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ULTRASONIC ATTENUATION AND PHASE VELOCITY
MEASUREMENTS OF ROTATIONAL IMPURITIES
IN ALKALI HALIDES

by

John Ruediger Mader Viertl

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Ph. D. Thesis
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ULTRASONIC ATTENUATION AND PHASE VELOCITY MEASUREMENTS
OF ROTATIONAL IMPURITIES IN ALKALI HALIDES

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Cornell University 1972

The ultrasonic attenuation and phase velocity change in pure RbCl and RbCl "doped" with CN^- and OH^- were measured from -2°K to -30°K and at approximately 500 MHz. In the low temperature region from -13°K to -2°K , the Nowick-Heller Selection Rules were verified for $\text{RbCl}:\text{CN}^-$ and $\text{KCl}:\text{Li}^+$ for all modes and directions of propagation. Both impurities are $\langle 111 \rangle$ defects, i.e., their motion is hindered by potential wells in the eight equivalent $\langle 111 \rangle$ directions. The elastic dipole moment v_0 ($\lambda_1 - \lambda_2$) of CN^- in RbCl is $1.0 \times 10^{-23} \text{ cm}^3$. In the high temperature region, from -13°K to -30°K , the total fractional compliance change and attenuation change vary approximately as T^n ($n \geq 4$) for both the pure and "doped" crystals. The elastic constants of pure RbCl at 4.2°K are: $c_{11} = 4.28 \times 10^{11} \text{ dynes/cm}^2$, $c_{12} = .66 \times 10^{11} \text{ dynes/cm}^2$, $c_{44} = .40 \times 10^{11} \text{ dynes/cm}^2$; and the Debye temperature Θ_D determined from these elastic data is 174°K . These values of elastic constants and Debye temperature agree with those found by Lewis, Lehoczky and Briscoe³¹.

I. INTRODUCTION

Very few measurements of ultrasonic attenuation^{4,27} and phase velocity of acoustic waves have been made in alkali halide crystals at high frequencies (- 500 MHz.) and at temperatures less than 30°K. Only recently⁸ has it been possible to easily generate ultrasonic waves at 500 MHz. by using vapor-grown cadmium sulfide transducers. In this work there are two areas of interest: the attenuation and phase velocity of (1) the pure crystal, and (2) the impure crystal.

For pure materials a number of authors^{16,17,18} derived expressions for the temperature dependence of the ultrasonic attenuation due to three phonon processes. They concluded that the temperature dependence of the attenuation is proportional to T^4 . The pure crystal attenuation will be measured to examine its temperature dependence.

The phase velocity is studied to determine its temperature dependence and to determine the low temperature region in which the phase velocity becomes constant.

The introduction of a substitutional molecular impurity ion into a crystal causes an anisotropic strain if the molecular impurity ion has a shape different from the ion it replaces. Frequently the molecular ion will have a set of preferred equilibrium positions corresponding to minima in its configurational energy. Hence, the possibility of ordering these ions through the application of a stress exists. The anisotropy of the ions implies a change of the elastic constants of the host due to the molecular ion system.

Experimentally the change of elastic constants as a function of temperature are measured as changes of the phase velocity of the acoustic wave.

For crystals with defects which have an anisotropic strain, Nowick and Heller³ derived a set of selection rules for stresses and defects of appropriate symmetry. These selection rules have been used by several authors to determine the direction of the potential minima, but have not been completely tested. Since the potential minima are well established from other measurements for the system $\text{KCl}:\text{Li}^+$, this system is used to test completely all the selection rules. Using the established Nowick-Heller Selection Rules, the dumb-bell molecular ion CN^- is studied in RbCl to determine the directions of its potential minima and demonstrate the utility and power of the acoustic measurements to determine these directions.

II. EXPERIMENTAL TECHNIQUES

A. Method of Measuring the Compliance Change and Attenuation Change

The compliance change in a specimen causes the velocity of an acoustic wave to change. This velocity change is measured as a frequency change. The connection of the compliance change to the velocity change can be found from the expression for the velocity of an acoustic wave. This is given by the expression² $v = \sqrt{c/\rho}$ where v is the velocity of the acoustic wave, ρ is the density of the medium, and c is the stiffness of the material for the particular wave being considered. It is a function of the elastic stiffnesses. Hence, the fractional change of the velocity is given by

$$\Delta v/v = \frac{1}{2} \Delta c/c$$

In order to understand the method used to measure the compliance change a block diagram of the electronic apparatus is shown in Fig. 1. The pulser (Applied Microwave Laboratory, Model Ph-5K) provides d.c. pulses to a triode coaxial cavity oscillator. This oscillator uses the 2C39A lighthouse tube to produce microwave pulses at approximately 500 MHz. The microwave pulses from the cavity oscillator pass through an attenuator (Microlab AA-03N) which reduces the coupling between the cavity oscillator and the rest of the system. From the attenuator, the pulses are sent into a three-port circulator (Scientific-Atlantic, Inc. Model 235-5C-480) and then into the re-entrant cavity, transducer and specimen.

Fig. 1. Block diagram of ultrasonic apparatus

The receiving section of the apparatus is protected with a diode limiter (Microwave Associates, Inc. Model SN-120). This unit allows sufficient power of the transmitter pulse to pass into the receiver to activate the phase locking oscillator and start the trigger circuit of the 454 Tektronix oscilloscope, but not enough power to damage the balanced mixer. The CWO oscillator operates at approximately 60 MHz. and is forced to be in phase with the 60 MHz. i.f. signal of the transmitter pulse through the technique of injection locking. This phase locking, which repeats for each transmitter pulse, allows the CWO to function as a 60 MHz. clock. The CWO signal is applied to the second channel of the Tektronix oscilloscope and the main receiver echos to channel one. Both channels one and two are triggered by the channel one transmitter pulse. Using the time delay to select a particular echo and sweeping at 5 nanoseconds per centimeter, both signals can be displayed on the oscilloscope. One can compare a single oscillation of the CWO signal with that of an echo. If the signals on channel one and channel two are added together by the oscilloscope, a null can be formed by adjusting the frequency and amplitude of the CWO. Any shift in velocity will shift the position of the null and necessitate a shift in frequency of the CWO to return the null to its former position. Hence, any velocity shifts appear as frequency shifts which are measured with a Hewlett-Packard frequency counter. The velocity change is related to the measured frequency change by the expression¹

$$\left| \frac{\Delta v}{v} \right| = \left| \frac{\Delta f_c}{f_c} \right| \left(\frac{f_l}{f_R} \right)$$

where $\Delta v/v$ is the fractional change in velocity of the acoustic wave, Δf_c is the change of frequency of the CWO, f_c is the frequency of the CWO, f_l is the frequency of the receiver i.f., and f_R is the frequency of the transmitter.

The overall accuracy of the fractional frequency change measurements are at least 2×10^{-5} . The error in $\frac{\Delta v}{v}$ is also at least 2×10^{-5} . In order to achieve this accuracy the system must undergo a long warm-up period of approximately four to six hours so that the frequency of the General Radio oscillator and the transmitter do not drift significantly.

The attenuation change is found by measuring the voltage amplitude of the echo pulses as a function of temperature. The voltage amplitude of the n^{th} echo at temperature T is given by

$$A_n(T) = A_0 \exp \left[-a(T) 2nD \right]$$

where $2nD$ is the distance traveled by the n^{th} echo in the crystal. This may be rearranged to give the attenuation change

$$a(T) - a_0 = \frac{1}{2nD} \ln \left[\frac{A_{n0}}{A_n(T)} \right]$$

The quantity a_0 is given by

$$a_0 = \frac{1}{2(n-m)D} \ln \left[\frac{A_{m0}}{A_{n0}} \right]$$

where $a(T)$ is the attenuation in nepers per centimeter, D is the thickness of the sample, and a_0 is the background attenuation in nepers per centimeter. The subscript "0" refers to

an arbitrary reference temperature. This reference temperature is chosen to be approximately 4.2°K . since it is found experimentally that the attenuation is independent of temperature for temperatures less than 4.2°K . The background attenuation contains the temperature independent contributions to the attenuation from such sources as diffraction of the acoustic beam, imperfections in the specimen's flatness and parallelism, distortion of the acoustic wavefront by internal strains, and transducer and equipment losses. For crystals with impurities the background attenuation is taken as the average value of the pure crystal attenuation at 4.2°K . Electrical noise limited the measurements of attenuation change $\alpha(T) - \alpha_0$ to approximately $0.025 \text{ cm}^{-1} \pm 0.1 \text{ db}/\mu \text{ sec}$. The reproducibility was limited by the fluctuations in the line power to about 0.025 cm^{-1} .

B. Microwave Cavity and Cryostat

The microwave cavity is a coaxial re-entrant cavity (Fig. 2) turnable from approximately 350 to 500 MHz. in its fundamental mode. Tuning is accomplished by adjusting the position of a contactless coaxial plunger within the cavity. The center coaxial post is fixed to the top end of the cavity. Its lower end has an adjustable screw which travels up to a hole in the end plate of the cavity in order to make contact with the cadmium sulfide transducer of a specimen.

The cryostat consists of an outer dewar for liquid nitrogen and an inner dewar for liquid helium. The microwave cavity plus specimen is contained inside a vacuum-tight

■ Copper ■ Stainless Steel ■ Brass

Fig. 2. Microwave cavity and cryostat

copper can. This specimen can is surrounded by a copper exchange gas can which sits in liquid helium. Five radiation shields prevent heat from entering through the top of the system. A large mechanical pump is used to lower the temperature by pumping on the liquid helium bath. A combination of a mechanical pump plus a diffusion pump is used to control the amount of helium exchange gas in the exchange gas can. A thermocouple gauge is used to monitor the pressure. During the cooling process the specimen can is filled with helium gas to a pressure of one atmosphere at 77°K . This pressure is sufficient at liquid helium temperatures to prevent microwave arcing in the cavity at the cadmium sulfide transducer. Two wire wound resistors (- 1500 ohms each) are cemented to the cavity with G.E. 7031 varnish.

C. Thermometry

The temperature of the specimen is measured with a Cryocal germanium resistor which is attached to the side of the copper re-entrant cavity immediately adjacent to the sample. G.E. 7031 varnish is used to attach the resistor. The sample chamber and cavity are filled with helium gas of one atmosphere pressure at (77°K .) liquid nitrogen temperature. This procedure ensures adequate thermal contact of the cavity, specimen, heater and germanium thermometer.

The resistance is measured with a three-wire a.c. bridge to eliminate the resistance due to the leads. The resistor was calibrated against a commercially available calibrated germanium resistor.

D. Sample Preparation and Optical Polishing

The crystals were grown by the Crystal Growing Facility of the Material Science Center. The boules were oriented in the $\langle 100 \rangle$ direction. Specimens with $\langle 100 \rangle$ orientation were cleaved from the boules, and those specimens with $\langle 110 \rangle$ and $\langle 111 \rangle$ orientations were cut with a string saw from a cleaved piece of the boule. A special fixture was prepared which used two adjacent $\langle 100 \rangle$ surfaces as references for cutting $\langle 111 \rangle$ specimens. The orientation was checked with an x-ray diffractometer and found to be within 0.5° . The final specimen thicknesses varied between approximately 4mm. and 12mm.

A cleaved or a string-sawed piece was mounted on a polishing jig (Fig. 3) consisting of a stainless steel cylinder approximately 4" long and 4" in outer diameter. The wall of the cylinder was approximately 1" thick. The specimen was held with mounting pitch against a movable spring-loaded piston which fit snugly into the cylinder. The mounting pitch consists of resin, hard black pitch and beeswax in approximately equal proportions. The polishing jig is worked with its specimen in 3 micron garnet powder and kerosine on a glass plate until the surface of the specimen is flat to within one-half wavelength of sodium light over its surface. The specimen is removed and remounted to prepare the second surface in a similar way. At this point the specimen is ready for optical testing and finishing to produce two parallel surfaces.

Fig. 3. Crystal polishing jig

Fig. 4. Optical test jig (Fabry-Perot)

The optical test set-up is a Fabry-Perot interferometer, consisting of two optical flats with surfaces with a flatness of 10^{-6} inch per inch and approximately $2\frac{1}{2}$ " diameter mounted vertically in an adjustable stage, a half-silvered mirror, and a sodium vapor lamp with a glass diffuser. This optical test jig is sketched in Fig. 4.

The specimen is cleaned briefly in kerosine and dried with tissue paper. The specimen is placed upon the lower optical flat of the Fabry-Perot interferometer and pressed lightly with a cotton tip until Newton interference fringes are seen between the lower optical flat and the specimen, showing that the specimen is in good contact with the optical flat. The specimen is moved adjacent to the upper optical flat. For parallel optical flats the Fabry-Perot fringe system consists of concentric circles with the same order visible and stationary as the observer moves across the viewing field. The Newton fringe system produced between the top of the specimen and the upper optical flat form a contour map of the upper surface with an interval of one-half wavelength of sodium light. This allows the determination of the degree of parallelism and flatness. Once the locations of the high spots have been found, they are polished away by hand with 3 micron powder in kerosine on a cotton tip. The testing procedure is continued until the surface contours show that the specimen is flat and parallel over more than 50% of its central area and to within one-tenth the acoustic wavelength to be propagated. The acoustic wave is propagated within this central area.

The concentration of CN^- in RbCl was determined from the infrared absorption α for the 2075 cm^{-1} line using the relation

$$N = \sigma \alpha$$

where σ is $1.8 \times 10^{19} \text{ cm}^{-2}$ as determined by Harrison, Peressini, and Pohl⁵.

The OH^- concentration of RbCl was determined by measuring the u.v. absorption coefficient at $2150\text{\AA}$ and σ is $3.4 \times 10^{16} \text{ cm}^{-2}$ according to Klein et al.⁶

For CN^- in KCl , the infrared absorption coefficient at 2105 cm^{-1} is measured and σ is $3.6 \times 10^{19} \text{ cm}^{-2}$.⁷ Similarly, CNO^- was measured at 2132 cm^{-1} and σ taken as $7 \times 10^{17} \text{ cm}^{-2}$.⁷

Since σ has not been determined for CNO^- in RbCl , the value of σ is taken as the same as for CNO^- in KCl . This should allow an order of magnitude estimate of the CNO^- concentration⁵.

E. Cadmium Sulfide Transducer Preparation

The transducer preparation technique is similar to that described by Auyang⁴ and deKlerk⁸. In this vapor deposition technique cadmium and sulfur are melted in separate crucibles within the evaporator and are deposited simultaneously upon the specimen. With the specimen at a temperature between 180°C and 200°C , the vapors combine to form a cadmium sulfide film on the substrate. A quartz crystal microbalance was used to determine the thickness during transducer growth. Small variations among the crucibles for cadmium and sulfur cause variations in the deposition rate. By monitoring the film thickness, quite reproducible transducers can be made.

III. COMPLIANCE CHANGE

A. Classical Theory: Nowick-Heller Selection Rules

In the classical theory of the anelastic relaxation of crystals, an interstitial or substitutional defect can produce an anisotropic distortion of the host lattice. Depending upon the symmetry of the host crystal, there are several equivalent equilibrium positions for which the defect has the same energy. If the system is unstressed and in thermodynamic equilibrium, these equivalent sites are equally populated. By the application of a stress with a non-hydrostatic component an imbalance of the populations of these sites may result so that they are no longer equivalent. Since the strain due to the defect is anisotropic, the macroscopic result is a change of the compliance relative to the host crystal. It is dependent upon the concentration of defects, the kind of defect, and the temperature. The populations of the various sites are governed by Boltzmann statistics.

In analogy with the interaction energy of an electric dipole in an applied electric field, the energy of an elastic dipole with an applied stress field is ³

$$u_p = - \sum_{ij} v_{ij}^p \sigma_{ij} = -v_o \sum_{ij} \lambda_{ij}^p \sigma_{ij}$$

Where u_p is the elastic interaction energy per unit volume per unit concentration of impurities or orientation p ; σ_{ij} is the ij^{th} component of the applied stress; v_{ij}^p is the ij^{th} component of the elastic dipole tensor of one defect; and

v_0 is the volume of a primitive cell of the host crystal. The components λ_{ij}^p are dimensionless numbers and related to the elastic dipole tensor v_{ij}^p by the volume of a primitive cell of the host crystal. Since the v_{ij}^p are components of a homogeneous strain, the v -tensor is symmetric. Similarly, the λ -tensor is also symmetric and can be described by a strain ellipsoid with the principal values $\lambda_1, \lambda_2, \lambda_3$. Hence for a given defect orientation p , the components of the λ -tensor are given by

$$\lambda_{ij}^p = \sum_{m=1}^3 a_{im}^p a_{jm}^p \lambda_m$$

where a_{im}^p (a_{jm}^p) is the direction cosine between the i^{th} (j^{th}) direction and the principal axis m for the orientation p . The λ_m are the principal values of the λ -tensor. The principal axes of the λ -tensor can be found from the symmetry of the defect and its equilibrium sites.

For a low concentration of defects, the strain equation may be written as

$$\epsilon_{ij} = \sum_{k,l} s_{ijkl} \sigma_{kl} + \sum_{p=1}^n \lambda_{ij}^p c_p$$

where s_{ijkl} are the unrelaxed compliance coefficients and the reference strain is taken at $c_p = C_0/n$. The number of equilibrium orientations are given by n . The term

$\sum_{p=1}^n \lambda_{ij}^p c_p$ is the elastic part of the strain. The quan-

tity $c_p = C_p - C_0/n$ is the difference between the concentration of the defects of orientation p and the unstressed

equilibrium situation. Hence the anelastic strain due to the defects is given by

$$\eta_{ij} = \sum_{p=1}^n \lambda_{ij}^p c_p = \sum_{p=1}^n \lambda_{ij}^p (c_p - c_o/n)$$

The mole fraction of defects in orientation p at temperature T is given by the expression

$$c_p = \frac{c_o e^{-u_p/kT}}{\sum_{g=1}^n e^{-u_g/kT}}$$

where u_p and u_g are the elastic interaction energies. The change in compliance due to the defects relative to the pure crystal is

$$\delta s_{ijkl} = \frac{\partial \eta_{ij}}{\partial \sigma_{kl}} = \sum_{p=1}^n \frac{\partial c_p}{\partial \sigma_{kl}} \lambda_{ij}^p$$

This equation may be reduced to³

$$\delta s_{ijkl} = \frac{v_o c_o}{n k T} \left[\sum_{p=1}^n \lambda_{ij}^p \lambda_{kl}^p - \frac{1}{n} \left(\sum_{p=1}^n \lambda_{ij}^p \right) \left(\sum_{p=1}^n \lambda_{kl}^p \right) \right]$$

where the approximation of the elastic energy u_p is small compared to kT .

The stress is related to the strain by Hooke's Law

$$T_i = c_{ij} S_j \quad \text{or} \quad S_i = s_{ij} T_j$$

where these equations are written in two index notation².

The convention of summing over repeated indices applies to these equations. The subscripts i and j may have values from one to six. T_i is the i^{th} component of the stress and S_i is

the i^{th} component of the strain. The quantities s_{ij} and c_{ij} are the elastic compliance and the stiffness.

For a cubic crystal, the elastic compliances are found to be related to the stiffnesses as follows:

$$s_{44} = \frac{1}{c_{44}}; \quad s_{11} - s_{12} = \frac{1}{c_{11} - c_{12}}; \quad s_{11} + 2s_{12} = \frac{1}{c_{11} + 2c_{12}}$$

Since the group theoretical compliances for crystals of cubic symmetry are

$$s_{A_{1g}} = s_{11} + 2s_{12}$$

$$s_{E_g} = s_{11} - s_{12}$$

$$s_{T_{2g}} = \frac{1}{2} s_{44}$$

the fractional changes of the group theoretical compliances can be related to the fractional changes of the stiffnesses.

$$\text{Hence, } \frac{\Delta c_{44}}{c_{44}} = - \frac{\Delta s_{44}}{s_{44}} = - \frac{\Delta s_{T_{2g}}}{s_{T_{2g}}}$$

$$\frac{\Delta(c_{11} - c_{12})}{c_{11} - c_{12}} = - \frac{\Delta(s_{11} - s_{12})}{s_{11} - s_{12}} = - \frac{\Delta s_{E_g}}{s_{E_g}}$$

$$\frac{\Delta(c_{11} + 2c_{12})}{c_{11} + 2c_{12}} = - \frac{\Delta(s_{11} + 2s_{12})}{s_{11} + 2s_{12}} = - \frac{\Delta s_{A_{1g}}}{s_{A_{1g}}}$$

The velocities of propagation of an acoustic wave along the various principal directions in a cubic crystal are given in Table I. These velocities can be expressed in terms of the group theoretical compliance coefficients. Using these equations the fractional change of the compliance can be found

from the fractional velocity change. For a single defect species, a hydrostatic stress cannot produce a compliance change, i.e. $\Delta S_{\lambda_{1g}}$ is zero.

The three types of substitutional defects which occur in cubic crystals are the $\langle 100 \rangle$ tetragonal dipole, the $\langle 111 \rangle$ trigonal dipole, and the $\langle 110 \rangle$ orthorhombic dipole. From the symmetry of the substitutional site in the cubic crystal we have the following principal values of the λ -tensor:

$\lambda_1, \lambda_2 = \lambda_3$ for the $\langle 100 \rangle$ defect; $\lambda_1, \lambda_2 = \lambda_3$ for the $\langle 111 \rangle$ defect; and, in general, $\lambda_1 \neq \lambda_2 \neq \lambda_3$ for the orthorhombic defect. Using these principal values and taking the major axis of the elastic dipole tensor in one of these principal directions, the compliance changes are of various types of substitutional defects as follows:

$$\langle 100 \rangle \quad \delta S_{Eg} = \delta(S_{11} - S_{12}) = \frac{C_o v_o}{3kT} (\lambda_1 - \lambda_2)^2; \quad \delta S_{T_{2g}} = 0$$

$$\langle 111 \rangle \quad \delta S_{T_{2g}} = \frac{\delta S_{44}}{2} = \frac{2C_o v_o}{9kT} (\lambda_1 - \lambda_2)^2; \quad \delta S_{Eg} = 0$$

$$\langle 110 \rangle \quad \delta S_{Eg} = \frac{C_o v_o}{3kT} \left(\frac{\lambda_1 + \lambda_2}{2} - \lambda_3 \right)^2;$$

$$\delta S_{T_{2g}} = \frac{\delta S_{44}}{2} = \frac{C_o v_o}{6kT} (\lambda_1 - \lambda_2)^2$$

Table I summarizes the expressions for the velocity and lists which defect type will or will not produce a compliance change.

TABLE I.

Nowick-Heller Selection Rules

An interaction is indicated by an 'x' under the appropriate defect type. No interaction is shown by '0'. The velocity of a given acoustic wave times the square root of the density is expressed in terms of the appropriate elastic moduli (C_{ij}). The 'stress symmetry' indicates the representations of the cubic group according to which the stress tensor of a given acoustic mode transforms.

Acoustic Wave Direction Polarization		Velocity x $\rho^{1/2}$	Stress Symmetry	Defect Type <100> <111> <110>		
<100>	<100>	$\left[\frac{1}{3}(C_{11}+2C_{12}) + \frac{2}{3}(C_{11}-C_{12}) \right]^{1/2}$	A_{1g}, E_g	X	0	X
<100>	any normal to <100>	$C_{44}^{1/2}$	T_{2g}	0	X	0
<110>	<110>	$\left[\frac{1}{2} \left(\frac{2}{3}(C_{11}+2C_{12}) + \frac{1}{3}(C_{11}-C_{12}) + 2C_{44} \right) \right]^{1/2}$	A_{1g}, E_g, T_{2g}	X	X	X
<110>	<001>	$C_{44}^{1/2}$	T_{2g}	0	X	0
<110>	<110>	$\left[\frac{1}{2}(C_{11}-C_{12}) \right]^{1/2}$	E_g	X	0	X
<111>	<111>	$\left[\frac{1}{3} \left((C_{11}+2C_{12}) + 4C_{44} \right) \right]^{1/2}$	A_{1g}, T_{2g}	0	X	0
<111>	any normal to <111>	$\left[\frac{1}{3} \left((C_{11}-C_{12}) + C_{44} \right) \right]^{1/2}$	E_g, T_{2g}	X	X	X

B. Quantum Theory

The quantum theory of the interaction of an acoustic stress wave, with a defect has been developed by Shuman⁹ by extending the Gomez, Bomen, Krumhansl¹⁰ theory of a defect in a set of overlapping spherical harmonic wells. By considering a stress interaction term H_0 to the Hamiltonian of the tunneling impurity, perturbation theory yields the corrections to the energy levels of the unperturbed defect system. To calculate the compliance change, the free energy of the system can be found from the expression

$$F = -KT \ln Z$$

where Z is the partition function and is given by

$$Z = \sum_i e^{-E_i/KT} \quad (1)$$

for a system of discrete energy levels. The energy E_i of the i^{th} level includes the perturbation correction.

The change in compliance can be found from²⁹

$$\delta s_{ij} = n \lim_{\sigma_{ij} \rightarrow 0} \frac{\partial^2 F}{\partial \sigma_{ij}^2}$$

where n is the number of defects per unit volume,

δs_{ij} is the compliance change, and σ_{ij} is the acoustic stress. Using the expressions for the partition function and the free energy, the compliance change can be written as

$$\begin{aligned} \delta s_{ij} = \lim_{\sigma_{ij} \rightarrow 0} & \left(\frac{n}{Z^2 KT} \left[\sum_i \frac{\partial E_i}{\partial \sigma_{ij}} e^{-E_i/KT} \right]^2 \right. \\ & \left. + \frac{n}{Z} \sum_i \left[\frac{\partial^2 E_i}{\partial \sigma_{ij}^2} - \frac{1}{KT} \left(\frac{\partial E_i}{\partial \sigma_{ij}} \right)^2 \right] e^{-E_i/KT} \right) \end{aligned} \quad (2)$$

The acoustic stress interaction energy is

$$H(\sigma) = v_o \sum_{ij} \lambda_{ij} \sigma_{ij}$$

Both Nowick and Heller³ and Welsh¹¹ treated the elastic dipole tensor as a rigid ellipsoid and rotated it to find the appropriate λ_{ij} 's which interact with the stress. Shuman expanded the λ_{ij} components of the elastic dipole tensor in a three-dimensional Taylor series about the lattice defect site and found that, for a cubic system, the λ -tensor can be written as

$$\lambda = \begin{pmatrix} ax^2 & bxy & bxz \\ bxy & ay^2 & byz \\ bxz & byz & az^2 \end{pmatrix} + c(x^2+y^2+z^2) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The three constants a, b and c completely determine the distortion around the defect. This λ -tensor reflects the symmetry appropriate to a given position for cubic symmetry and is not a rigid ellipsoid. The connection of the λ -tensor to the Nowick-Heller λ -tensor can be seen by considering a $\langle 111 \rangle$ defect. In this case $x = y = z = x_o$. Hence

$$\lambda = x_o^2 \begin{pmatrix} a & b & b \\ b & a & b \\ b & b & a \end{pmatrix} + 3cx_o^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Diagonalizing this λ -tensor and writing it in principal coordinates, it is found that

$$\lambda^p = x_o \begin{pmatrix} a+2b+3c & 0 & 0 \\ 0 & a-b+3c & 0 \\ 0 & 0 & a-b+3c \end{pmatrix}$$

By comparing this with Nowick-Heller's λ -tensor in principal coordinates, the following identification results: for the $\langle 111 \rangle$ defect, $\lambda_1 - \lambda_2 = 3bx_o^2$; for the $\langle 100 \rangle$ defect $\lambda_1 - \lambda_2 = ax_o^2$; and for the $\langle 110 \rangle$ defect $\lambda_1 - \lambda_2 = 2bx_o^2$ and

$\lambda_1 + \lambda_2 - 2\lambda_3 = 2ax_0^2$. It should be noted that if the λ -tensor is required to be rotationally symmetric for all positions for a $\langle 111 \rangle$ or $\langle 100 \rangle$ defect, a is equal to b .

Then the above equation represents the rotation of a rigid ellipsoid expressed in Cartesian coordinates as was used by Welsh¹¹ and Hayes¹². The elastic interaction energy of the Hamiltonian for a given stress wave is found by considering the displacements produced by the acoustic wave and calculating the strains, hence identifying the appropriate elements of the stress tensor. To find the energies E_i needed for the free energy the Hamiltonian $H_T + H_0$ must be diagonalized. In those cases in which an explicit expression for the energy in closed form cannot be found by diagonalization, the energies E_i are found from second order perturbation theory, i.e.

$$E_i(\sigma) = E_i(0) + H_{ii}'(\sigma) + \sum_{i \neq j} \frac{|H_{ij}'(\sigma)|^2}{E_i - E_j}$$

This is used to find the compliance changes. The results of the quantum mechanical calculation of the compliance changes for the three defect types are tabulated in Table II. The quantity $S = e^{\frac{-m\omega x_0^2}{\hbar}} 0$ is the overlap integral between neighboring wells. The quantity Δ is the energy splitting between the levels due to tunneling and is given by $\Delta = \hbar\omega (2V_b/\hbar\omega)^{1/2} \exp(-2V_b/\hbar\omega)$ where V_b is the barrier height between the wells and $\hbar\omega$ is the energy difference between adjacent states for a single well¹³.

There are two important conclusions which may be drawn from the quantum mechanical calculations. The quantum

TABLE II.

Quantum Mechanical Compliance Change Results

Defect Type	Stress Symmetry	Compliance Change per Unit Concentration
<100>	T_{2g}	$\delta s_{44} = \frac{-a^2 s^2}{\Delta} \left[\frac{e^{-2\beta\Delta}}{1+3e^{-2\beta\Delta}+2e^{-3\beta\Delta}} \right]$
	E_g	$\delta(s_{11} - s_{12}) = \frac{-a^2}{9\Delta} \left[\frac{6\beta\Delta(3e^{-2\beta\Delta}+e^{-3\beta\Delta}) + (1-e^{-3\beta\Delta})}{1+3e^{-2\beta\Delta}+2e^{-3\beta\Delta}} \right]$
<110>	T_{2g}	$\delta s_{44} = \frac{b^2}{Z_o} \left[\frac{3\beta\Delta(e^{-\beta\Delta}+e^{-3\beta\Delta})}{2} + 1 + \frac{3}{2} e^{-\beta\Delta} + e^{-2\beta\Delta} - \frac{7}{2} e^{-3\beta\Delta} \right]^*$
	E_g	$\delta(s_{11}-s_{12}) = \frac{-a^2}{2\Delta Z_o} \left[\beta\Delta \left(\frac{3}{4} e^{-\beta\Delta} + 3 e^{-2\beta\Delta} + \frac{7}{4} e^{-3\beta\Delta} \right) + 1 + \frac{9}{4} e^{-\beta\Delta} - \frac{13}{4} e^{-3\beta\Delta} \right]$
<111>	T_{2g}	$\delta s_{44} = \frac{4}{9} \frac{v_o^2 (\lambda_1 - \lambda_2)^2}{\Delta} \left[\tanh \frac{\beta\Delta}{2} + \frac{\beta\Delta}{2} \operatorname{sech}^2 \frac{\beta\Delta}{2} \right]$
	E_g	$\delta(s_{11} - s_{12}) = \frac{4}{9} \frac{v_o^2 (\lambda_1 - \lambda_2)^2}{\Delta} s^2 \left[\frac{\beta\Delta}{2} \operatorname{sech} \frac{\beta\Delta}{2} \right]$
* $Z_o = 1 + 3e^{-\beta\Delta} + 3e^{-2\beta\Delta} + 5e^{-3\beta\Delta}$		

mechanical compliance change in all cases yields the appropriate classical result for high temperatures and deep wells, i.e. $S = 0$. The selection rules are still obeyed although some of the quantum mechanical expressions for the compliance change have slightly different numerical coefficients from the classical results.

C. Discussion of Random Internal Stress on the Compliance Change

The fact that internal stresses are important can be seen, for example, in the stress dichroism measurements on KCl:CN by Seward and Narayamurti⁷. The inclusion of random internal stresses as an additional term to the Hamiltonian has resulted in the successful description of the complex dielectric constant of RbCl:CN by Hayes¹².

In order to determine the effect of a random stress upon the compliance change, the wavefunctions of the Hamiltonian for tunneling and random stress can be found. These wave functions can be expressed as a linear combination of wavefunctions of the isolated "deep well" wavefunctions to good approximation, that is,

$$|\psi_k(\sigma_R, 0)\rangle = \sum_{i=1}^N c_i^k |i\rangle$$

where the coefficients are dependent on the particular values of stress chosen for the random stress and the index "i" labels the equilibrium sites. These coefficients are found by diagonalizing the Hamiltonian consisting of a tunneling part plus a random stress part, i.e.

$$H_0 = H_T + H(\sigma_R)$$

In general, $H(\sigma_R)$ contains all the components of stress. Then, using perturbation theory, the energy of the system including the interaction of the measuring stress with the elastic dipoles is given by

$$E_k(\sigma_R, \sigma_m) = E_k(\sigma_R, 0) + H'_{kk}(\sigma_m) + \sum_{k \neq l} \frac{|H'_{kl}|^2}{E_k - E_l}$$

Once the energies E_k are known, the compliance change can be found from equation (1). The matrix elements H'_{kl} can be written as

$$\langle \psi_k(\sigma_R, 0) | H(\sigma_m) | \psi_l(\sigma_R, 0) \rangle = \sum_{i,j} c_i^k c_j^l \langle i | H(\sigma_m) | j \rangle$$

Hence, these matrix elements for the perturbation theory correction to the energy are known in terms of the matrix elements $\langle i | H(\sigma_m) | j \rangle$.

For a shear wave propagating in the $\langle 100 \rangle$ direction with polarization in the $\langle 010 \rangle$ direction, the displacements of the atoms may be taken as $u = 0$; $v = v_0 e^{-i(kx - \omega t)}$; $w = 0$

where the displacements u , v , and w refer to the $\langle 100 \rangle$, $\langle 010 \rangle$, and $\langle 001 \rangle$ directions, respectively. The strains due to this displacement is $e_{xy} = -iKv$ and the resulting measuring stress is

$$\sigma = \begin{pmatrix} 0 & \sigma & 0 \\ \sigma & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Hence the perturbation due to the measuring stress is given

$$\text{by} \quad H(\sigma_m) = 2 v_o b \sigma_{xy}$$

The matrix elements of $H(\sigma_m)$ are given by

$$\begin{aligned} \langle i | H(\sigma_m) | j \rangle &= 2 v_o b \sigma \quad \langle i | xy | j \rangle \\ &= \pm 2 v_o b \sigma x_o^2 \text{ for } i = j \\ &= \pm s x_o^2 \text{ or } 0 \text{ if } i \neq j \end{aligned}$$

where the plus sign refers to odd numbered states and the negative sign to even numbered states. Substituting this result into the equation for the energy and taking the appropriate derivatives to find the compliance, the compliance can be found from equation (2). Similarly, for a shear wave in the $\langle 110 \rangle$ direction with polarization $\langle 1\bar{1}0 \rangle$, the perturbation Hamiltonian is

$$H(\sigma_m)_{1\bar{1}0} = a v_o (x^2 - y^2)$$

The matrix elements of $H(\sigma_m)_{1\bar{1}0}$ can be written in terms of the matrix elements:

$$\begin{aligned} \langle i | x^2 - y^2 | j \rangle &= 0 \quad \text{if } i = j \\ &= O(s) \text{ if } i \neq j \end{aligned}$$

Hence for this wave the compliance change depends on s^2 ,

that is $\delta S_{Eg} = O(s^2)$. Therefore even in the presence of

a random stress the selection rules are obeyed for a $\langle 111 \rangle$ defect and an E_g or T_{2g} measuring stress. Analogous results are obtained for the $\langle 100 \rangle$ and $\langle 110 \rangle$ defects in the presence of random stress. The temperature dependence and elastic dipole dependence of the compliance changes are unchanged.

In Appendix I, the matrix elements of the stress perturbation are tabulated for the $\langle 111 \rangle$ defect.

D. Experimental Results

KCl:Li⁺

The system KCl:Li⁺ has been thoroughly studied by a number of authors¹⁴. It has been established that the lithium ion which substitutes for potassium in KCl does not sit at the lattice site. Rather, the lithium ion is displaced in the $\langle 111 \rangle$ crystal directions. Since the potential minimas of the Li⁺ ion in KCl are in the $\langle 111 \rangle$ directions, the Li⁺ ion in KCl is a $\langle 111 \rangle$ defect. This system has been used to test the Nowick-Heller Selection Rules.

Figures 5 and 6 present the compliance change measured for KCl:Li⁺ for all the acoustic modes listed in Table I except the last mode. This mode, a shear wave propagating in the $\langle 111 \rangle$ direction, was measured by B. Yap. The data of Figure 5 are normalized to unit concentration and demonstrate the linear dependence of the compliance change on concentration. The compliance change of KCl:Li⁺ shows a $1/T$ behavior below 15°K for interacting acoustic modes. Figure 6 combines measurements of pure KCl and KCl:Li⁺. The pure crystal data indicates that the compliance change of the pure crystal is independent of temperature below 15°K. For those acoustic

Fig. 5. KCl:Li⁺ Compliance change per unit concentration vs. $1/T$

Fig. 6 KCl and KCl:Li⁺ Compliance change vs. $1/T$

TABLE III.

Table of Experimental Results

Acoustic Wave		Nowick-Heller		
<u>Direction</u>	<u>Polarization</u>	<u>Rules</u> <u><111> Defect</u>	<u>RbCl:CN⁻</u>	<u>KCl:Li⁺</u>
$\langle 100 \rangle$	$\langle 100 \rangle$	0	0	0
$\langle 100 \rangle$	any normal to $\langle 100 \rangle$	X	X	X
$\langle 110 \rangle$	$\langle 110 \rangle$	X	X	X
$\langle 110 \rangle$	$\langle 001 \rangle$	X	X	X
$\langle 110 \rangle$	$\langle 1\bar{1}0 \rangle$	0	0	0
$\langle 111 \rangle$	$\langle 111 \rangle$	X	X	X
$\langle 111 \rangle$	any normal to $\langle 111 \rangle$	X	X	X

Fig. 7. RbCl:CN⁻: T_{2g} Compliance change per unit concentration vs. $1/T$

Fig. 8. RbCl:CN^- ; E_g Compliance change vs. $1/T$

Fig. 9. RbCl (pure): Compliance change vs. $1/T$

modes which do not interact with Li^+ in KCl, Figure 6 also indicates that no interaction occurs.

The results of the compliance change measurements on $\text{KCl}:\text{Li}^+$ are tabulated in Table III and compared with the Nowick-Heller Selection Rules for a defect with potential minima in the $\langle 111 \rangle$ crystal directions. From this comparison it is concluded that the Nowick-Heller Selection Rules are valid.

$\text{RbCl}:\text{CN}^-$

The fractional compliance change per unit concentration is presented as a function of $1/T$ for the system $\text{RbCl}:\text{CN}^-$ in Figure 7. This system was chosen to test the power of the Nowick-Heller Selection Rules to determine the potential minima of the defect CN^- . The conclusions of specific heat⁵ measurements and paraelectric²⁹ resonance experiments do not agree upon the directions of the potential minima for the impurity CN^- in RbCl. The compliance changes of Figures 7 and 8 show that there is a stress interaction with acoustic waves which have a T_{2g} symmetry component. Figure 9 shows the compliance change versus $1/T$ for pure RbCl. All the longitudinal and shear acoustic¹⁴ wave modes have been measured on $\text{RbCl}:\text{CN}^-$. They show that for acoustic waves with a T_{2g} component, there is an interaction; and for acoustic waves with an E_g component, there is no interaction. The results of the compliance changes measured on $\text{RbCl}:\text{CN}^-$ are also tabulated in Table III.

The compliance data for RbCl:CN^- (Fig. 7) display a slope change at approximately 0.175°K^{-1} . This is believed due to internal stress. Microwave dielectric measurements¹² on RbCl:CN^- were satisfactorily explained only after random internal stresses were included with the potential minimas in the $\langle 111 \rangle$ directions. Again, calculation²¹ of the specific heat of RbCl:CN^- agreed with experiment only after a random internal stress was included with the eight potential minima in the $\langle 111 \rangle$ directions. Figure 10 shows that the peak height is directly proportional to the concentration. The compliance changes measured at 30 MHz. and approximately 450 MHz. show no frequency dependence.

An estimate of the overlap integral S may be made by using the quantum mechanical expressions of the compliance listed in Table II for a $\langle 111 \rangle$ defect. Taking the high temperature limit, we find that

$$\frac{\delta(s_{11} - s_{12})}{\delta s_{44}} = \frac{s^2}{2}$$

Using this expression, the overlap integral S is .06. From the Nowick-Heller expression for the compliance change for a $\langle 111 \rangle$ defect, the values of the elastic dipole CN^- in RbCl are tabulated in Table IV.

Figures 11 and 12 present the high temperature compliance change as a function of temperature plotted on double log scale to illustrate any power law behavior. The compliance change plotted is that obtained from the equation

$$2 \left| \Delta v/v \right| = 2 \left| (\Delta f_c/f_c) (f_I/f_R) \right|$$

Fig. 10. $\text{RbCl}:\text{CN}^-$: Peak of T_{2g} compliance change vs. concentration

TABLE IV.

Values of the Elastic Dipole of CN^- in RbCl .

Concentration $10^{17}/\text{cm}^3$	Temperature Region $(1/T) \text{ } ^\circ\text{K}^{-1}$	Slope of Compliance versus $1/T$ $10^{-3} (^\circ\text{K})$	Elastic Dipole $v_o (\lambda_1 - \lambda_2)$ 10^{-23} cm^3
1.5	.25-.60	2.20	.98
1.2	.25-.5	2.06	1.0
3	.20-.40	5.56	1.1
4	.25-.55	5.97	.99
5.7	.25-.55	7.48	.93

$$\text{Average } v_o (\lambda_1 - \lambda_2) = 1.0 \times 10^{-23} \text{ cm}^3$$

Fig. 11. RbCl:CN⁻ Total high temperature compliance change vs. temperature.

Fig. 12. RbCl (pure) and KCl (pure): Total high temperature compliance change vs. temperature

The power law behavior of the attenuation is shown in the next chapter. Considering the compliance and attenuation as the real and imaginary parts of a response function, they must be related by the Kramers-Kronig relations. These equations relate the real and imaginary parts of a response function to each other as a function of frequency. They imply that the temperature behavior of the real part and the imaginary part should be the same. The high temperature compliance change is approximately T^4 for a few cases and seems to be a bit stronger for the pure crystals. This power law behavior resembles that exhibited by the attenuation in the next chapter.

IV. ATTENUATION CHANGE

A. Theoretical Predictions For Pure Crystals

The absorption of acoustic waves in solid substances has been treated by a number of authors^{16,17,18}. Their quantum mechanical treatment for $\omega\tau > 1$ considers collisions between acoustic and thermal phonons. The acoustic frequency is $\omega/2\pi$ and the average phonon lifetime is τ . It is assumed that the average phonon lifetime is long enough so that the energy and momentum of the phonons are well defined. This implies that energy and momentum conservation are obeyed for collisions between acoustic and thermal phonons. It is found that the velocity of the acoustic wave must be less than or equal to the velocity of the thermal phonons of the acoustic branch. Hence, high velocity longitudinal acoustic waves can interact with collinear, low frequency thermal phonons only if all three phonons are longitudinal and collinear. Thus the attenuation of longitudinal waves should be negligible. Since these calculations consider only third order strains in the potential energy of the lattice, the attenuation calculated only takes account of three phonon processes. The attenuation of a transverse wave interacting with a longitudinal phonon in an isotropic substance is given¹⁶ by

$$a_T = \frac{\pi}{80} \frac{\gamma_{tl}^2}{\rho} \left[1 - \left[\frac{v_t}{v_l} \right]^2 \right] \frac{k_B^4}{v_l^6 \hbar^3} \omega T^4 \quad (\text{cm}^{-1})$$

In this expression, k_B and $\hbar$ are Boltzmann's and Planck's constants, v_l and v_t are the longitudinal and transverse

velocities, ρ is the density, and γ_{tl} is an anharmonicity factor composed of second and third order elastic constants. Shiren¹⁷ derived an expression for γ_{tl} for transverse acoustic waves propagating in the $\langle 100 \rangle$ direction which is

$$\gamma_{tl} = \frac{c_{11} + c_{12} + 4c_{44} + 4c_{166}}{2c_{11}}$$

It was observed by Simon¹⁸ that the attenuation of longitudinal waves is due basically to the finite thermal phonon lifetime which relaxes the conservation of energy condition of three phonon collisions. It seems that this process dominates the attenuation of longitudinal waves. Shiren found the following expression for the attenuation of longitudinal waves in a cubic crystal:

$$a_1 = \frac{\pi^2 \hbar \omega}{60 \rho^3 v^{10} \beta^5} \left[\frac{kT}{h} \right]^4 \left[\omega r \int_{-1}^{+1} \frac{[G(x)]^2 dx}{1 + [\omega r(1-\beta x)]^2} \right] (\text{cm}^{-1})$$

where $x = \cos \theta$; θ is the angle between the acoustic and thermal phonon propagation directions; and $G(x) = A_{111}x^2 + A_{112}(1-x^2)$; $A_{111} = 3c_{11} + c_{111}$; $A_{112} = c_{12} + c_{112}$.

The quantity ωr is the ratio of the thermal phonon to ultrasonic wave velocity. Again, in the region of $\omega r > 1$, the square-bracketed factor is expanded in a power series of $(1/\omega r)$ and yields the terms $A_1 + A_2$, and these are given by the expressions

$$A_1 = A_{111}^2 \left[\arctan (1+\beta)\omega r - \arctan (1-\beta)\omega r \right],$$

$$A_2 = 1/\omega r \left[\frac{8}{3} (A_{111} - A_{112})^2 + 4A_{111} (A_{111} - A_{112}) (1 - \log_e 2\omega r) \right].$$

For the condition $(1+\beta)\omega r \gg 1 \gg (1-\beta)\omega r$, the term A_1 is temperature independent and neglecting terms of $1/\omega r$, the attenuation yields a T^4 behavior for longitudinal sound waves. If $\omega r(1-\beta) \gg 1$, the attenuation is proportional to $T^4/\omega r$; and since r is temperature dependent, the attenuation of longitudinal waves is proportional to T^n ($n \geq 4$). For the case $\omega r \gg 1 \gg (1-\beta)\omega r$, the attenuation of longitudinal waves given above becomes¹⁷

$$a = \frac{\pi^3}{120} \frac{\gamma_{11}^2}{\rho v_1^6} \frac{k_B^4}{h^3} \omega T^4 \quad (\text{cm}^{-1})$$

where, for the waves propagating in the $\langle 100 \rangle$ direction

$$\gamma_{11} = (3c_{11} + c_{111}) / c_{11}$$

for the $\langle 110 \rangle$ direction

$$= 3 + \frac{6c_{166} + c_{112}/2 + c_{111}/2}{c_{11} + c_{12} + 2c_{44}}$$

and for the $\langle 111 \rangle$ direction

$$= 3 + \frac{c_{111} + 6c_{112} + 2c_{123} + 12c_{144} + 24c_{166} + 16c_{456}}{3(c_{11} + 2c_{12} + 4c_{44})}$$

When $\omega r < 1$, the mean free path of a thermal phonon is less than the acoustic wavelength and the acoustic wave interacts with an entire set of thermal phonons. This region is treated by Akhieser¹⁹ by considering the thermal phonons as a phonon gas and the acoustic wave as a uniform, time-dependent strain which upsets the thermal equilibrium. The origin of the attenuation arises from the fact that straining isothermally and adiabatically, i.e. at constant phonon occupation number, is not the same and each mode relaxes to its

equilibrium temperature by phonon-phonon collisions. The results of Akhieser¹⁹ and Mason²⁰ are that the attenuation is independent of temperature and varies as the square of the acoustic frequency.

B. Theoretical Predictions For Impure Crystals

The attenuation due to impurities in a crystal can be understood in terms of the Nowick-Heller Theory which was described in Chapter III on the compliance change. If a stress wave is propagated in a crystal containing impurities with several equivalent sites, the original thermodynamic equilibrium is disturbed, and the populations of the various impurity sites changes. The result is a change of compliance if the applied stress is of the correct symmetry for the particular type defect. Since the reorientation of the elastic dipole is not instantaneous, there is an energy loss and a time lag between the applied stress and the resultant strain. Then the propagation of an acoustic wave may be considered as being governed by a complex compliance, the real part of which gives the compliance change, and the imaginary part gives the attenuation change. Since these follow a Debye equation³, the attenuation coefficient is given by

$$\alpha = \frac{\delta \omega}{2\pi v} = \frac{\Delta s}{s} \frac{1}{2\pi v} \frac{\omega^2 r}{(1 + \omega^2 r^2)}$$

where Δs is the compliance change as given in Chapter III, r is the orientation relaxation time, v is the velocity of the acoustic wave, and δ is the logarithmic decrement. The

real part of the complex compliance change is given by

$$\frac{\delta s(T, \omega)}{s} = \frac{\Delta s}{s} \frac{1}{1 + \omega^2 r^2}$$

For a single thermal activation process, the relaxation time for orientation can be written as

$$r = r_0 e^{E/kT}$$

where E is the activation energy and $1/r_0$ is the "attempt frequency". If $\omega \ll 1/r$, the attenuation becomes

$$\alpha \approx \frac{\Delta s}{s} \frac{1}{2\pi\nu} \omega^2 r(T)$$

and for $E \ll kT$, $r \approx r_0$ and the temperature dependence of the attenuation is given by the temperature dependence of the compliance change (s) which is $1/T$.

For a tunneling system which implies a resonance system, one can assume a Lorentzian frequency dependence. Then the attenuation is given by^{4, 30}

$$\alpha \approx \frac{\Delta s}{s} \frac{\omega_0^2 \omega^2 \Gamma}{[\omega_0^2 - \omega^2]^2 + \omega^2 \Gamma^2}$$

which yields for $\omega \ll \omega_0$,

$$\alpha \approx \frac{\Delta s}{s} \frac{\omega^2 \Gamma}{\omega_0^2}$$

If the half-width Γ of the resonance peak is temperature independent, the attenuation is again proportional to the square of the ultrasonic frequency and inverse temperature.

The results of these two cases imply that the cases of thermal relaxation and of tunneling cannot be distinguished.

However, since it is known from dielectric measurements^{12, 21} that the rearrangement of the dipoles occurs by tunneling, the

attenuation suggested for a tunneling system would be expected to be more appropriate.

C. Experimental Results of Attenuation Change

The attenuation change is presented in this section for several alkali halides with or without an impurity. Figure 13 shows the dependency of r the thermal phonon lifetime on temperature. This allows as estimate of the temperature at which $\omega r = 1$, and was obtained from the relation

$$r = \frac{3K}{C_v \bar{v}^2}$$

where K is the thermal conductivity, C_v is the specific heat per unit volume and $\bar{v}$ is the average Debye velocity. The low temperature specific heat and thermal conductivity was obtained from Harrison, Peressini, and Pohl²², the high temperature specific heat from Kirkham and Yates²³, and the mean Debye velocity from the expression²⁴

$$\frac{1}{\bar{v}^3} = \frac{1}{3} \left(\frac{2}{\bar{v}_T^3} + \frac{1}{\bar{v}_L^3} \right)$$

The quantity $\bar{v}_T$ is the average of the principal shear wave velocities, and $\bar{v}_L$ is the average of the principal longitudinal wave velocities. Since the velocities depend on the density of the material, low temperature densities as determined by Urvas²⁵ were used. The elastic constants at 4.2°K. to 5% are found to be:

TABLE V.

Elastic Constants at Low Temperature

RbCl (pure)		
C_{11}	=	4.28×10^{11} dynes/cm ²
C_{12}	=	$.66 \times 10^{11}$ dynes/cm ²
C_{44}	=	$.40 \times 10^{11}$ dynes/cm ²
Density (4.2°K.) = 2.868 gm/cm ³

Fig. 13. RbCl (pure): Temperature vs. phonon relaxation time

The Debye temperature was calculated using the equation²⁴

$$\Theta_D = \frac{h}{k} \left[\frac{3n}{4\pi} \right]^{1/3} v_m$$

where h and k are Planck's and Boltzmann's constants, n is the number of atoms per cubic centimeter, and v_m is the mean Debye velocity. The results for RbCl are: $\Theta_D = 174^\circ\text{K}$.

This value compares with Rollefson and Peressini's²⁶

$$\Theta_D = 169^\circ\text{K. for RbCl.}$$

The attenuation results for pure and impure crystals can be divided into two parts. The first part demonstrates the power law behavior of the attenuation change versus temperature and shows the T^4 behavior in the high temperature region. The second part presents the attenuation versus the inverse temperature. These show the increase of the attenuation as low temperatures are approached as predicted by Nowick and Heller for impurities which have several equilibrium sites. Each graph gives the value of the background attenuation which is subtracted from the raw data. Figure 14 shows that the attenuation is approximately proportional to T^4 for pure RbCl for the $\langle 100 \rangle$ and $\langle 111 \rangle$ longitudinal waves. Figure 15 presents the high temperature region of the attenuation of RbCl:CN for longitudinal waves in the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions. The slope is not changed significantly by the various increasing concentrations measured up to $6 \times 10^{17} \text{ CN}^-/\text{cm}^3$. Figure 16 presents the high temperature attenuation for OH^- impurities in RbCl, and again the

Fig. 14. RbCl (pure): Attenuation change vs. temperature

Fig. 15. RbCl:CN⁻: Attenuation change vs. temperature

Fig. 16. RbCl:OH^- : Attenuation change vs. temperature

attenuation is approximately T^4 . Auyang⁴ presented the same results for the high temperature attenuation in KCl and KCl:Li⁺.

To illustrate the effect of a re-orienting impurity, the attenuation is replotted as a function of $1/T$ since the temperature dependence of the attenuation due to this type of impurity is expected to be proportional to $1/T$. Figures 17 and 18 present the results for RbCl:CN⁻ for the E_g and T_{2g} symmetry modes of an acoustic wave. They also show the results for pure RbCl. It is seen that CN⁻ in RbCl interacts with acoustic waves with a T_{2g} symmetry component, and there is no interaction with waves with E_g symmetry components. Hence, the attenuation due to the impurity depends on the relaxation strength ΔS , just as the compliance does; and confirms the Nowick-Heller Selection Rules. The attenuation results for CN⁻ cannot confirm a linear $1/T$ behavior because of the presence of a peak in the attenuation, but the attenuation does increase as the temperature decreases.

This peak occurs at the same temperature at which the compliance change displays a slope change. The measurements of the microwave dielectric constant¹², specific heat⁵ and low frequency dielectric constant²¹ of RbCl:CN⁻ show that a satisfactory explanation of the experimental results could not be made by only using a model of the potential minima of the CN⁻ ion in its eight equivalent potential wells. In each case the inclusion of a random internal stress was required to broaden the energy levels of the system. With this random

Fig. 17. RbCl (pure) and RbCl:CN⁻: Attenuation of 100 longitudinal waves vs. 1/T

Fig. 18. RbCl (pure) and RbCl:CN⁻: Attenuation of $\langle 111 \rangle$ longitudinal waves vs. $1/T$

internal stress, it was found that the experimental and theoretical results agreed quite well. This suggests that random internal stresses play an important role on measurements in RbCl:CN^- and that the peak in the attenuation of RbCl:CN^- in Figure 18 is produced by these random internal stresses.

V. CONCLUSIONS

1. The Nowick-Heller Selection Rules are verified for RbCl:CN^- and KCl:Li^+ for all modes and principal directions of propagation for the first time. Both the impurities CN^- in RbCl and Li^+ in KCl are $\langle 111 \rangle$ defects. The high temperature compliance is approximately proportional to T^4 .
2. For small random internal stresses the Nowick-Heller Selection Rules remain valid.
3. Although the high temperature attenuation has been measured for several substances, it had not been measured for pure RbCl or "doped" RbCl . It is found that the high temperature attenuation of pure RbCl is approximately proportional to T^4 as it is for "doped" RbCl . Although the attenuation due to Li^+ in KCl was seen by Auyang⁴ and Byer¹⁵, it was not measured for RbCl:CN^- . It was found that the low temperature attenuation of RbCl:CN^- obeys the Nowick-Heller Selection Rules.
4. The average value of the CN^- elastic dipole RbCl is $1.0 \times 10^{-23} \text{ cm}^3$.

APPENDIX I.

Matrix Elements of the Elastic Dipole Tensor

For the XY-8 model the matrix elements of the elastic dipole tensor are presented in the basis of the isolated "deep well" wave functions. A typical function is

$$|a\rangle = \left(\frac{m\omega}{\pi\hbar}\right) \exp\left(-\frac{m\omega}{2\hbar} [(x-x_0)^2 + (y-x_0)^2 + (z-x_0)^2]\right)$$

These functions follow the labeling of the GBK¹⁰ paper.

Since the matrices are symmetric, only half of the elements are explicitly presented. The results are tabulated below for the following operators:

$$\langle i | x^2 | j \rangle = \begin{bmatrix} C & SA & S^2A & SC & SC & S^2A & S^3A & S^2C \\ & C & SC & S^2A & S^2A & SC & S^2C & S^3A \\ & & C & SA & S^3A & S^2C & SC & S^2A \\ & & & C & S^2C & S^3A & S^2A & SC \\ & & & & C & SA & S^2A & SC \\ & & & & & C & SC & S^2A \\ & & & & & & C & SA \\ & & & & & & & C \end{bmatrix}$$

$$\langle i | y^2 | j \rangle = \begin{bmatrix} C & SC & S^2A & SC & SC & S^2C & S^3A & S^2A \\ & C & SA & S^2A & S^2C & SC & S^2A & S^3A \\ & & C & SC & S^3A & S^2A & SC & S^2C \\ & & & C & S^2A & S^3A & S^2C & SC \\ & & & & C & SC & S^2A & SA \\ & & & & & C & SA & S^2A \\ & & & & & & C & SC \\ & & & & & & & C \end{bmatrix}$$

$$\langle i | z^2 | j \rangle = \begin{bmatrix} C & SC & S^2C & SC & SA & S^2C & S^3A & S^2A \\ & C & SC & S^2C & S^2A & SA & S^2A & S^3A \\ & & C & SC & S^3A & S^2A & SA & S^2A \\ & & & C & S^2A & S^3A & S^2A & SA \\ & & & & C & SC & S^2C & SC \\ & & & & & C & SC & S^2C \\ & & & & & & C & SC \\ & & & & & & & C \end{bmatrix}$$

$$\langle i | xy | j \rangle = x_0^2 \begin{bmatrix} 1 & 0 & 0 & 0 & S & 0 & 0 & 0 \\ & -1 & 0 & 0 & 0 & -S & 0 & 0 \\ & & 1 & 0 & 0 & 0 & S & 0 \\ & & & -1 & 0 & 0 & 0 & -S \\ & & & & 1 & 0 & 0 & 0 \\ & & & & & -1 & 0 & 0 \\ & & & & & & 1 & 0 \\ & & & & & & & -1 \end{bmatrix}$$

$$\langle i | yz | j \rangle = x_0^2 \begin{bmatrix} 1 & S & 0 & 0 & 0 & 0 & 0 & 0 \\ & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ & & -1 & -S & 0 & 0 & 0 & 0 \\ & & & -1 & 0 & 0 & 0 & 0 \\ & & & & -1 & -S & 0 & 0 \\ & & & & & -1 & 0 & 0 \\ & & & & & & 1 & S \\ & & & & & & & 1 \end{bmatrix}$$

$$\langle i | xz | j \rangle = x_0^2 \begin{bmatrix} 1 & 0 & 0 & S & 0 & 0 & 0 & 0 \\ & -1 & -S & 0 & 0 & 0 & 0 & 0 \\ & & -1 & 0 & 0 & 0 & 0 & 0 \\ & & & 1 & 0 & 0 & 0 & 0 \\ & & & & -1 & 0 & 0 & -S \\ & & & & & 1 & S & 0 \\ & & & & & & 1 & 0 \\ & & & & & & & -1 \end{bmatrix}$$

where $C = x_0^2 + \hbar/2m\omega$, and $A = \hbar/2m\omega$. The quantity S is the overlap integral.

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