THE RICE INSTITUTE

ELASTIC CONSTANTS OF POTASSIUM IODIDE
AND POTASSIUM CHLORIDE

by

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FOREWORD

Since one of the primary goals of physical research is to be able to disseminate the results through the medium of the various journals, the author has attempted to write Section A of the thesis in a manner such that it can be submitted for publication with as few changes as possible. This would seem to be an advantage to both the writer and the school since it eliminates some duplication of effort on the part of the former and it leads to a quicker submittal for publication.

In order to try to bridge the gap between the amount of information usually included in a published article and that included in theses, the author has included three appendices in Section B which would fill in details and be of help to anyone attempting to do similar research.

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SECTION A

ELASTIC CONSTANTS OF POTASSIUM
IODIDE AND POTASSIUM CHLORIDE

ELASTIC CONSTANTS OF POTASSIUM IODIDE
AND POTASSIUM CHLORIDE

Abstract

The sound velocities and elastic constants have been measured for pure single crystals of KI and KCl by the ultrasonic pulse technique over the temperature range from 4°K to 300°K. In KI, $c_{11}=3.38$, $c_{12}=0.22$, $c_{44}=0.368$ in units of 10^{11} dyne/cm² at 0°K according to our extrapolations. In KCl, measurements of all three constants were made over the entire temperature range down to 4°K and their values are: $c_{11}=4.83$, $c_{12}=0.54$, $c_{44}=0.663$ in units of 10^{11} dyne/cm². The Debye Theta has been calculated from these very low temperature values of the elastic constants to give 129°K for KI and 234°K for KCl. An analysis has been made of the error in these calculated θ_D due to experimental error in the elastic constants. The specific heats of KI, KCl, and KBr have been calculated in this paper by using a combination of a Debye and an Einstein term in the expression for the specific heat. These calculations indicate that the fit of such a simple theory becomes better as the ratio of ionic radii and masses increases in these three salts. We point out that in the alkali halides thus far studied in this laboratory, there is evidence that $c_{12}=c_{44}$ at about $T=\theta_D$. No reason is offered for this coincidence.

Introduction

This work has been done as part of a continuing program at The Rice Institute for furnishing more fundamental information on the elastic constants of alkali halides. Simultaneously, work is being done on the specific heats of these crystals by Scales¹ so that a comparison can be made of the value of the characteristic temperature (θ_D) obtained from low temperature specific heat measurements and from the elastic constants near the absolute zero. We are interested in seeing how well these evaluations of θ_D by different methods agree not only as a check on the experimental errors of each method but also as a further check on the methods^{2,3,4} of averaging the velocity over different directions in the crystal in order to calculate θ_D from the elastic constants. Last, we are interested in trying to gain a little insight into what sort of improvements can be made in a simple manner to the frequency spectrum in order to give a better representation of the specific heat of these materials. We attempt to do this by considering the smaller ion in the lattice to behave somewhat like an independent Einstein oscillator while the larger ion behaves as a Debye oscillator with an adjusted value of θ_D since we then consider the larger ion to occupy the whole volume. We wish to see if such a simple fit improves as the ratio of ionic radii and masses increases.

Experimental

The experimental apparatus used in this experiment is for the most part, the same as was used by Overton and Swim⁵, and Briscoe and Squire⁶, for similar measurements in this laboratory. A block diagram of this equipment is included in this section. The echo ranging technique was used to measure velocities of longitudinal and transverse waves along various directions in the single crystal specimens. Due to the differential contraction between the quartz transducer, the binder, and the specimen, very slow rates of cooling were necessary in order to minimize the chance of cleavage in the specimen. Generally, we cooled from room temperature to liquid air temperature in about twenty four hours and in the case of KI, the crystal developed cracks on all but one occasion as Helium was transferred into the dewar. As a result of this, actual measurements were made only for the longitudinal velocity in the (0,0,0) direction at helium temperature. The binders used on KI were Dow Corning silicones XC-270 and C-271.

During the experiments on KCl, we decided to try to find a binder which would not solidify until a temperature was reached where the expansion coefficient of the specimen had dropped appreciably from its room temperature value. For KI and KCl, this does not occur until about 60°K. The first such binder tried was the natural gas from the wall outlet. After cooling the specimen to liquid air temperature out of contact with the transducer, a glass tube from

BLOCK DIAGRAM OF APPARATUS

Figure 1

the top of the dewar was rotated such that its tip was placed above the specimen. The natural gas was run through a trap of dry ice and acetone to remove water vapor and the flow was regulated in the tube such that liquefaction took place at the bottom. After a few drops of liquid were deposited on the specimen, the tube was rotated out of the way and the transducer lowered until contact was made.

In the case of X-cut quartz crystals, measurements could be made immediately. In using Y-cut crystals, the appearance of echos indicated that the natural gas did not solidify until about 45°K. This freezing point perhaps can be explained by the fact that the gas is a mixture of about 94% Methane, 5% Ethane, and the rest other light hydrocarbons. Echos obtained with this binder at 4°K were surprisingly good.

Using this binder, the transverse and longitudinal velocities in the (1,0,0) direction were obtained quite accurately at Helium temperature. In measuring the constant c_{12} , we tried to do this by measuring the velocity of a longitudinal wave in the (1,1,0) direction and of a transverse wave in the (1,1,0) direction polarized perpendicular to the z axis. We obtained measurements in the latter case at Helium temperature but the echos were not as sharp as in the other cases. In the former case, the specimen was cooled too rapidly during the Helium transfer and the specimen cracked. The data from 90°K was extrapolated however

giving two independent estimates of c_{12} at very low temperature.

The relations from which the constants are calculated are listed in many books on Solid State Physics^{4,7} (See Appendix III).

Results

The elastic constants for KI and KCl are listed in Tables I and II. For KCl, the measurements of Durand⁸, by

Table I. Elastic constants of KI in units of 10^{11} dyne/cm².

T	c_{11}	c_{12}	c_{44}
4.2	3.383 $\pm$ 2%	.217 $\pm$ 30%	.3680 $\pm$ 2%
20	3.356	.236	.3681
40	3.323	.256	.3683
60	3.277	.280	.3687
80	3.233 $\pm$ 1%	.303 $\pm$ 15%	.3691 $\pm$ 1%
100	3.191	.319	.3692
120	3.144	.330	.3689
140	3.099	.354	.3687
160	3.050	.367	.3684
180	3.009	.375	.3679
200	2.962	.387	.3676
220	2.922	.392	.3670
240	2.869	.410	.3667
260	2.818	.420	.3660
280	2.763	.437	.3652
300	2.705 $\pm$ 1%	.449 $\pm$ 9%	.3639 $\pm$ 1%

Table II. Elastic constants of KCl in units of 10^{11} dyne/cm².

T	Present work c_{11}	c_{12}	c_{44}	Durand c_{11}	c_{12}	c_{44}
4.2	4.832	.542	.6626			
20	4.811	.543	.6614			
40	4.780	.554	.6602			
60	4.743	.553	.6584			
80	4.697	.550	.6566	4.81		.664
100	4.644	.570	.6550			
120	4.582	.576	.6523			
140	4.510	.588	.6502	4.62		.658
160	4.453	.591	.6484	4.55		.655
180	4.394	.600	.6457	4.48		.651
200	4.331	.613	.6430	4.40		.648
220	4.274	.616	.6404	4.33		.645
240	4.218	.622	.6377	4.24		.641
260	4.158	.632	.6350	4.16		.637
280	4.095	.645	.6323	4.08	.6	.634
300	4.032	.664	.6292

Figure 2

Figure 3

an earlier technique known as the composite oscillator, are listed for comparison. In Table I, the estimated maximum errors are listed with the numbers. For KCl, the room temperature maximum errors for c_{11} and c_{44} are $\pm 0.3\%$ and $\pm 0.5\%$. At 4°K we estimate the maximum errors to be $\pm 0.4\%$ and $\pm 0.6\%$. Since c_{12} must be determined by taking a difference between large numbers close together in value, an analysis of the propagation of errors shows that the % error in c_{12} can be large. For KCl, our analysis indicates a possible, but not probable, error of 35%. The effect of this error on the calculation of θ_D will be discussed in more detail. The second estimate of c_{12} by using a transverse polarized wave in the (1,1,0) direction indicates a value of c_{12} at 4°K equal to .597. The two values are about 9% apart indicating that the error is not nearly as large as 35%.

Table III shows a comparison between room temperature values of the elastic constants of KI done in the present work and that done by static methods in 1929 by Bridgman⁹. The compressibility of KI calculated from our constants is 8.33 at 300°K in units of 10^{-12} cm²/dyne. Slater¹⁰ gives a value of 8.54. Table IV shows a comparison between our constants at 4°K and the theoretical calculations of Krishnan and Roy¹¹ at absolute zero using a central force model.

Table V shows a comparison of our values of elastic constants at 4°K and our compressibility with the theoretical

calculations of Krishnan and Roy, and Lowdin¹². The units of all constants are 10^{11} dyne/cm² and 10^{-12} cm²/dyne for compressibilities.

Table III. Comparison of elastic constants at room temperature for KI.

	c_{11}	c_{12}	c_{44}
Present work	2.71	.449	.364
Bridgman	2.66	.425	.412

Table IV. Comparison of elastic constants of KI near absolute zero.

	c_{11}	c_{12}	c_{44}
Present work	3.383	.217	.3680
Krishnan and Roy	3.1	.5	.5

Table V. Comparison of elastic constants and compressibility of KCl with theoretical values.

	c_{11}	c_{12}	c_{44}	β
Present work	4.832	.542	.6626	5.60
Lowdin		.777	.909	6.0
Krishnan and Roy	3.9	.8	.8	

The values of θ_0 have been calculated for each of the crystals by using DeLauney's Tables¹³ and by the formulas in the extension of Houston's work² by Betts, Bhatia, and Wyman³. Table VI shows these values compared with specific heat work of Berg and Morrison¹⁴, and Scales¹. From these results it becomes apparent that specific heat data and elastic constant data lead to values of θ_0 in good agreement with each other.

In order to obtain an idea of the error in θ_0 due to

errors in the elastic constants, we programmed the computation of θ_0 by the relations derived by Betts, Bhatia and Wyman for the IBM 650 computer. We assumed the errors for c_{11} and c_{44} given previously and for c_{12} we assumed errors of 1, 10, and 35%. For each error in c_{12} we calculated

Table VI. Values of θ_0 from elastic constant work and specific heats at low temperatures.

KI

	Elastic Constant	Specific Heat
DeLauney's Tables	131	
Betts, Bhatia, and Wyman	129	
Berg and Morrison		132.3
Scales		128
Krishnan and Roy (Theoretical)	140	

KC1

	Elastic Constant	Specific Heat
DeLauney's Tables	236	
Betts, Bhatia, and Wyman	234	
Berg and Morrison		235.1
Durand (Extrapolated)	238	

the eight values of θ_0 obtained by taking all combinations of plus and minus errors. Each time we also calculated the eight θ 's listed in Betts, Bhatia, and Wyman's paper. We show the results for θ_0 only since it is assumed to be the best approximation. The results of this error analysis show as does an examination of DeLauney's Tables that the calculation is extremely insensitive to errors in c_{12} . Even with the 35% assumed error in c_{12} , all values fell between 232.5 and 235.8°K. For 10% error all values fell

between 233.3 and 235.1. As a result of this analysis on KCl and a less extended one on KI we conclude that the respective errors in θ_0 due to experimental errors in the constants are $\pm 1^\circ\text{K}$ and $\pm 2^\circ\text{K}$.

Discussion

The history of early attempts by Einstein and Debye to describe theoretically the specific heats of materials is well known and will not be discussed here in detail. It suffices to say that only a detailed knowledge of the lattice vibration spectrum can lead to the correct theoretical values of the specific heat.

Briscoe and Squire⁶ have applied a rather simple technique in trying to improve the fit of the Debye specific heat to experimental data on LiF. They assume that in a crystal such as LiF where one ion is considerably larger than the other, that the smaller ions are partly shielded from one another by the electron clouds of the larger, and that the smaller ions tend to act like independent Einstein oscillators. They compute the specific heat as a combination of an Einstein and a Debye function. The θ_E used comes from the Reststrahlen frequency or frequency of maximum infrared

$$c_v = 3R F_D(\theta'_D/T) + 3R F_E(\theta_E/T)$$
reflection. The θ'_D shown is not the usual θ_D but $\theta_D/(2)^{1/3}$ since the larger ion is now considered to occupy the whole volume. It is worth noting that this manipulation gives back the correct specific heat at low temperatures.

As T goes to 0 $F_E(\theta_E/T) \ll F_D(\theta'_D/T)$

$$c_v \approx 3R F_D(\theta'_D/T) = 3R (4\pi^4/5) (T/\theta'_D)^3 = 6R (4\pi^4/5) (T/\theta_D)^3$$

Using this scheme, specific heats of KI, KCl, and KBr were calculated using the data of Galt¹⁵ on KBr. The results are shown in the included graphs. It is seen that the fit becomes increasingly better as the ratio of the ionic radii and masses increase in going from Cl to Br and to I. For KI, this simple fit is quite good and indicates that the method may throw a little light on the true frequency spectrum of ionic cubic crystals where one ion is somewhat larger than the other. In no case is the Debye fit adequate. It is intended that more work be done on alkali halides with higher ratios of ionic radii and masses as soon as techniques of polishing and handling hygroscopic crystals are improved a little more.

One point of interest arising from this work is that in noticing the temperatures where $c_{12} = c_{44}$ for crystals whose constants have been measured, it appears there is a tendency for this to happen at about the Debye temperature of the crystal. A summary of available data follows.

Substance	Temp. where $c_{12} = c_{44}$	θ_D	Investigator
KCl	265	235	Present work
KI	164	130	Present work
NaCl	300	322	Overton and Swim
LiF	well above 500	735	Briscoe and Squire

It is realized that there is considerable error involved in locating this point but the tendency does seem to exist. The data of Galt¹⁵ on KBr does not show the constants

Figure 4

Figure 5

Figure 6

equal for any temperature, but they are close together in value everywhere so that the usual error in c_{12} might account for this.

In regard to agreement between elastic constant methods and specific heat methods of obtaining the Debye Theta at absolute zero, it should be pointed out that very recent work by Ludwig³⁰ using anharmonic terms in the atomic potentials indicates that one should not necessarily expect the two to be exactly the same in alkali halides, even at absolute zero. In his model for Krypton, he shows that one expects a difference between the measured values of the order of 2%, and that for alkali halides, the difference should be about half of this figure. In the case of KI and KCl, it would be difficult to try to see differences of this sort because of experimental errors involved in each technique. In the case of KI however, it is observed that the two estimates of θ made at The Rice Institute differed by about 1 part in 129 and that the specific heat estimate was lower as Ludwig indicates.

SECTION B
APPENDICES

APPENDIX I. BRIEF HISTORY OF RELATED WORK

The elastic constants, which are the elements in a matrix relating the six independent stress components to the six independent strain components, have been measured for many solids in various ways. The earlier attempts at measurements of this sort consisted of directly introducing a distortion such as an elongation or a twist in the body and measuring the strains caused by the distortion. The early papers of Slater¹⁰ and Bridgman⁹ are cited as among the more important contributions to the technique of static measurements. None of these measurements were carried to low temperatures.

In 1934, Balamuth¹⁶ devised a technique of measuring elastic constants which is called a composite oscillator. This device consists of a piece of piezoelectric material, coated on the ends with a conducting material, and cemented to the specimen of interest. Standing waves are set up in the combination of materials by the transducing material and the amplitude of the wave at any point depends on the geometry, the frequency of excitation, and the properties of the materials. If the properties of the transducer, quartz for example, are well known, the elastic constants of the specimen may be measured. Balamuth used this technique to measure s_{11} , the constant relating longitudinal stresses and strains in Sodium Chloride single crystals from 78°K to 273°K.

After the development of the composite oscillator, other investigators used this technique on elastic constants of single crystals. Among them are Durand⁸ (NaCl, KCl, MgO), Hunter and Siegel¹⁷ (NaCl--all 3 constants to high temperatures), and Rose¹⁸ (NaCl--extension of Balamuth work to all 3 constants from 78°K up). Hearmon¹⁹, in an article in the Reviews of Modern Physics, 1946, describes the techniques and the work done in measuring elastic constants up to that time.

During the second World War, advances in electronics made possible the generation of short radio frequency pulses in the megacycle range. The ideas and equipment used in radar were adapted to the idea of measuring velocities of propagation of sound waves in various media. The technique will be described briefly.

In the ultrasonic method, a short radio frequency pulse is applied to a piezoelectric transducer which is in contact with the material of interest. These pulses propagate from the transducer through the medium and are detected by the same transducer after a reflection or are detected by another transducer after only one trip through the medium. If the reflection method is used, then a series of "echos" are obtained by each additional round trip through the medium. These echos are displayed on the time base sweep of an oscilloscope and the times of flight can be obtained. Upon measuring the length of the path of propagation, the veloc-

ity in the medium is obtained. This method has been applied to solids, liquids, and gases. In solids, one uses the other end of the specimen as the reflector while in liquids and gases, the walls of the container or an internal reflector are used.

In recent years, many measurements have been made using the ultrasonic technique. Of interest to this work and Low Temperature Research in general are the following examples.

Pellam and Galt²⁰ studied velocities and absorption in liquid Nitrogen, Hydrogen, and Oxygen. Pellam and Squire²¹ investigated these quantities in liquid Helium. Studies of velocity and attenuation in superconductors have been made by Overton²², and by Bommel²³.

Measurements of velocities and elastic constants in single crystal alkali halides are of particular interest in this work. The available data is found in the following references. Huntington²⁴ has made measurements on single crystals of NaCl, KCl, and KBr at room temperature. Galt¹⁵ measured the elastic constants of KBr from room temperature to liquid helium temperature. Swim²⁶ measured the constants of NaCl by the ultrasonic method from 60°K to 300°K. Briscoe and Squire⁶ obtained the constants for LiF from room temperature to 4°K.

This does not pretend to be a complete review of ultrasonic measurements. An adequate source of information in this

regard is furnished by Bergmann²⁹ in his book, Ultrasonics and Their Scientific and Technical Applications.

In completing this brief history of research related to this thesis, something must be said about the calculation of the Debye Theta from the elastic constants. In the Debye theory, the quantity Θ_D involves the velocity of sound waves in the medium. In an isotropic medium, this presents no difficulty but in a single crystal, longitudinal and transverse waves have different velocities which also vary with the direction of propagation. Therefore in order to calculate the Debye Theta, some sort of average velocity must be used in the formula. Work along this line has been done by Blackman (Repts. Prog. Phys. 8, 11, 1941), Houston², and more recently by Betts, Bhatia, and Wyman³. Betts et al. have modified Houston's suggestion on averaging the velocity and have derived eight expressions for the Debye Theta, each succeeding one involving averages over different combinations of the six directions in the crystal lattice used.

DeLaunay⁴ has published a set of tables which simplifies the calculation of the Debye Theta from the elastic constants and he has extended tables not published which can be obtained on request.

APPENDIX II. ADDITIONAL INFORMATION ON EXPERIMENTAL APPARATUS AND PROCEDURE

Electronic equipment. The electronic apparatus used in this experiment is essentially the same as used in this lab by Overton and Swim⁵, and by Briscoe and Squire⁶. Since the circuit diagrams and details of most of the equipment are described in some detail in the theses of Overton²⁵ and Swim²⁶, only a simple block diagram is included in this thesis. There are two points in regard to the electronics which will be discussed in some detail. One of these is the use of a delay circuit in order to see the first pulse and the other is the use and need of a new oscilloscope of higher sensitivity.

During the work on Potassium Iodide, echos at low temperatures were poor due to gradual changes in the binder during the cooling process. It became desirable to see the initial pulse on the scope in order to be able to use the first interval as a time measurement since echos were poor after the third or fourth pulse. In order to do this, a delay circuit was built and used between the Dumont 256-D scope and the pulse forming unit. The output pulse from the scope caused the pulses going to the crystal to arrive later and to be displayed later on the sweep. This process can be visualized by examining the block diagram of the apparatus shown earlier. The delay was constructed with a three posi-

Figure 7

tion switch which changed capacitors in the circuit, thereby changing an RC time constant. These three positions correspond to maximum delays of approximately 10, 40, and 150 microseconds. A variable potentiometer allows continuous control of the delay time on each of the three ranges. For the benefit of anyone using the apparatus in the future a circuit diagram of the delay is included in this thesis.

The other point to be mentioned in regard to the electronics is the use of a more sensitive scope in the work on KCl. The scope used was the Tektronix 545 with a high gain preamplifier. The reason for obtaining this more sensitive instrument was to be able to look at the actual waveform of the returning echos rather than the demodulated pulses as had been done in the past. One of the greatest difficulties in measuring times between echos was in deciding where the pulses actually began. This meant that most of the error was in the human eye and in the process of decision. With the new scope, the beginnings of the pulses were made more distinct by the fact that the oscillations were displayed on both sides of the center position rather than on one side as in the detected pulses. The errors in time measurements on KCl were reduced to about one-half the errors in the KI measurements. Photographs of a single echo and a series of echos are included in this Appendix.

Low Temperature Apparatus. The low temperature equip-

DELAY CIRCUIT

Figure 8

Figure 9. Single Echo

Figure 10. Series of echos

ment used in this work is the same as was used by C. V. Briscoe⁶ in measurements on LiF1. Since a diagram of this equipment is included in his work along with a very complete description of it, this information will be omitted and a discussion will be given of the differences in method used between earlier work and the present work.

The primary experimental difficulty in measuring the elastic constants of these crystals is the difference in contraction between the specimen and the quartz transducer. In the case of "weaker" alkali halides such as KI and KCl, it is extremely difficult to use a single binder from room temperature to liquid helium temperature as was accomplished in the work on LiF1. This meant that in order to make measurements over the entire range, it was necessary to do this in different temperature ranges on different runs. The following procedures were applied to KCl and they worked quite well. In obtaining data from 300°K to about 200°K, a light lubricating oil was used with X-cut crystals while beeswax was used with Y-cut crystals. The beeswax is solid at room temperature and transmits transverse waves. The beeswax was applied by heating the specimen slowly to about 60°C with a small amount of the wax on top of the specimen. The transducer was then pressed onto the liquid until a uniform layer was obtained between the specimen and the quartz. The specimen was then cooled to room temperature again. In order to make measurements at lower temperatures, special

measures were taken. The crystal was cooled to about 125°K at a rate of about 12°K per hour. During this cooling, the specimen was not in contact with the transducer or the brass contact holding the transducer. This is important because the specimen cools more uniformly if it is not in contact with a good heat conductor. The chances of the crystal developing cleavage planes is reduced substantially this way. At 125°K, the binder is applied. The binder used was a mixture of ether, pentane, and ethyl alcohol as described in the thesis of Overton²⁵. The binder is applied through a glass tube from the top of the dewar. The glass tube is bent at the bottom so that the end of it can be rotated into position over the specimen. The liquid binder is then admitted at the top of the dewar until several drops are standing on the specimen. The transducer is then lowered onto the specimen and the cooling is continued. In the case of even lower temperatures, a solid natural gas binder was used as described earlier. It is important to use a trap of some kind to remove water vapor and yet not to liquefy gas in the trap itself. The dry ice and acetone trap mentioned earlier seems to work well.

The problem of devising a crystal holder which allows the quartz crystal to be lowered onto the specimen from above is more difficult than it first seems. Obviously if the quartz is smaller in diameter than the specimen, no retaining ring can be used below the quartz to hold it in a

mount. The solution to this problem seemed to be to use a specimen about $5/8$ " in diameter which would go inside a retaining ring so that a flat contact could be made between specimen and transducer. There was some concern over possible reflections from the side walls of the specimen but for samples about 1" long, no such effects were observed. This indicates that the transducer was producing a fairly good plane wave propagation of the pulses through the crystal.

A diagram is included of the two types of probes used in work of this kind in this laboratory. The one on the left shows the method of contact with the RF source when the transducer is bonded to the specimen at room temperature. The figure on the right shows the method of bonding the transducer to the specimen at low temperature. The most important improvement in technique in this work was the construction of the probe in which the quartz crystal was spring loaded in both the center and at the edges. A $5/8$ " bellows was used to spring load the outside of the crystal. This spring loading allowed the quartz to adjust itself until a flat contact was made with the specimen, even if the specimen was slightly tilted with respect to the crystal holder.

Correction of the length of the specimen due to thermal contraction. In order to measure the velocity of sound over a wide temperature range, it was necessary to know the length of the specimen at any temperature. Since no data on the

METHODS OF CONTACT WITH QUARTZ CRYSTAL

Figure 11

expansion coefficients of KI and KCl were available, they were calculated from a knowledge of the density as a function of the temperature. Information of this sort was available in the International Critical Tables published by the McGraw-Hill Publishing Co. This information was in the form of empirical formulas obtained from the work of Henglein²⁷. The empirical equations allowed calculation of the density to five significant figures down to a temperature of about 90°K. The expansion coefficients below this temperature were estimated by the Gruneisen relation which states that the expansion coefficient is approximately proportional to the specific heat. The specific heat work of Clusius, Goldman, and Perlick²⁸, and of Berg and Morrison¹⁴ were used. From the expansion coefficient as a function of temperature, the length at any temperature was calculated by a numerical integration using temperature intervals of ten degrees. The changes in length between room temperature and helium temperature for KI and KCl were of the order of 1%.

Velocities of Sound. In order to give the reader some idea of how the various velocities are related to each other and how they change with temperature, plots of these velocities for KI and KCl are included in this appendix.

Figure 12

Figure 13

APPENDIX III. THEORETICAL BACKGROUND

Elastic Constants. In considering the mathematical theory of elasticity it is found that the behavior of solid bodies can be described by a generalized form of Hooke's Law. There are nine stresses and nine strains involved. If it is required that an element not be rotated while it is being deformed, then it is found that there are only three independent shear stresses and strains. The general form of Hooke's Law may be written as follows:

$$(1) \begin{pmatrix} X_x \\ Y_y \\ Z_z \\ Y_z \\ Z_x \\ X_y \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{pmatrix} \begin{pmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \\ e_{yz} \\ e_{zx} \\ e_{xy} \end{pmatrix} \quad \begin{aligned} Y_z &= Z_y \\ Z_x &= X_z \\ X_y &= Y_x \end{aligned}$$

X_x is a stress due to a force in the x direction applied to a plane perpendicular to the x direction. Similarly, X_z is a stress due to a force in the x direction which is applied to a plane perpendicular to the z direction. The strains are defined by the following relations:

$$(2) \quad \begin{aligned} e_{xx} &= \frac{\partial u}{\partial x} & e_{yy} &= \frac{\partial v}{\partial y} & e_{zz} &= \frac{\partial w}{\partial z} \\ e_{xy} &= \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} & e_{yz} &= \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} & e_{zx} &= \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \end{aligned}$$

The strain components of the type e_{xy} may be interpreted as being made up of two simple shears. In one of the shears, planes of the material normal to the x axis slide in the y direction. In the other, planes normal to y slide in the x direction.

If one considers the work done on a small cube by a stress due to a force F , one finds relations of the type

$$(3) \quad \frac{\partial X_x}{\partial e_{yy}} = \frac{\partial Y_y}{\partial e_{xx}}$$

If these derivatives are taken in the linear equations relating the stresses and strains, an important result follows, namely that $c_{ij} = c_{ji}$. This means that the matrix is symmetric, reducing the thirty six constants to twenty one independent constants for any solid body.

In the case of a cubic crystal, the matrix is simplified much more due to its symmetry. If one permutes the letters x , y , and z , this corresponds to simply relabeling the axes and no difference in the physical law is expected to occur. When this is done, it is found that many of the constants are equal. Furthermore, if the axes are reversed one at a time in the first three equations of the system, one finds that many of the constants must be zero because the stress is the same after the reversal since it is not a vector quantity. These results are summarized below:

$$(4) \quad C_{11} = C_{22} = C_{33} \quad C_{44} = C_{55} = C_{66}$$

$$C_{12} = C_{13} = C_{23}$$

All other constants are zero.

Under these conditions, the general form of Hooke's Law may be rewritten for the special case of the cubic crystal.

$$(5) \quad \begin{pmatrix} X_x \\ Y_y \\ Z_z \\ Y_z \\ Z_x \\ X_y \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix} \begin{pmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \\ e_{yz} \\ e_{zx} \\ e_{xy} \end{pmatrix}$$

Putting in the expressions (2) for the strains, the following set of equations are obtained.

$$(6) \quad \begin{aligned} X_x &= (C_{11} - C_{12}) \frac{\partial u}{\partial x} + C_{12} \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) \\ Y_y &= (C_{11} - C_{12}) \frac{\partial v}{\partial y} + C_{12} \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) \\ Z_z &= (C_{11} - C_{12}) \frac{\partial w}{\partial z} + C_{12} \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) \\ Y_z &= C_{44} \left(\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} \right) \\ Z_x &= C_{44} \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) \\ X_y &= C_{44} \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \end{aligned}$$

Now consider the forces on a cubical element of volume. There is an inertial force due to its motion and an elastic force due to the difference in the stress on opposite sides of the element. These may be equated to give the equations of motion remembering that there are nine stresses even though only six of them are independent.

$$\begin{aligned}
 \rho \frac{\partial^2 u}{\partial t^2} &= \frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} \\
 \rho \frac{\partial^2 v}{\partial t^2} &= \frac{\partial Y_x}{\partial x} + \frac{\partial Y_y}{\partial y} + \frac{\partial Y_z}{\partial z} \\
 \rho \frac{\partial^2 w}{\partial t^2} &= \frac{\partial Z_x}{\partial x} + \frac{\partial Z_y}{\partial y} + \frac{\partial Z_z}{\partial z}
 \end{aligned}
 \tag{7}$$

If the expressions for the stresses in (6) are differentiated and substituted into (7), the three differential equations of motion for the element are obtained.

$$\begin{aligned}
 \rho \frac{\partial^2 u}{\partial t^2} &= (C_{11} - C_{12}) \frac{\partial^2 u}{\partial x^2} + C_{12} \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 v}{\partial x \partial y} + \frac{\partial^2 w}{\partial x \partial z} \right) \\
 &\quad + C_{44} \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} + \frac{\partial^2 v}{\partial x \partial y} + \frac{\partial^2 w}{\partial x \partial z} \right) \\
 \rho \frac{\partial^2 v}{\partial t^2} &= (C_{11} - C_{12}) \frac{\partial^2 v}{\partial y^2} + C_{12} \left(\frac{\partial^2 u}{\partial x \partial y} + \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 w}{\partial y \partial z} \right) \\
 &\quad + C_{44} \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial z^2} + \frac{\partial^2 u}{\partial x \partial y} + \frac{\partial^2 w}{\partial y \partial z} \right) \\
 \rho \frac{\partial^2 w}{\partial t^2} &= (C_{11} - C_{12}) \frac{\partial^2 w}{\partial z^2} + C_{12} \left(\frac{\partial^2 u}{\partial x \partial z} + \frac{\partial^2 v}{\partial y \partial z} + \frac{\partial^2 w}{\partial z^2} \right) \\
 &\quad + C_{44} \left(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} + \frac{\partial^2 u}{\partial x \partial z} + \frac{\partial^2 v}{\partial y \partial z} \right)
 \end{aligned}
 \tag{8}$$

In order to obtain a solution of these equations, plane wave expressions for u , v , and w are used.

$$\begin{aligned}
 u &= A_1 e^{2\pi i(\nu t - k_1 x - k_2 y - k_3 z)} \\
 v &= A_2 e^{2\pi i(\nu t - k_1 x - k_2 y - k_3 z)} \\
 w &= A_3 e^{2\pi i(\nu t - k_1 x - k_2 y - k_3 z)}
 \end{aligned}
 \tag{9}$$

When these expressions are substituted into the equations of motion, three more equations result involving a linear combination of A_1 , A_2 , and A_3 . In order that not all of the components of the amplitude vanish, the determinant of the coefficients must vanish. This is the well known secular equation which is the starting point of much theoretical research on crystals of this type.

$$(10) \quad O = \begin{vmatrix} (C_{11}-C_{44})k_1^2 + C_{44}k^2 - \rho v^2 & (C_{12}+C_{44})k_1k_2 & (C_{12}+C_{44})k_1k_3 \\ (C_{12}+C_{44})k_1k_2 & (C_{11}-C_{44})k_2^2 + C_{44}k^2 - \rho v^2 & (C_{12}+C_{44})k_2k_3 \\ (C_{12}+C_{44})k_1k_3 & (C_{12}+C_{44})k_2k_3 & (C_{11}-C_{44})k_3^2 + C_{44}k^2 - \rho v^2 \end{vmatrix}$$

The k 's are the propagation vectors, k_1 , k_2 , and k_3 being the components. This expression is a cubic equation in the square of the frequency. It is quite difficult to solve this equation for elastic waves propagating in an arbitrary direction. In certain special directions, however, rather simple relations between the elastic constants and the velocities of propagation in those directions result.

Wave parallel to the (1,0,0) direction:

$$(11) \quad k_1 = k \quad k_2 = k_3 = 0$$

$$\rho V_l^2 = C_{11} \quad \rho V_t^2 = C_{44}$$

The transverse wave may be polarized in any direction.

Wave parallel to the (1,1,0) direction:

$$(12) \quad k_1 = k_2 = k/\sqrt{2} \quad k_3 = 0$$

$$\rho V_e^2 = \frac{(c_{11} + c_{12} + 2c_{44})}{2}$$

$$\rho V_t^2 = c_{44}$$

$$\rho V_x'^2 = \frac{(c_{11} - c_{12})}{2}$$

V_t refers to a transverse wave with particle motion polarized parallel to the z axis. V_t' is the velocity of a transverse wave polarized perpendicular to the z axis.

Wave parallel to the (1,1,1,) direction:

$$(13) \quad k_1 = k_2 = k_3 = k/\sqrt{3}$$

$$\rho V_e^2 = \frac{(c_{11} + 2c_{12} + 4c_{44})}{3}$$

$$\rho V_x'^2 = \frac{(c_{11} - c_{12} + c_{44})}{3} \quad (\text{Any polarization})$$

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