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ULTRASONIC MEASUREMENTS ON SINGLE CRYSTALS

by

H. B. Huntington

Abstract

A pulsed technique at 10 Mc/sec has been used to measure acoustic velocity and attenuation of several alkali halides and Rochelle salt. Values for the elastic moduli of LiF, NaCl, KBr, and KI have been determined. The attenuation of the ultrasonic beam in these media is small. Corresponding measurements on the elastic moduli of Rochelle salt are reported. Under the assumption of plane-wave transmission many of these moduli automatically correspond to those measured on foiled crystals by other methods. Attenuation is considerable in Rochelle salt, and appears to be excessively high for transmission involving the temperature-dependent  $c_{44}$  (foiled case). Where this modulus is involved, marked effects have been observed from electric bias and mechanical pressure. A complete set of elastic moduli has been obtained and used to calculate the corresponding values for the moduli of compliance.



## 1. Introduction

The recent development of short-pulse techniques has made available pulsed ultrasonics as a very convenient tool for investigating the mechanical properties of matter. During the war, some work was carried out on liquids at the Radiation Laboratory at Massachusetts Institute of Technology<sup>1,2</sup>. More recently a systematic study of the velocity and absorption of certain organic liquids has been performed by workers<sup>3</sup> in this laboratory. Some research on solids has been done as part of the war effort in England<sup>4</sup> and also in this country<sup>5</sup>. The pulsed technique has also been used as a tool for detecting mechanical flaws in solids<sup>6</sup>.

Recently, the most widely used technique for measuring ultrasonic velocity and absorption in single crystals<sup>7</sup> has been the composite oscillator method initiated by Quimby's students<sup>8</sup> whereby a piezoelectric crystal is cemented to the specimen under test and the frequency is varied to obtain a resonance. Information on the velocity and elastic constants is obtained from the frequency of resonance. The breadth of the resonance measures the damping or internal friction.

With the pulse technique the same quantities are studied usually at a much higher frequency where the specimen is many wavelengths on a side. Traveling waves replace standing waves.

Briefly, the experimental procedure consists of exciting a piezoelectric crystal, which is also cemented to the specimen under test, by a short pulse of the carrier frequency. The pulse travels down through the specimen and may be detected by a second piezoelectric crystal or reflected from the end surface to the transmitting crystal. In either case successive echoes are converted into electric pulses, amplified, and displayed on a time-base sweep.

Actual elapsed times between the signals of successive echoes are measured to give velocity data. For the traveling wave the velocity is a directly measured quantity whose determination is uncomplicated by boundary conditions or mode coupling.

On the other hand, the measured attenuation of the successive echoes must be interpreted with caution, as there are many possible causes for such attenuation other than direct absorption by the medium itself. In the first place, any sort of inhomogeneity in the specimen under test will give rise to scattering which will break up the intensity of the beam. For work in the megacycle range minute impurities can cause scattering. Residual thermal stresses also have the same effect. Extensive scattering can also be caused by the individual polycrystals of the specimen if the grain size is not very small compared to the wavelength of the ultrasonics. In the second place, even for homogeneous specimens, there will be some spreading of the beam from straight diffraction effects. This spreading is ordinarily not serious because narrow-angle beams are obtained at high frequency. However, it is necessary for all specimens to be carefully prepared with two opposite surfaces flat and parallel. Any misalignment of these surfaces will cause a distortion in the pattern of the multiple echoes. As a result, the successive echoes decrease

unevenly and may show an oscillatory character where some echoes are actually larger than their immediate predecessor. In the third place, any thermal gradients in the specimens will cause refraction and consequent pulse distortion. Finally, the character of the film between crystal and specimen is increasingly critical at shorter wavelengths. It is essential that the surfaces be clean so that the film will be uniform. All particles and air bubbles should be carefully excluded. Precaution should be taken to keep the film as thin as possible and this is particularly important if the film has a low acoustic impedance. Otherwise, the crystal element will not be sufficiently broadband to maintain good pulse shape. For work with transverse waves it appears to be impractical to use liquid or wax films.

The effect of pulse distortion is naturally more pronounced in attenuation measurements. Mainly from this cause the results given here are only of a qualitative nature and tend to represent upper limits rather than actual values. To obtain more precise values would require repeated measurements on the same specimens to evaluate the reproducibility and influence of the film used, and on specimens of different size and shape to eliminate the effects of geometry, beam spreading, reflections, and the like.

The effect of pulse distortion on velocity measurements, though much smaller than on attenuation, was the limiting factor in the accuracy of the results. For successive pulses that maintained essentially the same shape the precision of velocity determination was easily as good as 0.1 per cent. With the appearance of pulse distortion for one reason or another, the determination of the time between pulses became difficult. Results varied depending on procedure and interpretation of the scope pattern so that inaccuracy in velocity measurement might be as high as  $1\frac{1}{2}$  per cent. For this reason the accuracy of measurement varies considerably throughout.

It was decided in this investigation to study single crystals to avoid as far as possible the pulse deterioration arising from polycrystalline inhomogeneities. Many of the alkali-halide crystals used were obtained from the Harshaw Development Company. Measurement on these substances was of particular interest as the attenuation was very low. We were fortunate to obtain two single crystals of copper from Mr. L. Gold of the M. I. T. Metallurgy Department which showed a considerably larger attenuation. Rochelle salt was chosen because of interest in its piezoelectric properties and its Curie point at room temperature. These crystals were supplied by the Brush Development Company.

## 2. Experimental Procedure

The equipment used in these measurements consisted of a Dumont 256B A/R Range Scope, a pulsed 10-Mc/sec oscillator, a broadband 10-Mc/sec receiver and a calibrated 70-ohm attenuator, arranged as shown in the block diagram (Fig. 1). The oscillator was adjustable in frequency, but for this work the frequency was held fixed at 10.6 Mc/sec. The trigger from the A/R scope initiated a video pulse. The pulse cut off a tube which previously loaded the grid circuit of the oscillator.

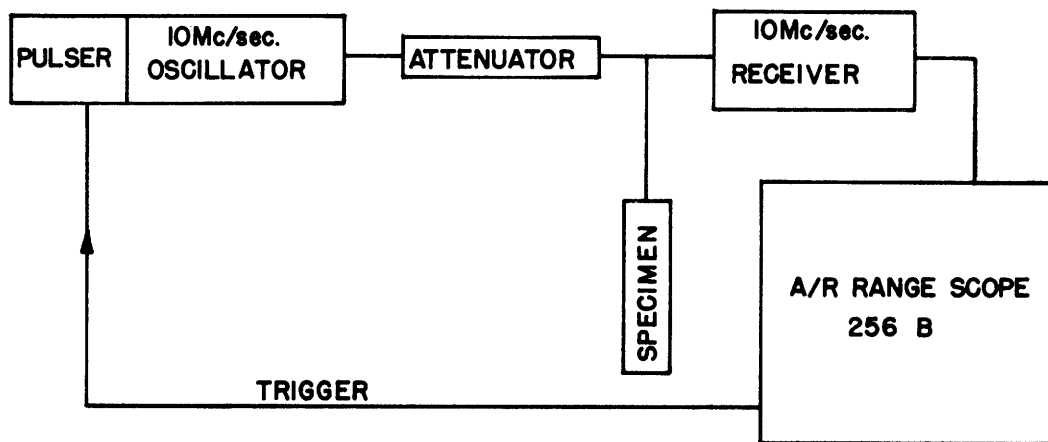


Figure 1. Block diagram

With the tube cut off, the high frequency pulse started with a short rise time. The duration of the pulse could be varied from  $3/4$  to  $2\frac{1}{2}$   $\mu$ sec. The 10-Mc/sec receiver consisted of five stages of high-frequency amplification followed by a detector and two stages of video amplification. The frequency response was such that the amplifier could pass pulses with 0.1  $\mu$ sec rise time with negligible distortion.\* The attenuator was variable from 0 to 101 db in steps of 1 db.

Quartz crystals were used for electromechanical transducers. In general, the same crystal, attached through a T-connector, was used to transmit and receive. The specimen under test was clamped in place on a small brass table with the crystal fastened to the prepared surface. The T-junction was physically near the amplifier input and transforming networks were not employed. Attenuation measurements were made only when sufficient attenuation had been inserted so that the driving impedance at the junction was effectively 70 ohms.

The preparation of electrodes for crystals to be used with alkali halides and Rochelle salt was complicated by the fact that the surfaces of these materials could not be cleaned by usual reagents. For this reason it appeared inadvisable to attempt to apply metal electrodes either by evaporation or Brashear's process. The interposition of a metal foil between crystal and specimen was undesirable since a second binding film would be needed between foil and specimen. Under such circumstances the production of good pulse shapes would have been difficult. Instead, electrodes were deposited on the crystal itself by the Brashear process so that the whole crystal, 1 in. in diameter, was plated everywhere except for a centered ring of bare quartz on one face. The inner and outer diameters of the ring were 0.5 in. and 0.75 in., respectively. The completely silvered face was attached to the specimen while on the other side press-fingers of beryllium copper made ground connection to the outer ring and a steel spring formed a coaxial lead to excite the central, silvered spot.

\* The pulser and amplifier units were developed for testing ultrasonic delay lines by R. D. Arnold at MIT Radiation Laboratory in 1945.

For the film between quartz and specimen several materials such as oil, vaseline, and Canada balsam were tried with indifferent success. Good pulse shape could be obtained with a thin layer of paraffin that had been allowed to cool under uniform pressure, but at temperatures for which the paraffin would flow freely it was extremely difficult to prevent dehydration of the Rochelle salt. Moreover, satisfactory transmission of transverse waves required a film of rigid material. It was decided to use an organic compound with a sharp melting point in the 40° - 50°C range. For this purpose, it was found\* that phenyl salicylate with a melting point near 42°C was completely satisfactory and it was used almost exclusively in the later measurements.

All experiments were performed at ambient temperature, except for some measurements on Rochelle salt where the specimen was cooled to a few degrees below the Curie point and allowed to warm up slowly over a period of several hours.

The A/R Scope is provided with two long sweeps, one of 122 microseconds and the other 1.22 milliseconds, (20,000 yds and 200,000 yds radar range), which start with the trigger. There are also available several delayed sweeps of which the fastest has a speed of 1 inch per microsecond. The procedure in taking the data was to put each echo in turn on this delayed sweep. By the use of the calibrated attenuator the echo was adjusted to give a fixed deflection, and the reading of the attenuator was recorded. Next, the attenuation was decreased by a fixed amount which caused the signal to overload. The delay time corresponding to the steep leading edge of the overloaded pulse could be read from a dial which measured the angular displacement of a helical potentiometer. Small corrections had to be applied to the dial readings for both the 122-microsecond and the 1.22-millisecond ranges. The instrument is supplied with an 82-kc crystal which gives markers every 12.192 microseconds. (The repetition rate is synchronized to be a subharmonic of this frequency.) From the markers, the correction curves for the helical potentiometer could be obtained. When it was possible to make time measurements on both the 122-microsecond and 1.22-millisecond range sweeps, the two agreed to within 0.1 per cent. This internal consistency served as a check on the accuracy and stability of the correction curves.

In any long series of successive echoes a gradual deterioration of pulse shape could be observed, so that an originally short flat pulse might appear after many reflections to be rounded off and extended in time. It seems likely that this was caused by diffusing reflections from the film and the back of the quartz as well as from the end of the specimen. Since measurements were made on the front of the

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\* We are much indebted to Dr. C. S. Pearsall of this Laboratory for his advice and assistance in this matter.



pulse, the distance of travel was always measured completely within the specimen.

For any particular series the time intervals between successively recorded echoes have been considered as independent measurements of an experimental quantity, which therefore determine an average value and a root mean error. Actually, the recorded values of the successive time intervals are not strictly independent, but are so interrelated that a deviation from the mean in one interval is likely to be counterbalanced by a deviation in the opposite direction in the next. For this reason the root-mean-square deviation of these quantities should actually be greater than the error in the average. A more exact treatment seems scarcely justified and, in the presentation of the data, this root mean error has been included in Tables II and III to give a comparative measure of the precision of the respective time measurements.

### 3. Alkali Halides

To arrive at the dynamic equations of an elastic anisotropic medium, one equates the product of the mass of an infinitesimal volume times its acceleration along a coordinate axis to the net force obtained by integrating the stress components over the surface of the volume element. This gives the result

$$\rho \ddot{u}_i = \sum_j \frac{\partial T_{ij}}{\partial x_j} \quad (1)$$

where  $\rho$  is the density,  $u_i$  is the displacement in the  $i$ th direction, and the  $T_{ij}$  are components of the stress tensor. All indices run over the range of the three Cartesian coordinates. The stresses can be related to the strains  $\epsilon_{kl}$  by a tensor equation involving the moduli of elasticity in the form of a fourth-order tensor.

$$T_{ij} = \sum_{kl} c_{ijkl} \epsilon_{kl} \quad (2)$$

The strains  $\epsilon_{kl}$  are here defined as a symmetric tensor\* in terms of the displacements:

$$\epsilon_{kl} = \frac{1}{2} \left( \frac{\partial u_k}{\partial x_l} + \frac{\partial u_l}{\partial x_k} \right) \quad (3)$$

The elastic equations for the medium are obtained by combining equations (1), (2) and (3).

$$\rho \ddot{u}_i = \frac{1}{2} \sum_{jkl} \frac{\partial}{\partial x_j} \left\{ c_{ijkl} \left( \frac{\partial u_k}{\partial x_l} + \frac{\partial u_l}{\partial x_k} \right) \right\} \quad (4)$$

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\* This definition of the strains is not the traditional one, but is nevertheless widely used. It is more convenient here because of the tensor character.

The tensor  $c_{ijkl}$  is symmetric with respect to interchange of  $i$  and  $j$ ,  $k$  and  $l$ , and the pair  $ij$  with the pair  $kl$ . For a homogeneous medium the moduli of elasticity are independent of position. Therefore

$$\rho \ddot{u}_i = \sum_{jkl} c_{ijkl} \frac{\partial^2 u_k}{\partial x_j \partial x_l} \quad (4a)$$

Under the conditions of measurements with pulsed ultrasonics, the wavelength is small compared with dimensions of the specimen. For a pulse of plane waves traveling through a medium in the  $x_1$  direction, one may expect all quantities to be independent of  $x_2$  and  $x_3$ . For this reason the elastic equations of motion become simplified,

$$\rho \ddot{u}_i = \sum_k c_{i1k1} \frac{\partial^2 u_k}{\partial x_1^2} \quad (4b)$$

If the expressions for the displacements of the plane waves are taken to be

$$u_i = A_i e^{i\omega(t - x_1/v)} \quad ,$$

then the equations for the amplitudes become

$$\rho v^2 A_1 - \sum_k c_{i1k1} A_k = 0 \quad (4c)$$

One can identify the components of the fourth-order tensor with the moduli  $c$  of elasticity as usually defined by combining paired indices.

$$\begin{array}{ll} 11 \rightarrow 1 & 23 \rightarrow 4 \\ 22 \rightarrow 2 & 31 \rightarrow 5 \\ 33 \rightarrow 3 & 12 \rightarrow 6 \end{array}$$

In the case of propagation parallel to one of the cubic axes of the alkali halides the determinantal equation for the allowed values for velocity of propagation takes on a particularly simple form

$$\begin{vmatrix} c_{11} - \rho v^2 & 0 & 0 \\ 0 & c_{44} - \rho v^2 & 0 \\ 0 & 0 & c_{44} - \rho v^2 \end{vmatrix} = 0$$

With an X-cut quartz crystal attached to a (100) face  $c_{11}$  could be obtained directly from measurements of the elapsed time between successive echoes and the distance traveled by the pulse. Density values as listed in Table 1 were obtained from the Handbook of Chemistry and Physics. Replacing the X-cut quartz by a Y-cut quartz one could generate transverse waves and obtain  $c_{44}$ .

Table 1. Measurements on alkali halides in units of  $10^{11}$  dynes/cm<sup>2</sup>.

		LiF	NaCl	KBr	KI
Density		2.295	2.165	2.75	3.13
I (a)	$c_{11}$	9.75			2.69
(b)	$c_{44}$				.362
II	$c_{11}$	9.96	4.79	3.54	
III (a)	$c_{11}$	9.74	4.85	3.45	
(b)	$c_{44}$	5.56	1.27 <sub>1</sub>	.508	
IV (a)	$c_{44}$	5.52	1.26 <sub>0</sub>	.515	
(b)	$(c_{11}-c_{12})/2$	2.85	1.80 <sub>9</sub>	1.45 <sub>3</sub>	
(c)	$c_{12}$ (calc)	4.04	1.23	.54	
(d)	$\left\{ \frac{c_{11} + c_{12}}{2} + c_{44} \right\}$	12.12	4.27	2.54	
(e)	$\left\{ \frac{c_{11} + c_{12}}{2} + c_{44} \right\}$	12.4 <sub>5</sub>	4.31	2.50	

A second specimen was necessary in each case for the determination of  $c_{12}$ . These additional specimens were supplied with a pair of plane parallel faces in the (110) direction. The determinantal equation for the values of the velocity becomes \*

$$\begin{vmatrix} \left[ \frac{1}{2}(c_{11} + c_{12}) + c_{44} \right] - \rho v^2 & 0 & 0 \\ 0 & \frac{1}{2}(c_{11} - c_{12}) - \rho v^2 & 0 \\ 0 & 0 & c_{44} - \rho v^2 \end{vmatrix} = 0$$

With the X-cut quartz one measures  $\frac{1}{2}(c_{11} + c_{12}) + c_{44}$ , and with the Y-cut quartz

\* For formulas giving the expressions for elastic constants, after a rotation, see W. G. Cady, "Piezoelectricity," McGraw Hill Book Company (1946).

one measures  $\frac{1}{2}(c_{11} - c_{12})$  and  $c_{44}$  simultaneously from two series of echoes. If the Y-cut crystal was oriented so that the x axis was parallel to the  $(\bar{1}10)$  axis in the  $(110)$  plane of the alkali halide, then only the transverse vibration with velocity  $[(c_{11} - c_{12})/2\rho]^{1/2}$  was excited. In a similar manner the other beam could be isolated by rotating the quartz through  $90^\circ$ . In addition to supplying values for  $c_{12}$ , measurements on the  $45^\circ$  alkali halides gave two internal checks on the accuracy of the measurements.

All the data taken on alkali halides are listed in Table I. The measurements tabulated in rows I(a) and (b) were taken on specimens kindly supplied by Professor D. C. Stockbarger of the M. I. T. Physics Department. Mr. D. L. Arenberg of the Physics Department of Brown University loaned the specimens from which the measurements given in row II were obtained. The measurements under III and IV refer to specimens purchased from the Harshaw Development Company. The specimens used for III were cut along cleavage planes and allowed ultrasonic propagation in the  $(100)$  direction. The measurements IV(a), (b) and (d) were made from a second set of specimens cut to provide flat parallel  $(110)$  planes. The values of IV(a) should be compared with III(b) to evaluate the degree of reproducibility of the same measurement in two different specimens. The values for  $c_{12}$  in IV(c) are obtained from III(a) and IV(b). The results tabulated in IV(e) are calculated from III(a), (b) and IV(c) and are to be compared with the measured values in IV(d). The internal agreement with the Harshaw crystals is better than 2 per cent in all cases except one (where the disagreement is less than 3 per cent). These crystals were cut to afford cross sections one inch square (or more) perpendicular to the path of the ultrasonic beam. The active area of the quartz crystals in every case was a circle 0.5 in. in diameter. Under these conditions good pulse-shape reproduction was maintained and accurate time determination was possible. The specimens loaned by Mr. Arenberg were also originally prepared by the Harshaw Company, but presented cross sections 0.5 in. square to the ultrasonic beams. With them the pulse-shape reproduction was poorer with consequent greater inaccuracy in the time measurement. This may have been the result of the smaller cross section or of inexperience in the technique of securing satisfactory films as the measurements were of a preliminary nature.

The weighted results of the measurements with the one-inch square specimens are given in Table II together with probable error figures based on the precision of the time measurements. In some cases, the internal checks (see Table I) show greater deviations than would be expected from the indicated precision and perhaps arise from an unknown source of systematic error. Values obtained by other investigators are also listed in Table II for comparison. The most marked discrepancies appear in the comparison of these measurements for LiF and those of Bergman<sup>9</sup> obtained by an optical method. For KBr and KI the  $c_{44}$  constant here measured is about 20 per cent less than that measured by Bridgman.<sup>11</sup> For NaCl, however, there appears to be fair agreement among all observers.

Table 2. Elastic constants of alkali halides in units of  $10^{11}$  dynes/cm<sup>2</sup>

	Pulsed Measurement	Bergman <sup>9</sup>	Durand <sup>10</sup>	Bridgman <sup>11</sup>	Hunter and Siegel <sup>12</sup>
<b>LiF</b>					
$c_{11}$	$9.74 \pm 0.01$	11.77			
$c_{12}$	$4.04 \pm 0.02$	4.33			
$c_{44}$	$5.54 \pm 0.03$	6.28			
<b>NaCl</b>					
$c_{11}$	$4.85 \pm 0.01$	4.67	4.99	4.70	4.86
$c_{12}$	$1.23 \pm 0.02$	1.23	1.31	1.23	1.19
$c_{44}$	$1.26 \pm 0.025$	1.19	1.27 <sub>0</sub>	1.28 <sub>1</sub>	1.28
<b>KBr</b>					
$c_{11}$	$3.45 \pm 0.07$			3.33	
$c_{12}$	$0.54 \pm 0.03$			.58	
$c_{44}$	$0.508 \pm 0.005$			.621	
<b>KI</b>					
$c_{11}$	$2.690 \pm 0.005$			2.67	
$c_{12}$	$.362 \pm 0.0014$			.421	

A few observations can be made about ultrasonic attenuation and pulse behavior in the alkali halides. In general the attenuation between successive echoes appeared to be far smaller than we have encountered in most substances. In this respect pulses of compressional vibration moving perpendicular to the cleavage planes made the best showing. In the case of the measurement of  $c_{11}$  for rock salt, over fifty echoes were observed on the 1.22-millisecond sweep. From first to last there was diminution in intensity of less than 15 db. In the potassium bromide specimen for the same period of time there was observed a drop in intensity of about 20 db for thirty-seven echoes. The order of magnitude of the results rather than the actual numbers is the significant quantity in isolated measurements of this sort. The results were very sensitive to the uniformity and character of the connecting film between the specimen and the quartz. Probably film losses account for the fact that transverse waves showed greater attenuation than compressional waves.

With lithium fluoride very marked mode conversion took place. Energy was lost from the main compressional beam on striking the sides of the specimen at small angles by conversion to transverse vibration. Some of the transverse beams so generated were later reconverted to a compressional excitation and detected by the X-cut quartz. It was possible to identify positively these smaller echoes by the times of their arrivals. The pronounced effect of large angle reflection in causing mode conversion, predominantly in LiF, may be accounted for (1) by the longer wavelength which causes a wider diffraction pattern for the same geometry and (2) possibly by greater efficiency of conversion in the region of an incident angle of  $75^\circ$  (as determined by the dimensions of the specimen). D. L. Arenberg has evaluated the efficiency of conversion as a function of angle and Poisson ratio for isotropic materials<sup>5</sup> and shown it to be very sensitive to the latter for large angles. The extension of this work to a cubic crystal presents difficulties. It should, however, be remarked that the ratio  $c_{11}/c_{44}$  is significantly smaller for LiF than for the other alkali halides so that a different behavior on reflection may be expected.

#### 4. Copper

We had the good fortune to borrow for test two large copper single crystals from Mr. L. Gold of the M. I. T. Metallurgy Department. Previous attempts to make measurements on polycrystalline copper specimens had been unsuccessful because of the very large scattering losses involved. With both single crystals of copper, however, return signals were received which showed well defined pulse shape and little evidence of scattering. These signals, however, fell off quite rapidly, something of the order of 1 db per cm. This large attenuation is in marked contrast with the behavior of the alkali halides discussed in the previous section. It should be pointed out that, while the Harshaw crystals had all been carefully annealed, the copper crystals were untreated. The frequency of the measurement is beyond the range of the frequency-dependent types of internal friction usually investigated for metals<sup>13</sup>. There is a possibility that the high losses in the copper may be associated with the mechanism of plastic deformation as the frequency dependence of this cause of internal friction has not been investigated over a very wide frequency range.

From each of the two copper crystals three ultrasonic velocities were measured in one direction, corresponding to one compressional and two transverse waves. If the crystal orientations had been known, it would have been possible to obtain values for the elastic constants of copper. Conversely, it is possible to use previously measured values of the elastic constants to compute the crystal orientation. The complexity of the mathematical relations involved makes this procedure more arduous than the results would justify, since the technique could never compete with X-rays in simplicity and accuracy.

## 5. Rochelle Salt

For a piezoelectric material additional terms must be added to Eq. (2) for the stresses to include the interactions between mechanical and electrical parameters.

$$T_{ij} = \sum_{kh} c_{ijkh} \epsilon_{kh} + \sum_m f_{ijm} P_m \quad (5)$$

where the  $P_m$  are the polarizations, and the  $f_{ijm}$  are the piezoelectric constants.

Also, the equations for the electric field strengths give

$$E_i = \sum_{kh} f_{khi} \epsilon_{kh} + \sum_m \chi_{im} P_m \quad (6)$$

where the  $\chi_{im}$  are the reciprocal susceptibilities of the clamped crystal. Under this selection of thermodynamic variables, the elastic constants with constant polarization are involved.

If one writes down Maxwell's equations for the piezoelectric crystal, it is practical to disregard the magnetic quantities and charge concentrations inside the crystal. One then obtains the following equations,

$$\text{Curl } \mathbf{E} = 0 \quad \text{and} \quad \text{div } \mathbf{D} = 0.$$

Under the conditions of the pulsed ultrasonic experiment one can assume that the only spatial variation the field quantities will exhibit will be along the direction of propagation, say the  $x_1$  direction. This shows that  $E_2$ ,  $E_3$ , and  $D_1$  are all constants and affect the ultrasonic velocity only by their biasing action. It follows that Eq. (6) becomes

$$E_1 = \sum_{kh} f_{khl} \epsilon_{kh} + \sum_m \chi_{1m} P_m = -4\pi P_1 \quad (6a)$$

$$0 = \sum_{kh} f_{kh2} \epsilon_{kh} + \sum_m \chi_{2m} P_m \quad (6b)$$

$$0 = \sum_{kh} f_{kh3} \epsilon_{kh} + \sum_m \chi_{3m} P_m. \quad (6c)$$

These equations can be solved for the components of the polarization and the results substituted back into Eq. (5). The equations of motion which replace (4b) for the non-piezoelectric crystal have the same form

$$\rho \ddot{u}_i = \sum_k c_{ilk}^* \frac{d^2 u_k}{dx_1^2} \quad (7)$$

except that now the moduli of elasticity (now starred) have been altered by the inclusion of the piezoelectric terms. Since the added terms depend in a special way on the direction of propagation, they do not necessarily have the symmetry of the crystal and may make the crystal appear to have a lower symmetry than it is known to possess. This effect was first observed by Atanasoff and Hart<sup>14</sup> in their measurements on standing waves in quartz. The correct explanation of the effect

was put forward by A. W. Lawson.<sup>15</sup>

In the case of Rochelle salt the crystal symmetry remains unaffected, but at least one of the added terms has a profound effect of a different sort. For this material the  $\chi_{ij}$  is a matrix with no off-diagonal terms and the  $f_{kli}$  connect only polarization parallel to a given axis with the shear stress about that axis. Again use is made of the fact that all field quantities are a function of  $x_1$  alone so that it remains only to relate the  $T_{il}$  with the  $\epsilon_{kl}$ ,

$$T_{il} = \sum c_{ilk} \epsilon_{kl} - \left( \frac{f^2}{\chi_{mm}} \right)_{m=i=1} \epsilon_{il} \quad (8)$$

As a result the starred moduli of elasticity can be written

$$c_{ilk}^* = c_{ilk} \quad \text{for } i \neq k \text{ or for } i = 1 \quad (9)$$

and

$$c_{i111}^* = c_{i111} - \frac{f^2}{\chi_{mm}} \quad \text{for } m, i \text{ and } 1 \text{ all different.}$$

In the usual nomenclature this last relation would be written

$$c_{55}^* = c_{55} - \frac{f^2}{\chi_2} \quad (9a)$$

$$c_{66}^* = c_{66} - \frac{f^2}{\chi_3} \quad (9b)$$

It is of interest to note that the starred quantities are identically the reciprocals of the elastic compliances for the foiled crystals.

Since  $c_{15}$ ,  $c_{16}$ , and  $c_{56}$  vanish for Rochelle salt from symmetry conditions (which are not removed by inclusion of piezoelectric terms), the determinantal equation for velocities in the  $x_1$  direction is

$$\begin{vmatrix} c_{11} - \rho v^2 & 0 & 0 \\ 0 & c_{55}^* - \rho v^2 & 0 \\ 0 & 0 & c_{66}^* - \rho v^2 \end{vmatrix} = 0 \quad (10)$$

It is possible then to generate a pure compressional wave by an X-cut quartz crystal or two transverse waves with a Y-cut crystal, respectively. In this way one can measure  $c_{11}$ ,  $c_{55}^*$  and  $c_{66}^*$ . By attaching X-cut quartz crystals to the faces perpendicular to the  $x_2$  and the  $x_3$  directions, measurements can also be made



of  $c_{22}$  and  $c_{33}$ . These five values are listed in Table 3 in the first block which refers to the so-called "90° cuts" or those specimens whose sides were perpendicular to the principal axes of the Rochelle salt.

Table 3. Elastic moduli of Rochelle salts in units of  $10^{11}$  dynes/cm<sup>2</sup>

	Pulsed Measurements	Unstarred Values	Mason
90° Cuts (100)			
$c_{11}$	$2.550 \pm .005$		2.64
$c_{22}$	$3.81 \pm .011$		3.18
$c_{33}$	$3.705 \pm .013$		3.91
$c_{55}^*$	$0.286_3 \pm .008$	$c_{55} = 0.321 \pm .008$	0.304
$c_{66}^*$	$0.960 \pm .027$	$c_{66} = 0.979 \pm .027$	0.996
		$\frac{c_{55} + c_{66}}{2} = 0.650 \pm .014$	
45° Cuts (110)			
$c_{12}$	$1.41 \pm .03$		1.81
$c_{23}$	$1.46 \pm .06$		2.13
$c_{13}$	$1.16 \pm .04$		2.23
$\frac{(c_{44} + c_{66})^*}{2}$	$1.145 \pm .003$	$\frac{(c_{44} + c_{66})}{2} = 1.159 \pm .003$	
		$c_{44} = 1.34 \pm .03$	1.25
$\frac{(c_{55} + c_{66})^*}{2}$	$0.637 \pm .002$	$\frac{(c_{55} + c_{66})}{2} = 0.644 \pm .002$	

In the same table (second column) are given values for  $c_{55}$  and  $c_{66}$  as calculated from Eq. (9) by using Mason's values:<sup>16</sup>

$$f_{14} = 7.8 \times 10^4; \quad f_{25} = 7.05 \times 10^4; \quad f_{36} = 5.40 \times 10^4$$

$$\text{and } \chi_2 = 1.43, \quad \chi_3 = 1.53; \quad \text{and } K_2 = 9.8, \quad K_3 = 9.2 \text{ c.g.s. units.}$$

The differences between  $c_{55}^*$  and  $c_{55}$ ,  $c_{66}^*$  and  $c_{66}$  are not large but, while  $c_{44}$  varies only slowly with temperature, it is known that the foiled elastic constant for shear about the  $x_1$  axis,  $c_{44}^*$ , effectively vanishes at 23.0°C. For the temperature range -18°C to +23.0°C the Rochelle salt crystal is deformed by a set strain  $\epsilon_4$ , its symmetry class changes from orthorhombic to monoclinic, and it becomes ferroelectric. This anomalous behavior has been successfully treated by the phenomenological theory of Mueller.<sup>17</sup> We shall return to a discussion of the transverse vibration with velocity  $(c_{44}^*/\rho)^{\frac{1}{2}}$  later. It is sufficient to point out here that the quantity was too temperature-dependent to allow precise calculation of  $c_{44}$  and values for these quantities are omitted from the upper block of Table 3.

The lower block of Table 3 gives the results obtained from the 45° cut specimens. These were principally measurements of the off-diagonal elements  $c_{12}$ ,  $c_{23}$ , and  $c_{13}$ . For a 45° rotation about the axis in the  $x_1$  direction the transformed matrix\* which relates strains and polarizations to stresses and electric field strength [see Eq. (5) and (6)] is given below:<sup>18</sup>

$c_{11}$	$\frac{c_{12}+c_{13}}{2}$	$\frac{c_{12}+c_{13}}{2}$	$\frac{c_{13}-c_{12}}{2}$	0	0	0	0	0
$\frac{c_{12}+c_{13}}{2}$	$\frac{c'+c_{23}+2c_{44}}{2}$	$\frac{c'+c_{23}-2c_{44}}{2}$	$\frac{c_{33}-c_{22}}{4}$	0	0	$f_{14}$	0	0
$\frac{c_{12}+c_{13}}{2}$	$\frac{c'+c_{23}-2c_{44}}{2}$	$\frac{c'+c_{23}+2c_{44}}{2}$	$\frac{c_{33}-c_{22}}{4}$	0	0	$-f_{14}$	0	0
$\frac{c_{13}-c_{12}}{2}$	$\frac{c_{33}-c_{22}}{4}$	$\frac{c_{33}-c_{22}}{4}$	$\frac{c'-c_{23}}{2}$	0	0	0	0	0
0	0	0	0	$\frac{c_{55}+c_{66}}{2}$	$\frac{c_{55}-c_{66}}{2}$	0	$\frac{f_{25}-f_{36}}{2}$	$\frac{f_{25}+f_{36}}{2}$
0	0	0	0	$\frac{c_{55}-c_{66}}{2}$	$\frac{c_{55}+c_{66}}{2}$	0	$\frac{f_{25}+f_{36}}{2}$	$\frac{f_{36}-f_{25}}{2}$
0	$f_{14}$	$-f_{14}$	0	0	0	$\chi_1$	0	0
0	0	0	0	$\frac{f_{25}-f_{36}}{2}$	$\frac{f_{25}+f_{36}}{2}$	0	$\frac{\chi_2+\chi_3}{2}$	$\frac{\chi_3-\chi_2}{2}$
0	0	0	0	$\frac{f_{25}+f_{36}}{2}$	$\frac{f_{36}-f_{25}}{2}$	0	$\frac{\chi_3-\chi_2}{2}$	$\frac{\chi_2+\chi_3}{2}$

where  $c'$  stands for  $\frac{c_{22}+c_{33}}{2}$ .

\* Mason's starred quantities are equivalent to our unstarred quantities.

For plane-wave propagation in the new  $x_2$  direction (actually a (011) axis in the unrotated lattice) the strains  $\epsilon_1, \epsilon_3$ , and  $\epsilon_5$  will not be excited. One can solve for the  $P_i$  from equations which resemble 6a, b, and c after interchange of indices 1 and 2 and obtain

$$\begin{aligned}
 P_1 &= -\frac{f_{14}}{\chi_1} \epsilon_2 \\
 P_2 &= -\frac{f_{25}\chi_3 + f_{36}\chi_2}{2[\chi_2\chi_3 + 2\pi(\chi_2 + \chi_3)]} \epsilon_6 \\
 P_3 &= \frac{f_{25}(\chi_3 + 4\pi) - f_{36}(\chi_2 + 4\pi)}{2[\chi_2\chi_3 + 2\pi(\chi_2 + \chi_3)]} \epsilon_6
 \end{aligned} \tag{11}$$

It follows that the determinantal equation for the velocities in this direction is:

$$\begin{vmatrix}
 \frac{c_{11} + c_{23} + 2c_{44}^*}{2} - \rho v^2 & \frac{c_{33} - c_{22}}{4} & 0 \\
 \frac{c_{33} - c_{22}}{4} & \frac{c_{11} - c_{23}}{2} - \rho v^2 & 0 \\
 0 & 0 & \frac{(c_{55} + c_{66})^*}{2} - \rho v^2
 \end{vmatrix} = 0 \tag{12}$$

The quantity  $(c_{55} + c_{66})^*$  is accordingly an abbreviation

$$(c_{55} + c_{66})^* = c_{55} + c_{66} - \frac{\frac{f_{36}^2}{\chi_3} + \frac{f_{25}^2}{\chi_2} + (f_{25} - f_{36})^2 \frac{2\pi}{\chi_2\chi_3}}{1 + \frac{2\pi}{\chi_2} + \frac{2\pi}{\chi_3}}$$

Inspection of this determinantal equation indicates that there will be one purely transverse wave propagated in the (011) direction and polarized in the (100) direction. The other transverse mode and the compressional mode are coupled together, but fortunately the coupling is weak enough so that excitation with X-cut quartz appears to

give only one set of signals. The velocity of this nearly compressional wave has a measured value of  $(c_b/\rho)^{\frac{1}{2}}$  where  $c_b$  is given as  $2.64 \times 10^{11}$  dynes/cm<sup>2</sup> in column 1 of Table 4.

Table 4. Data and results for the non-diagonal elastic moduli of Rochelle salt (all quantities in units of  $10^{11}$  dynes/cm<sup>2</sup>)

Crystal Surface	(011)	(101)	(110)
$c_d$	1.182	0.94 <sub>2</sub>	0.858
$c_b$	2.64	2.53 <sub>2</sub>	3.32 <sub>8</sub>
$c_b + c_d$	3.82	3.47 <sub>4</sub>	4.18 <sub>6</sub>
Right side of Eq. (13)	3.76	3.41 <sub>4</sub>	4.14 <sub>0</sub>
Non-diagonal Moduli	1.52 - 1.40	1.19 - 1.13	1.44 - 1.38

Excitation with Y-cut quartz oriented to give transverse vibration polarized along the  $x_1$  axis led to a measurement of a velocity  $(c_d/\rho)^{\frac{1}{2}}$ , where  $c_d$  is given by  $1.182 \times 10^{11}$  dynes/cm<sup>2</sup> in Table 4. The quantities given in columns 2 and 3 of Table 4 refer to the other 45-degree cuts as indicated by the Miller indices at the head of each column, respectively. The  $c_b$  and  $c_d$  in each case refer to quantities experimentally measured from respectively compressional and transverse excitations. For the moduli of elasticity a cyclic interchange of subscripts is understood on going from column 1 to column 2, and from column 2 to column 3.

The observed data in Table 4, namely the values for  $c_b$  and  $c_d$  are used to calculate the off-diagonal moduli of elasticity  $c_{23}$ ,  $c_{13}$ , and  $c_{12}$ . The internal consistency of the data is checked by the diagonal-sum rule which requires that

$$(c_{22} + c_{33})/2 + c_{44}^* = c_b + c_d \quad \text{for (011) direction} \quad (13a)$$

$$(c_{11} + c_{33})/2 + c_{55}^* = c_b + c_d \quad \text{for (101) direction} \quad (13b)$$

$$(c_{11} + c_{22})/2 + c_{66}^* = c_b + c_d \quad \text{for (110) direction} \quad (13c)$$

These internal checks ( see rows 3 and 4 in Table 4 ) show discrepancies of one to three per cent, which unfortunately introduce uncertainties in the values of the non-diagonal moduli of the order of 5 or 10 per cent. The quantities of Eq. (13a)

require special comment because of the temperature sensitivity of  $c_{44}^*$ . A temperature run was made on the measurement of  $c_b$  for the (011) direction and the velocity of propagation was found to go through a minimum at 23.7°C near the Curie point. The value of  $c_b$  at this minimum is given as  $2.64 \times 10^{11}$  dynes/cm<sup>2</sup> in Table 4. Since  $c_{44}^*$  vanishes at the Curie point, only  $(c_{22} + c_{33})/2$  or  $3.76 \times 10^{11}$  dynes/cm<sup>2</sup>, has been used for the right side of Eq. (13) in row 4.

The evaluation of the non-diagonal elements was carried out twice in every case, by solving the quadratic equation for the desired quantity first with  $\rho v^2$  equal to  $c_b$  and next with  $\rho v^2$  equal to  $c_d$ . Both values are given in Table 4 as an indication of the probable error of the results. A first-order approximation to the value for any non-diagonal modulus could be obtained by neglecting the coupling between the modes. The exact value could then be quickly obtained by Horner's method. Only the mean values of  $c_{12}$ ,  $c_{23}$ , and  $c_{13}$  are given in Table 3.

The modulus of elasticity as determined from the pure transverse vibrations in the 45° Y-Z specimen has been used to give an additional check on  $c_{55}$  and  $c_{66}$ . The result for  $\frac{1}{2}(c_{55} + c_{66})$  as given at the bottom of Table 3 checks to 1 per cent the same quantity as calculated from measurements on the (100) specimens, as given in the same table. The value for  $\frac{1}{2}(c_{44} + c_{66})$  was also found from the 45° X-Z specimen and from it a value for  $c_{44}$  was obtained.

Table 3 also shows for comparison Mason's values for the moduli of elasticity for constant polarization as computed from his measured moduli of compliance. In Table 5 are given the values of the moduli of compliance as calculated from the data<sup>16</sup> obtained by the pulsed method. Values obtained directly for these quantities by Mason and Hinz<sup>19</sup> are given in adjoining columns. Here the agreement with Mason is quite satisfactory for all the moduli listed except  $s_{13}$ .

Table 5. Moduli of compliance for Rochelle salt in units of  $10^{-12}$  cm<sup>2</sup>/dynes.

	Pulsed Measurement	Mason <sup>16</sup>	Hinz <sup>19</sup>
$s_{11}$	5.24	5.18	5.23
$s_{22}$	3.50	3.49	3.43
$s_{33}$	3.37	3.34	3.24
$s_{12}$	-1.54	-1.53	-2.18
$s_{13}$	-0.98	-2.11	-1.68
$s_{23}$	-0.91	-1.03	-1.33

\* Hinz's measurements were made by a static method.

The attenuation of the ultrasonic beam in Rochelle salt was much greater than in the alkali halides. No systematic quantitative measurements were made, but it was observed that the loss was never less than 1 db per inch of travel and sometimes a great deal more. The attenuation was always large in those measurements which involved  $c_{44}^*$  and, for the propagation of the transverse wave which involved this modulus alone, the attenuation increased so rapidly as the Curie point was approached that it was not possible to extend our measurements below 26.5°C. An ultrasonic signal which was observed after it had traversed a half inch of Rochelle salt, dropped by 24 db as the temperature fell by 2° C in this range. There is some evidence that the rate of cooling was too rapid to maintain thermal equilibrium throughout the run, but it is quite doubtful that the associated dispersion could account for all the observed attenuation.

The measured values of  $c_{44}^*$  taken as a function of temperature checked within rather wide experimental error Mason's values for  $(s_{44})^{-1}$  and also Mueller's phenomenological theory\* (see Fig. 2):

$$c_{44}^* \simeq (s_{44})^{-1} = c_{44} \left[ 1 + \frac{\sigma c_{44}}{t-t_0} \right]^{-1}$$

where  $t_0$  has been taken to be 23.0°C,  $\sigma = 66.7 \times 10^{-12}$  deg cm<sup>2</sup>/dyne and  $\epsilon_{44} = 1.25 \times 10^8$  dynes/cm<sup>2</sup>. The run was taken with decreasing temperature starting at 29°C and there is an indication that the specimen was not at complete thermal equilibrium for the first few measurements. The open circles represent Mason's measurements of  $(s_{44})^{-1}$  by a resonance technique. In the pulsed experiment the Y-cut quartz crystal was affixed to the X-Y surface of the Rochelle salt with the x-axes of the crystals parallel. Even so, a small shear wave was propagated with its transverse vibration perpendicular to the y-axes of the Rochelle salt. The beating caused by this signal interfered with the measurements at the lower temperatures and it was impractical to continue the run for  $c_{44}^* \leq c_{55}^*$ .

As might be expected, mechanical stress and electrostatic bias along the  $x_1$  axis caused marked effects on those waves whose velocity depended on  $c_{44}^*$ . In general only qualitative information was obtainable concerning the influence of such external forces on the ultrasonic velocity. On the other hand, very pronounced changes in pulse size and shape accompanied the application of stress or bias and indicated clearly changing interference effect from different portions of the ultrasonic beam. These effects were more pronounced the nearer the Curie point<sup>17</sup>. At 24°C the velocity of the compressional wave in the (011) direction increased by 3 per cent on the application of a d-c field of 4 esu.

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\* See Ref. 17. Specifically this particular relation is stated in Eq. (10) of the second paper.

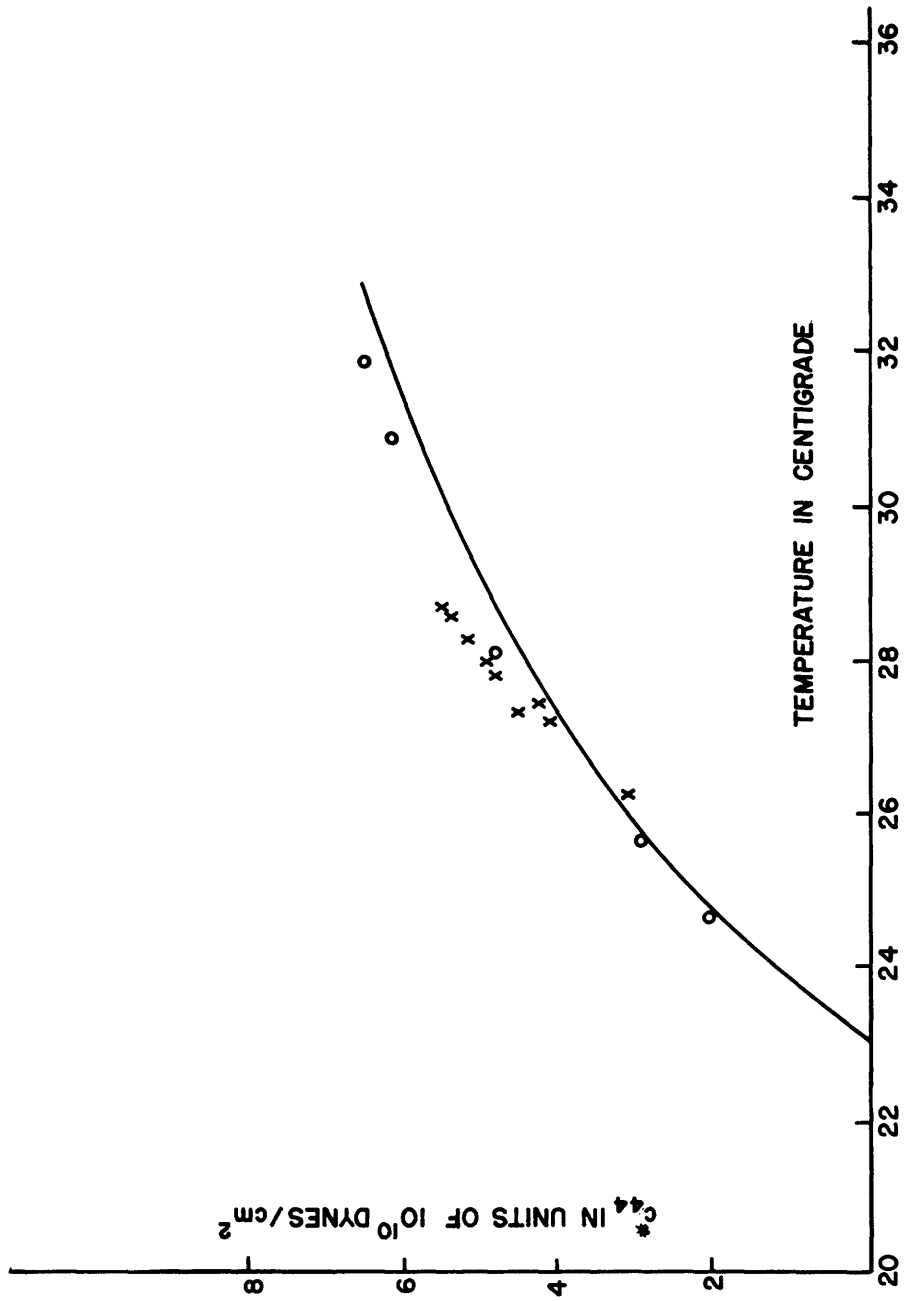


Figure 2.

## 6. Discussion and Acknowledgments.

A pulsed ultrasonic technique has been applied to measure the mechanical properties of some single crystals at 10 Mc/sec. The results for the elastic constants in general are self-consistent to 2 per cent or better and in most cases agree satisfactorily with previously measured values. The attenuation in the alkali-halide single crystals is small so that one can do little more than put an upper limit on the internal friction as measured by the decrement. Internal friction in the copper single crystal is high in comparison with that found at lower frequencies, even for unannealed specimens\* 18. Attenuation in Rochelle salt is also quite high, probably as a result of conversion of mechanical energy into electrical losses. Particularly high attenuation is evident in those cases which involve the shear constant  $c_{44}^*$  for the crystal with zero field in the  $x_1$  direction. It is known that for this modulus the departure from Hooke's law is appreciable for strains of  $10^{-4}$  within a few degrees of the Curie point. It seems possible that anharmonic terms in the stress-strain relation could be responsible for some of the observed loss. By causing an interaction with the Debye waves of the lattice these terms could bring about frequency conversion of the energy of the ultrasonic beam so that its intensity would decrease rapidly with distance traveled.

It is a great pleasure for me to thank Professor Mueller for having pointed out to me the interesting possibilities in Rochelle salt for such investigation and for his advice and lively interest in the research. Also I wish to thank individually Professor Stockbarger, Mr. Arenberg, and Mr. Gold for the use of their single crystal specimens.

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\* Our attenuation corresponds to a value of  $\Delta_1 = 8 \times 10^{-5}$  for the logarithmic decrement in Read's notation.



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