\[ A_2 = \frac{3\omega^2}{8c_L^2} \left( 1 + 2 \frac{C_{111}}{c_{11}} \right) aA_1^2, \tag{21} \]

where \( A_2 \) is the 60 MHz amplitude at the end of the sample, \( \omega \) is the frequency, \( c_L \) is the velocity of sound in the sample, \( C_{111} \) is the third-order elastic constant in the [100] direction, \( c_{11} \) is the second-order elastic constant in the [100] direction, \( a \) is the length of the sample, and \( A_1 \) is the 30 MHz amplitude introduced into the sample. Solving equation (21) for \( C_{111} \) yields
At the free end of the sample, the amplitude is twice that in the bulk material, so that $A_1$ and $A_2$ must be reduced by a factor of two from their value in equation (42). This modification yields

\[
C_{111} = \left\{ \frac{8C_L^2 A_2}{6 \omega^2 a^2} + \frac{1}{2} \right\} c_{11} \cdot \tag{43}
\]

The formula for $C_L$ is

\[
C_L = \frac{a}{t}, \tag{44}
\]

where $a$ is the sample length and $t$ is the pulse transit time. Substituting equation (44) in equation (43) yields

\[
C_{111} = \left\{ \frac{8a A_2}{3 \omega^2 t^2} + \frac{1}{2} \right\} c_{11} \cdot \tag{45}
\]

If the ratio $A_2/A_1^2$ is represented by $X$, equation (45) becomes

\[
C_{111} = \left\{ \frac{8aX}{3 \omega^2 t^2 A_1^2} + \frac{1}{2} \right\} c_{11} \cdot \tag{46}
\]

Substituting the values in equation (46) yields

\[
C_{111} = \left\{ \frac{8(5.08 \text{ cm}) (9.31 \times 10^{-4} \text{ cm})}{3(2\pi) (30 \times 10^6 \text{ sec}) (7.7 \times 10^{-6} \text{ sec})} + \frac{1}{2} \right\} (9.9 \times 10^{11} \text{ dynes/cm}^2) \tag{47}
\]
and

\[ C_{111} = -1.08 \times 10^{12} \text{ dynes/cm}^2 . \]  \hspace{1cm} (48)

Brugger's notation is commonly used for \( C_{111} \) and is equal to \( 6C_{111} \) in equation (45). Thus, \( C_{111} \) in Brugger's notation is

\[ C_{111} = (6) (-1.08 \times 10^{12} \text{ dynes/cm}^2) , \]  \hspace{1cm} (49)

which is

\[ C_{111} = -6.48 \times 10^{12} \text{ dynes/cm}^2 . \]  \hspace{1cm} (50)
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