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DETERMINATION OF THE ELASTIC CONSTANTS OF BENZENE

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and
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OF BENZENE

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CONSTANTS OF BENZENE

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Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
PHYSICS

United States Naval Postgraduate School
Monterey, California

1 9 6 2

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from the

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ABSTRACT

Large single crystals of benzene (C_6H_6) were aligned by an optical method. The aligned crystals were pulsed with ultrasonic waves at a frequency of approximately 10 megacycles per second using quartz crystal transducers. The velocity of the ultrasonic waves was measured by comparing the echo transit time with that of simultaneously generated waves moving through a variable length path in a medium in which the velocity of sound was known precisely.

Velocities of longitudinal and transverse waves along each of the principal axes of the orthorhombic crystal were used to compute the main diagonal terms of the C_{ij} matrix. The off-diagonal terms were then determined by velocity measurements along arbitrarily selected directions.

Velocity measurements were made and the elastic constants computed over the temperature range $170^{\circ}K$ to $250^{\circ}K$.

Absorption in the crystal was measured over the same temperature range for each of the directions used for velocity measurements. The absorption was determined to be aelotropic.

The writers wish to express their appreciation for the assistance and encouragement given them by Professor O. B. Wilson of the U. S. Naval Postgraduate School in this work.

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INTRODUCTION

Benzene, the fundamental aromatic hydrocarbon, possesses an orthorhombic crystalline structure in the solid state.

The low melting point of benzene (5.2°C) renders the use of standard diffraction methods for the determination of orientation difficult. Benzene crystals are, however, transparent to visible light and possess a high positive birefringence; thus their optical properties provide a suitable means of alignment using simple optical methods.

The formulation of the strain energy equation for an orthorhombic crystal results in nine independent elastic constants[1]. By measurement of the velocities of longitudinal and transverse ultrasonic waves along the three principal axes, the six main diagonal terms of the C_{ij} matrix can be computed. The remaining three elastic constants must then be determined by velocity measurements along arbitrarily selected directions, using the previously determined values for the main diagonal terms.

Using the techniques for alignment, pulsing and velocity measurement described in this thesis, the velocity data was obtained for the computation of the elastic constants over the temperature range 170°K to 250°K.

In obtaining the velocity data, the opportunity was taken to observe and record the absorption of the ultrasonic pulses at a frequency of 10 megacycles per second as a function of crystal orientation and of temperature.

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CRYSTAL GROWING AND CRYSTALLINE STRUCTURE OF BENZENE

The large single crystals, necessary in order to follow the alignment and cutting procedures developed, were grown in a melt of reagent grade benzene. The melt was contained in a sealed container which was maintained at a temperature of approximately 5°C. After degassing, the bath was left at this temperature for approximately two weeks during which time the crystals formed.

The conglomerate mass of crystals was then broken apart and large single crystals of irregular shape were obtained and stored at a temperature of about -10°C until required.

Crystalline benzene is of the orthorhombic class, space group Pbca, the unit cell having the dimensions (2):

$$a = 7.292 \text{ A}^o$$
$$b = 9.471 \text{ A}^o$$
$$c = 6.742 \text{ A}^o \quad \text{at } -195°C$$

Optically the crystal is transparent with indices of refraction (3):

$$\gamma \ 1.64$$
$$\beta - \alpha = 0.004$$
$$\gamma - \alpha > 0.12$$

The crystals were thus very suitable for examination by optical methods.

CRYSTAL ALIGNMENT

In order to obtain the necessary data to solve the strain energy equation and thereby compute the elastic constants, crystals were required which were accurately aligned along each of the principal axes together with at least one sample which could be aligned along

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some arbitrary axis.

The method of alignment used consisted of examining the raw irregularly shaped crystals under a conical beam of polarized light.

For this purpose, a conoscope was constructed in the form shown schematically (Fig. 1). For actual examination the instrument was located in a refrigerated compartment maintained at a temperature of about $-10^{\circ}C$.

In the raw state, since there seems to be no apparent preferred direction of growth for benzene crystals, initial examination was made with the crystal immersed in a glass bottomed tank containing a mixture of benzene (C_6H_6) and methyl salicylate ($C_8H_8O_3$). This mixture was in the proportions of 440 parts methyl salicylate to 300 parts benzene by volume. The refractive index of this mixture is approximately 1.52, close to that of benzene at $-10^{\circ}C$. The actual mixture proportions were found to be not critical. Changes occur due to evaporation and the solubility of the crystalline benzene in the mixture. Fortunately the mixture is close to the solubility limit of benzene in methyl salicylate, so that loss of crystal by dissolution is small.

The tank was positioned in the conoscope so that the bottom of the fluid was at the focal point of the convergent lens, with the divergent beam spreading up through the fluid.

In this beam the raw crystal was examined for the location of the optic axes, the bisectrix of which locates the b axis of the crystal (Fig. 8).

Examination was carried out by rotating the crystal, held in a pair of tongs, in the beam to determine two extinction planes. Since

3

Ground Glass Screen

Analyser

Immersion Tank

Single Crystal

Glass Bottom

Lens

Polariser

Plane Mirror

Light Source
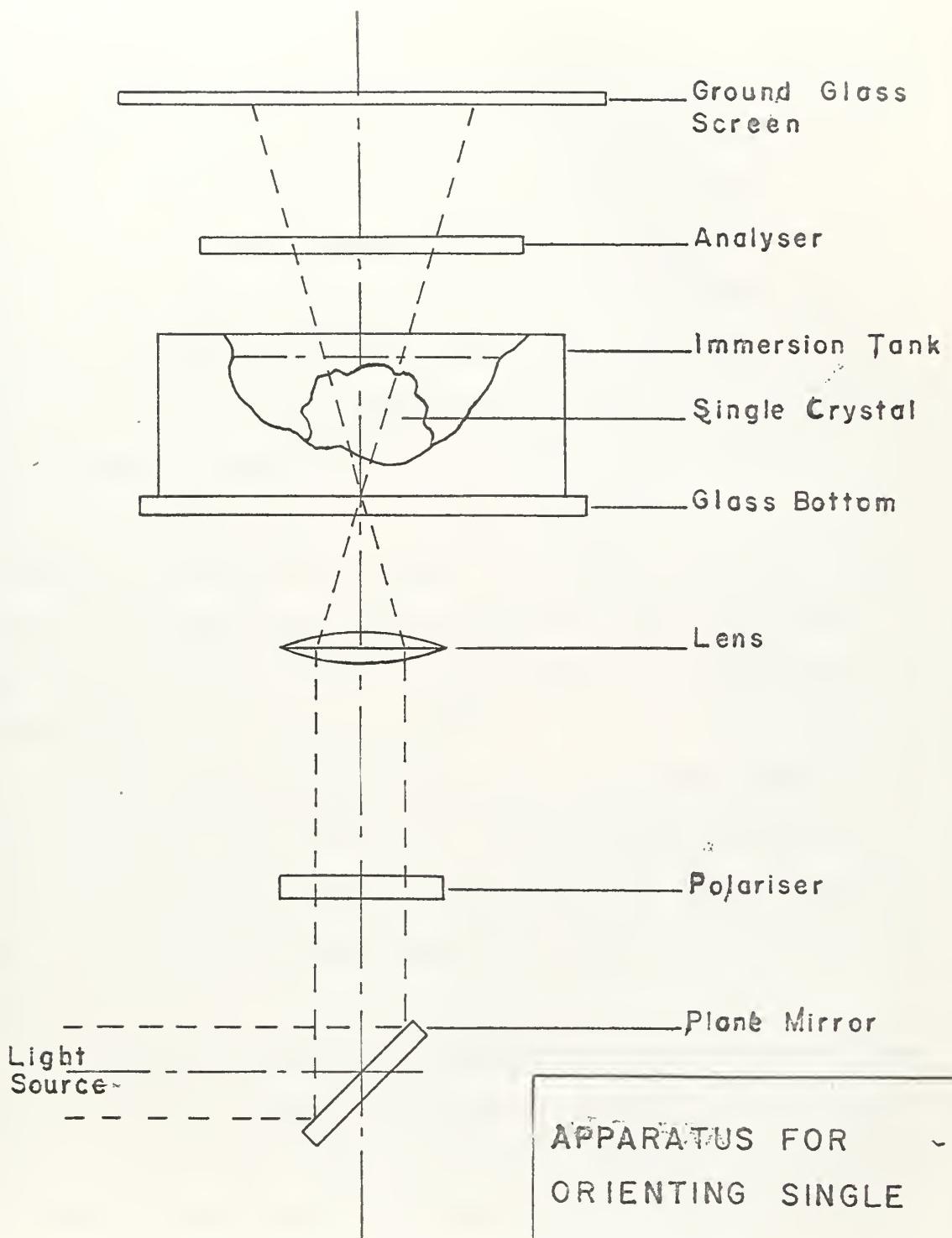
APPARATUS FOR ORIENTING SINGLE CRYSTALS. SCHEMATIC ARRANGEMENT

FIG. I.

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the normals to these extinction planes form an orthogonal system with one of the optic axes, this axis was visible at 90 degrees to both these normals.

This alignment was retained by transferring the crystal to a special clamp (Fig. 2), designed to accommodate a range of shapes and sizes of crystals and at the same time permit a more accurate alignment. The clamp consisted of a short length (about 5cm) of 10cm diameter aluminum tubing into which were mounted in gimbal fashion two aluminum rings. On the inside of the inner gimbal were secured four strips of spring steel bent into the center forming a spring collar which retains the crystal. Spring pressure was just sufficient to hold the crystal firmly in position.

Mounted in this clamp, the crystal was returned to the bath with the base of the clamp forming a reference face resting on the glass bottom of the bath and was thus in a plane normal to the optic axis of the conoscope.

With the freedom afforded by the gimbals, the crystal could be rotated with respect to the optic axis of the conoscope to bring the bisectrix into coincidence with this axis. Since the crystal was held firmly in the clamp, the interference pattern (Fig. 3) could be clearly observed.

The alignment was preserved by removing the clamp and crystal from the bath and, using the base of the clamp as reference, melting parallel faces on the crystal, which were finally covered with glass slides.

A check on this alignment was made by mounting the crystal on a goniometer attachment, which could be fitted to the conoscope.

INTERFERENCE
PATTERN.

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FIG. 3.
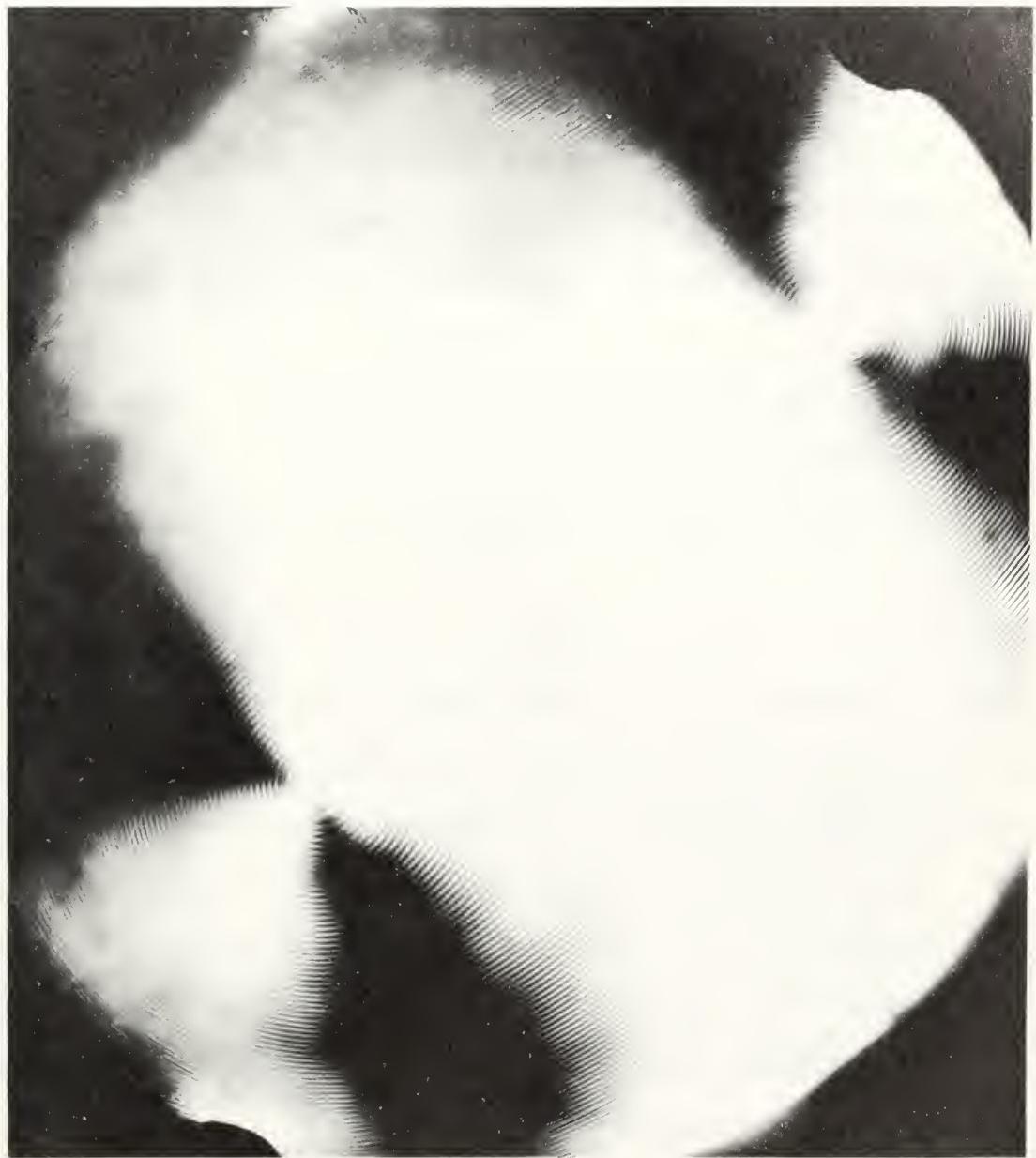
Small corrections to the alignment could be made by melting new faces on the crystal, the corrections being computed from the goniometer angles using the knowledge of the refractive indices of benzene.

Alignment to the other principal axes was accomplished by rotating the goniometer 90 degrees in the plane of the optic axes (100), or in a plane normal to the plane of the optic axes (001). After rotation, new parallel faces are melted on the crystal and glass slides secured to preserve the particular orientation.

Any other orientation could be obtained by appropriate rotation of the goniometer. In all cases, a knowledge of the direction of the optic plane was preserved by appropriately marking the glass covering slides.

MOUNTING OF CRYSTALS

For the purpose of ultrasonic pulsing, it was necessary to mount the crystals in such a manner as to permit electrical connection of a radio frequency source and a receiver to a transducer, which was in mechanical contact with the crystal. At the same time, it was necessary to ensure that the crystal orientation was maintained and the effects of sublimation eliminated. The crystal holder (Fig. 4) was therefore designed and manufactured to meet these requirements.

To prepare a crystal for mounting in this holder, it was transferred to a glass plate and frozen in place using the preserved face as reference; the desired axis was thus maintained normal to the glass plate. The cylindrical shape required to fit the holder was then obtained by melting the periphery of the crystal, using metal cylinders maintained at room temperature to melt the crystal. When the desired

End Plate

Mylar Seal

Crystal

Coated Mylar Seal
& Contact

Transducer

End Plate

CRYSTAL HOLDER.
SHOWING METHOD OF
MOUNTING AND SEALING
CRYSTAL.
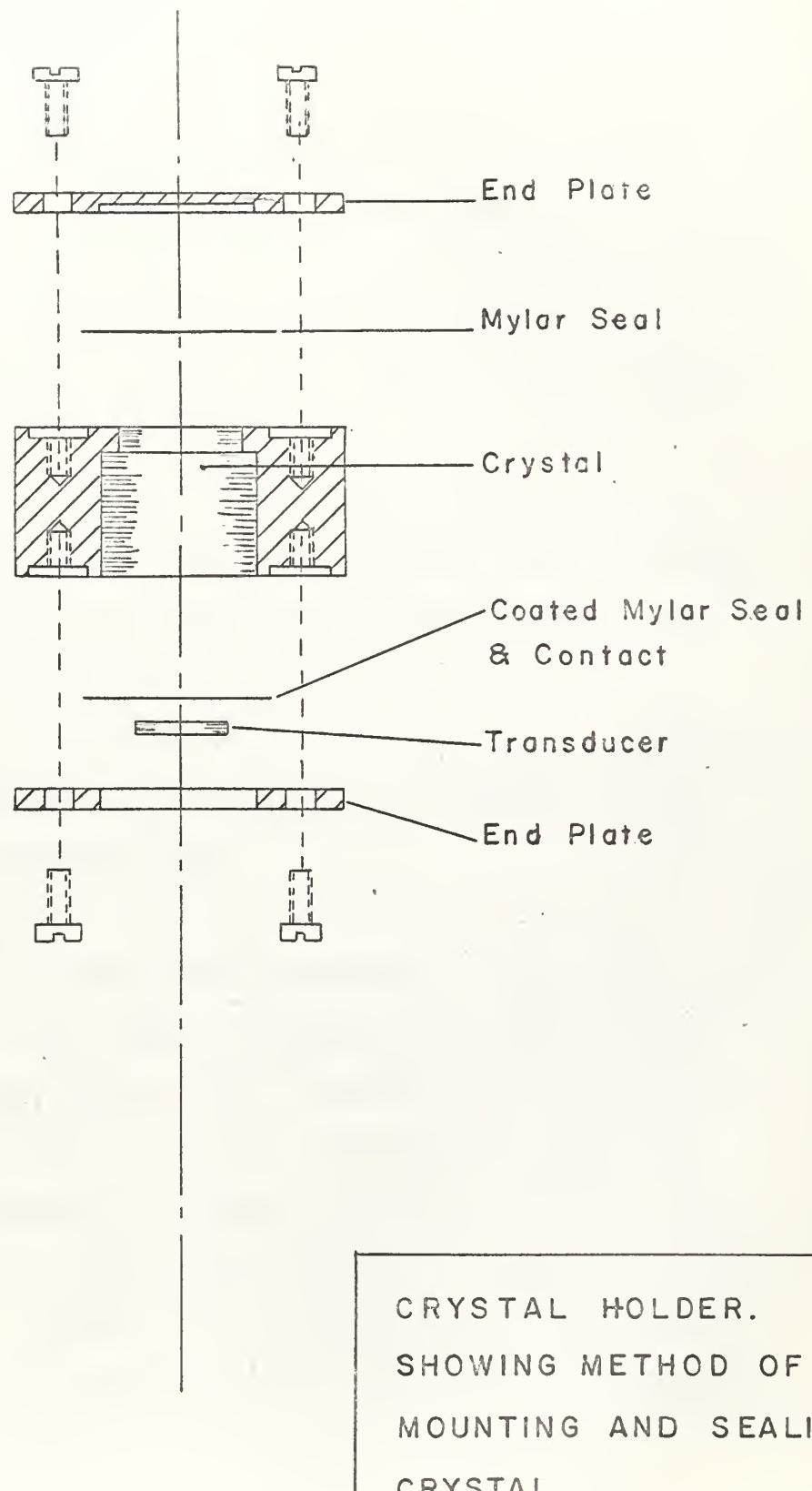
FIG. 4.

cylindrical shape was obtained, the holder was slipped over the sample and frozen in place. During this process, the sample and holder were maintained at refrigerator temperature.

With the crystal in the holder, the end faces were finished parallel to the holder faces by polishing on fine emery cloth. The end faces were then sealed with 1/4 mil clear Mylar for the free end and 1/4 mil aluminum coated Mylar for the end receiving the transducer, using glycerine as a sealing agent. The end seals were secured in place using the holder end plates.

The transducer was mounted on the aluminum coated Mylar using Nonaq stopcock grease. These bonding materials were found satisfactory for the transmission of both shear waves and longitudinal waves over the temperature range for which data was obtained.

The transducers employed were 0.5 inch diameter quartz crystal. X cut crystals were used for the generation of longitudinal waves; Y cut for shear or transverse waves.

PULSING OF CRYSTALS

For pulsing, the crystal holder was mounted in the pulsing assembly (Fig. 5). This assembly provided a secure support for the holder and at the same time permitted connection of the transducer to the radio frequency source. The ground connection was made through the body of the assembly and the crystal holder, the other connection being made through the spring loaded electrode. The method of mounting the holder allowed adjustment of the electrode pressure on the transducer; a light pressure was found best for the generation of longitudinal waves and a heavier pressure for transverse waves.

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Cover

End Plate

Crystal Holder

End Plate

Electrode Assembly
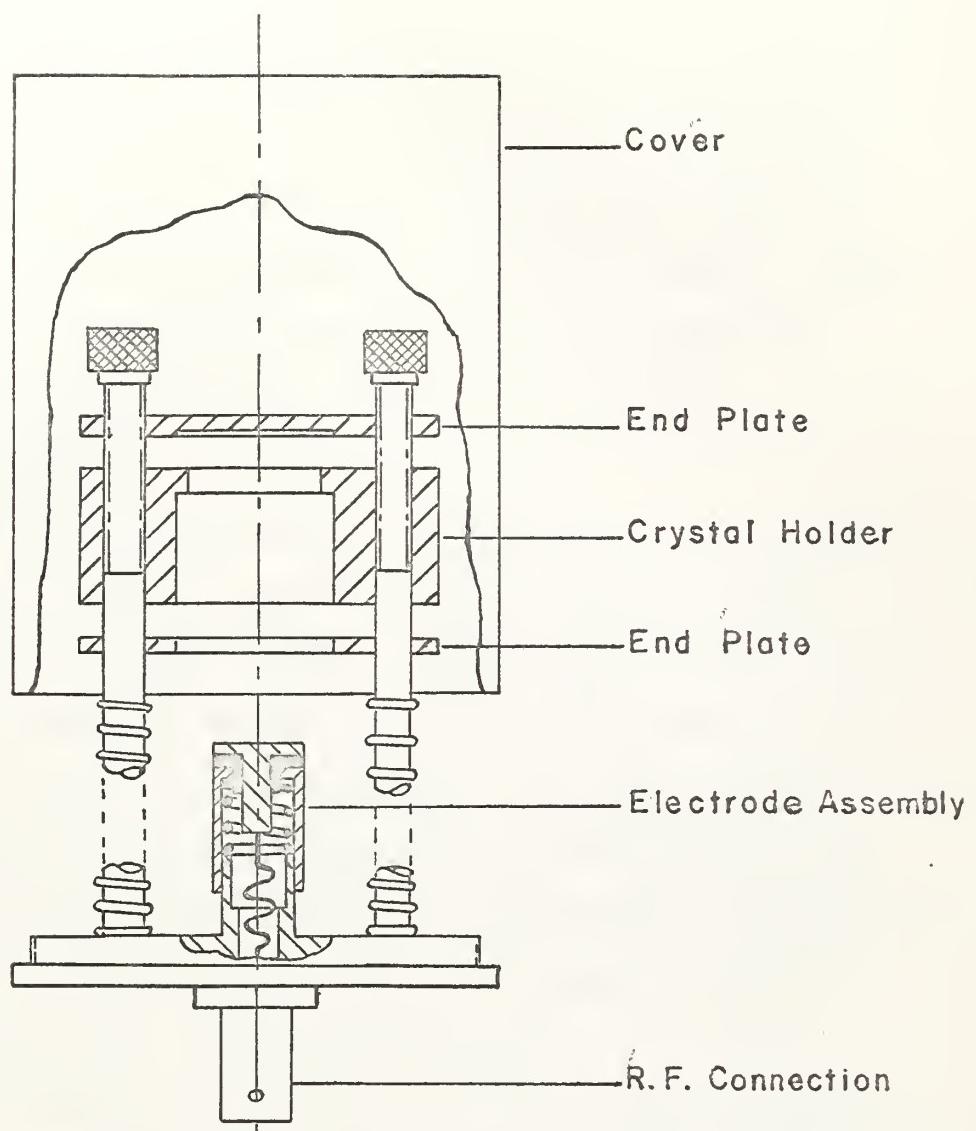
R.F. Connection

CRYSTAL PULSING
ASSEMBLY.
GENERAL ARRANGEMENT.

FIG.5.

Radio frequency pulses were generated by an Arenberg pulsed
oscillator, Model PG 650-C, connected by low impedance coaxial cable
to the pulsing assembly. The return echoes after reflection from the
free end of the crystal were amplified by an Arenberg wideband ampli-
fier WA-600 and displayed on a Tektronix Type RM45A oscilloscope. A
Tektronix Type RM 181 time mark generator was used for control of pulse
repetition rate and for external sweep control of the oscilloscope.
Figure 6 shows a schematic arrangement of the pulsing system.

MEASUREMENT OF VELOCITY

To obtain accurate measurements of the velocity of the ultrasonic
waves through the crystal, a modification of the method of velocity
measurement described in (4) was used. Figure 7 shows the construction
of the velocity comparator designed and built for this modified method.
In the velocity comparator, pulses generated by the quartz crystal
transducer immersed in the liquid medium were reflected off the rigid
boundary and received at the transducer. The path length and thus the
transit time of the pulse was made variable by altering the position
of the boundary by means of the micrometer screw.

In making a measurement, the pulse trains from both the comparator
and the crystal were superimposed on the oscilloscope and the path
length adjusted to bring corresponding echoes into coincidence. Pre-
cise matching could be obtained by observing the interference effects
as the echoes were brought into coincidence, since the comparator and
benzene transducers were pulsed in parallel.

The velocity in the crystal was then computed from the known
velocity in the liquid medium by the relation:
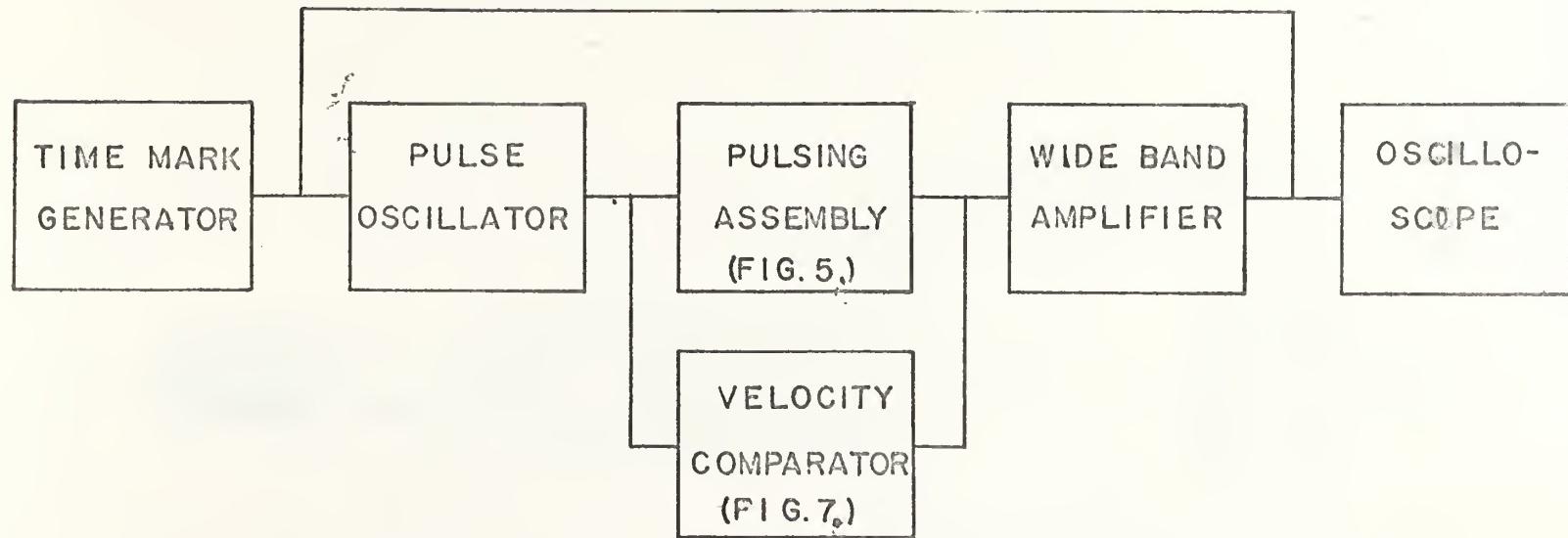
PULSING SYSTEM.

CIRCUIT SCHEMATIC

FIG. 6.

R. F. Connection

Insulator

Coated Mylar, Seal &
Contact

Quartz Transducer

Reflecting Boundary

Ethyl Alcohol
& Water

Micrometer,
Travel   0 - 2.5 cm.

VELOCITY COMPARATOR

GENERAL ARRANGEMENT

FIG. 7.

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$$V_c = \left[\frac{1 - l_o}{l_c} \right] V_1$$
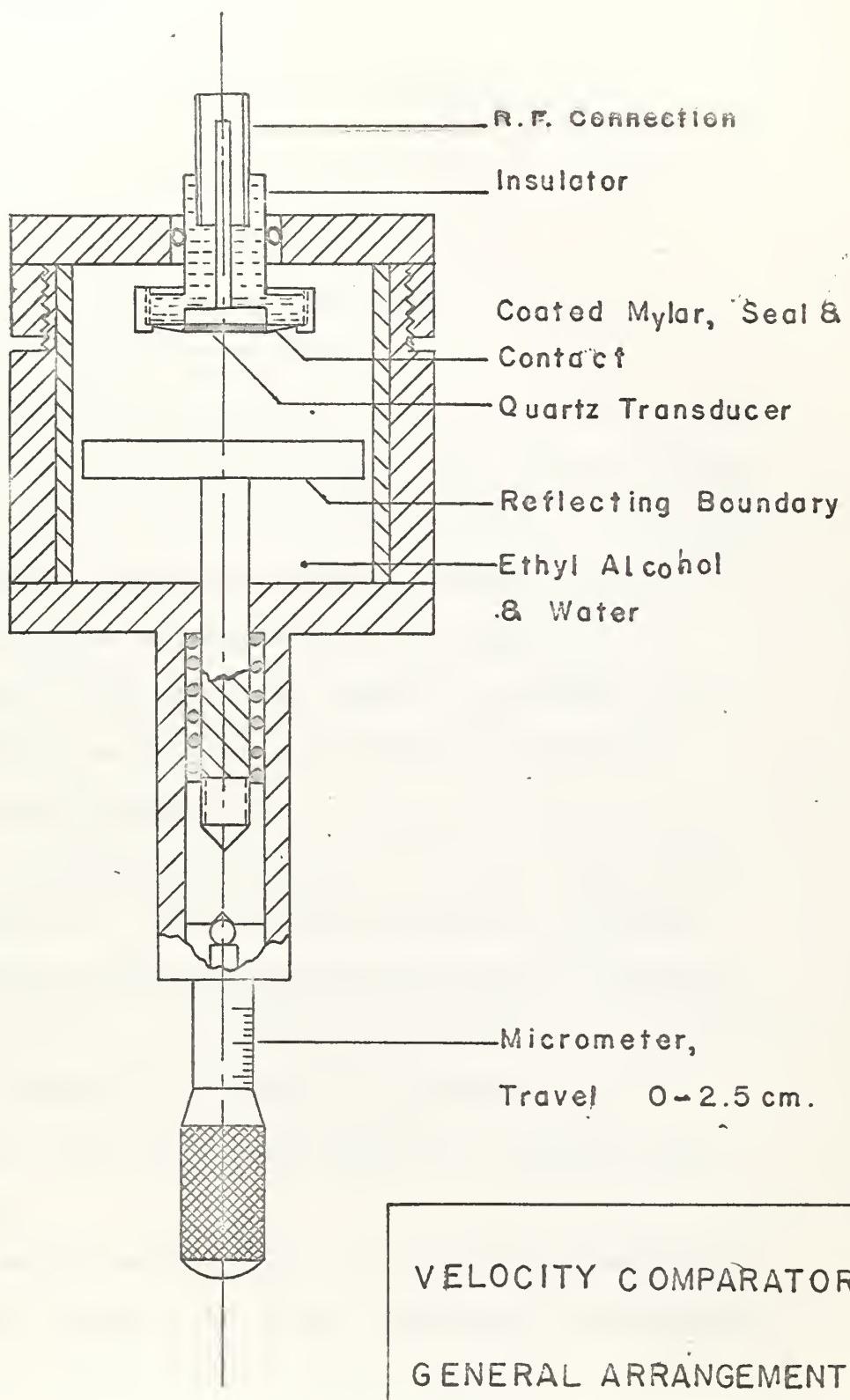
where: l_o = initial micrometer reading corresponding to zero
        path length.

l_c = length of path through crystal.

l = micrometer reading at coincidence.

V_1 = sound velocity in the liquid medium.

V_c = sound velocity in the crystal.

The liquid medium used was a mixture of 100 parts distilled water to 22 parts absolute ethyl alcohol by volume. This mixture transmits sound waves at a velocity given by Willard (5) which is of a magnitude suitable for comparison with the velocities of benzene crystals and is substantially independent of temperature in the region of 25°C. Temperature control of the device was, therefore, unnecessary. The temperature, however, was monitored and corrections made for the small variations which occurred.

Corrections to the measured length of the crystal were necessary to take into account the effect of thermal contraction of benzene. These corrections were made from the data on the thermal expansion of benzene given by Cox (2), and by Euchen and Lindenberg (6), and applied as a percentage decrease in the length of the crystal.

The accuracy of the velocity measurements was dependent on two dominant factors:

(a) Measurement of crystal length: this length was measured to .001 cm and, after correction for thermal contraction, was considered accurate to within .01 cm for the 3 cm path length.

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(b) Pulse matching between the crystal and velocity comparator; the two 10 mc pulses were matched to within one half of one wave length, resulting in a possible error of .05 μ sec in 12 μ sec.

The possible errors introduced by other factors were not of significant magnitude in comparison to these two factors. Based on this estimate, the velocity error was determined to be less than 1%.

Measured velocities, using the same crystal, were reproduced to within 1% over the temperature range 250°K to 170°K.

TEMPERATURE CONTROL AND MEASUREMENT

Velocity measurements were made over the temperature range 250°K to 170°K by cooling the crystal mounted in the pulsing assembly using liquid air. In order to maintain an even cooling rate the sealed pulsing assembly was inserted in a silvered Dewar containing liquid air. Contact with the liquid air was made through a heat leak, which permitted control of the cooling rate.

Temperature was measured using a Copper-Constantan thermocouple placed in contact with the crystal holder.

TEMPERATURE RANGE

The upper limit 250°K was predetermined by the need to preserve the crystal from sublimation and also ensure the maintenance of a satisfactory bond between the transducer and the crystal.

Bond failure occurred in the temperature range 150°K to 170°K, thus determining the lower limit of 170°K. The precise nature of the failure was not ascertained but it was believed that differential contraction of the crystal and the Mylar end seal resulted in separation at the glycerine bond producing a void between the transducer and the crystal.

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DETERMINATION OF ELASTIC CONSTANTS

For a crystal of orthorhombic symmetry, Group 3, the nine inde-
pendent elastic constants may be arrayed in accordance with Cady (1),
as shown:

$$
\begin{array}{cccccc}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\
C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{55} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66}
\end{array}
$$

Since it was possible to align and mount crystals oriented along
each of the principal axes, the main diagonal terms C_{ii} of the matrix
were computed directly from longitudinal and transverse wave velocity
measurements along each of these axes.

The crystal orientation, measured velocity and associated elastic
constant determined by this method were as given in Table 1.

Table 1.

DIRECTION OF WAVE PROPAGATION	DIRECTION OF WAVE DISPLACEMENT	VELOCITY MEASURED	ELASTIC CONSTANT
100	100	V_{aa}	$C_{11} = \rho\, V_{aa}^2$
	010	V_{ab}	$C_{66} = \rho\, V_{ab}^2$
	001	V_{ac}	$C_{55} = \rho\, V_{ac}^2$
010	100	V_{ba}	$C_{66} = \rho\, V_{ba}^2$
	010	V_{bb}	$C_{22} = \rho\, V_{bb}^2$
	001	V_{bc}	$C_{44} = \rho\, V_{bc}^2$
001	100	V_{ca}	$C_{55} = \rho\, V_{ca}^2$
	010	V_{cb}	$C_{44} = \rho\, V_{cb}^2$
	001	V_{cc}	$C_{33} = \rho\, V_{cc}^2$

Note: For axial velocities, the first letter indicates the axis of

   propagation, second letter indicates axis of wave displacement.

To determine the off-diagonal terms C_{ij}, the transformation equations (App. I) were used. Crystal orientations were chosen so that each off-diagonal constant could be computed in terms of a measured velocity and certain of the previously determined main diagonal constants. For the orthorhombic crystal the desired form of the equations was obtained by considering a rotation in an axial plane to an angle of 45 degrees from two of the principal axes (Fig. 8). This produced three different orientations giving three independent sets of equations, each of which could be solved for one of the three off-diagonal terms.

The three independent sets of equations were obtained by substituting the appropriate values for the direction cosines l, m, and n in the equations as demonstrated in Appendix I.

Substitution of these particular values reduced two of the C_{ij}' terms to zero. The remaining terms when substituted into the secular equation for irrotational plane waves traveling in the X' direction gave rise to the simplified determinant solution:

$$(C_{ii}' - \rho V^2)(C_{jj}' - \rho V^2) - C_{ij}'^2 = 0.$$

This may be reduced to:

$$\rho V^2 = \tfrac{1}{2}(C_{ii}' + C_{jj}') \pm \left\{\tfrac{1}{4}(C_{ii}' - C_{jj}')^2 + C_{ij}'^2\right\}^{\tfrac{1}{2}}$$

where the C' terms are defined in terms of the elastic constants and the direction cosines (App. I). This results in an equation in terms of the longitudinal velocity and previously determined elastic constants (C_{ii}):

$$C_{ij} = \left\{\left[2\rho V^2 - \tfrac{1}{2}(C_{ii} + C_{jj} + 2C_{kk})\right]^2 - \tfrac{1}{4}(C_{jj} - C_{ii})^2\right\}^{\tfrac{1}{2}} - C_{kk}$$

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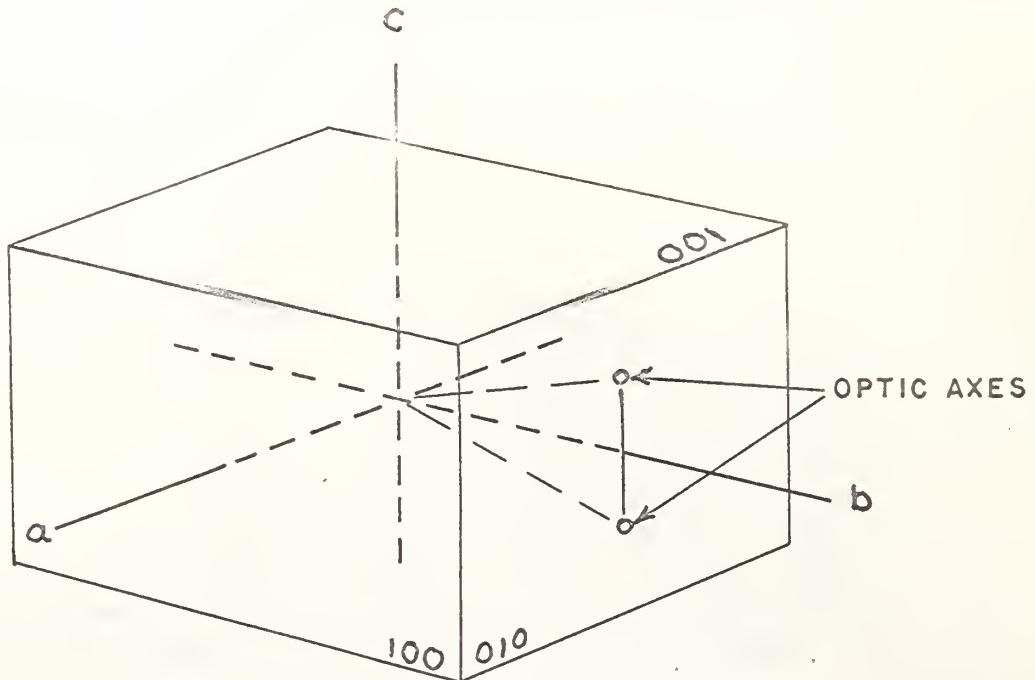
(a) Principal Axes and Principal Planes
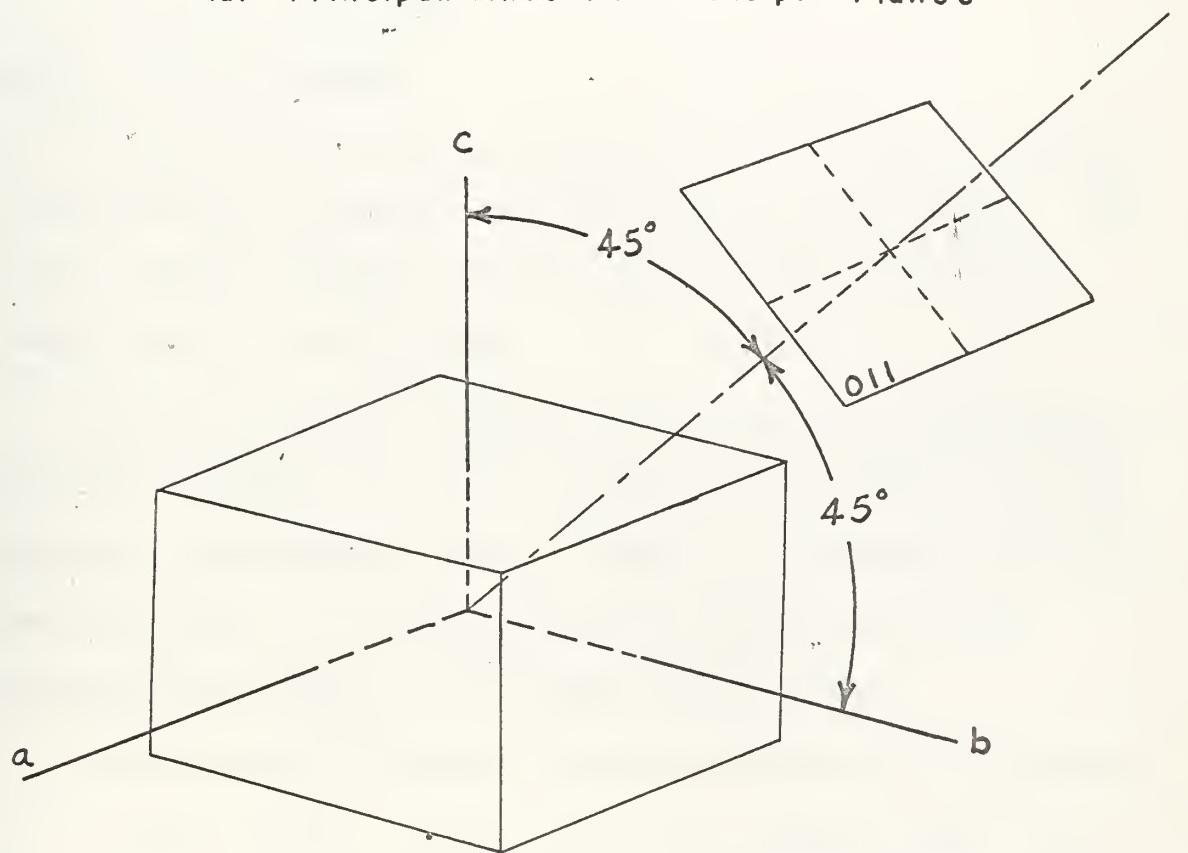
(b) 45° OII Orientation.

PLANES AND AXES

OF BENZENE (C_6H_6)

FIG. 8.

The crystal orientation, measured velocity and associated elastic constants were as given in Table 2:

Table 2

Direction of Wave Propagation	Velocity Measured	C_{ij}	C_{ii}	C_{jj}	C_{kk}
110	V_{110}	C_{12}	C_{11}	C_{22}	C_{66}
101	V_{101}	C_{13}	C_{11}	C_{33}	C_{55}
011	V_{011}	C_{23}	C_{22}	C_{33}	C_{44}

All of the data pertinent to the computations and the actual values of the elastic constants have been presented in both graphical and tabular form, page 21-26.

ERROR IN ELASTIC CONSTANTS

The sources of error in the determination of the elastic constants from the measured velocities could be divided into two categories - the error in crystal alignment, and the error in computing the elastic constants from the velocity data.

The error in crystal alignment depended not only on the accuracy of the optical alignment, but also on the method of preserving this alignment during the mounting procedure. Since for all alignments other than that along the b axis, the alignment of the crystal could not be rechecked after mounting, no correction could be applied.

Another source of alignment error was introduced in the alignment of the shear transducer to produce shear waves along the axes. To eliminate this error, only longitudinal wave velocities were used to determine the off-diagonal elastic constants.

TABLE OF MEASURED VELOCITIES (meters per second)

| $T^{o}K$	V_{aa}	V_{ab}	V_{ac}	V_{ba}	V_{bb}	V_{bc}	V_{ca}	V_{cb}	V_{cc}	V_{110}	V_{101}	V_{011}
250	2344	1412	1888	1362	2487	1200	1832	1193	2404	2572	2879	2530
240	2381	1469	1940	1419	2567	1216	1897	1207	2455	2644	2946	2611
230	2426	1519	1984	1479	2628	1241	1947	1227	2505	2727	3009	2675
220	2487	1569	2038	1532	2708	1258	1990	1247	2550	2796	3069	2737
210	2536	1617	2091	1576	2767	1275	2031	1264	2593	2865	3130	2793
200	2580	1659	2139	1618	2821	1295	2072	1281	2632	2921	3185	2849
190	2629	1702	2188	1660	2862	1314	2113	1300	2675	2975	3241	2899
180	2677	1735	2237	1693	2905	1336	2147	1317	2713	3026	3291	2943
170	2725	1773	2284	1731	2954	1355	2181	1333	2747	3071	3350	2988

AXIAL VELOCITIES
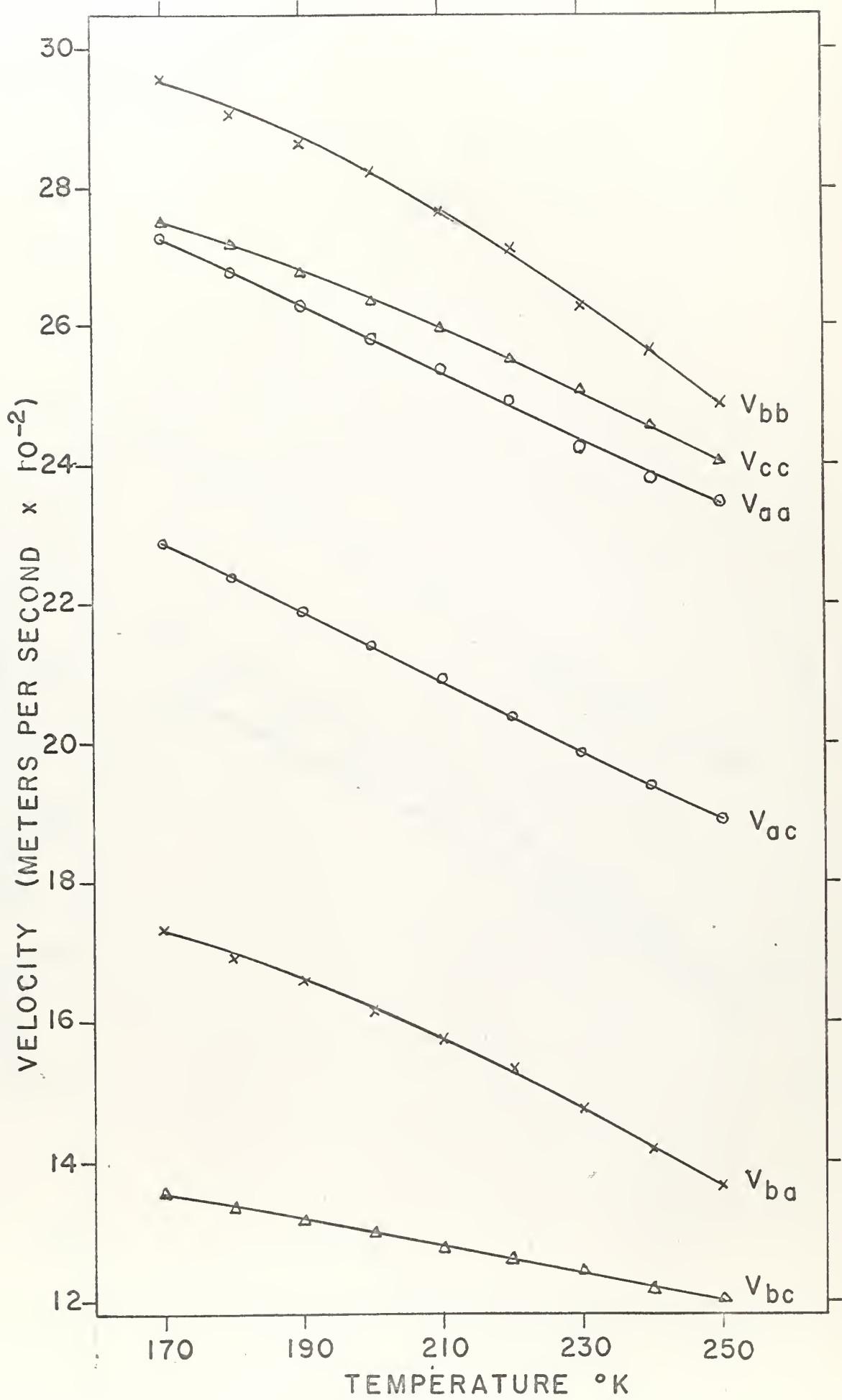
LONGITUDINAL VELOCITIES
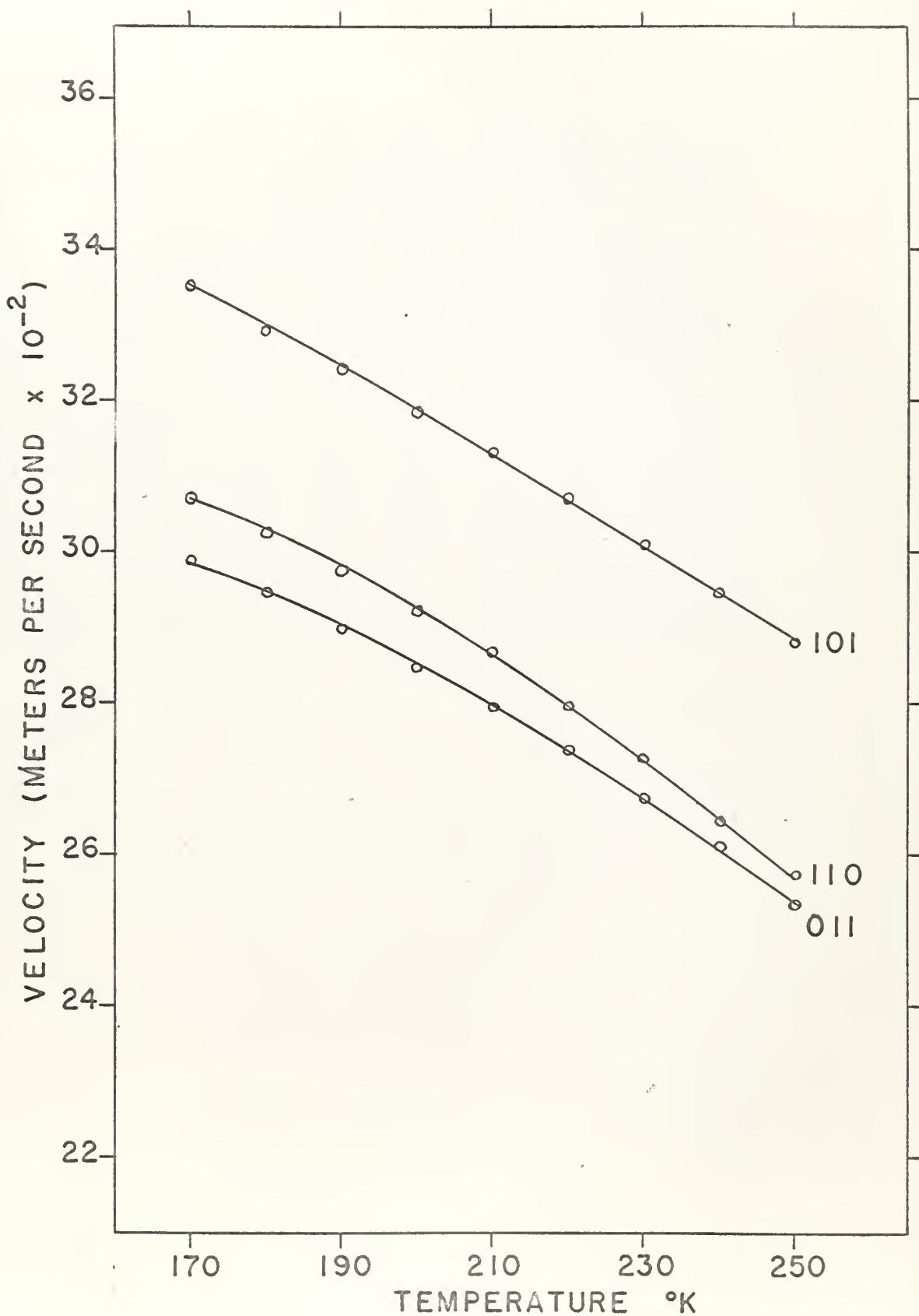
ELASTIC CONSTANTS OF BENZENE (C_6H_6)

$$x \ 10^{-10} \ \text{dynes/cm.}^2$$

Temperature $^\circ$K	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{23}	C_{13}
250	5.83	6.56	6.14	1.53	3.78	1.97	3.90	3.52	4.01
240	6.01	6.99	6.39	1.57	3.99	2.14	4.06	3.57	4.22
230	6.24	7.33	6.66	1.63	4.17	2.32	4.34	3.67	4.41
220	6.56	7.78	6.90	1.68	4.41	2.49	4.44	3.68	4.43
210	6.82	8.12	7.13	1.72	4.64	2.63	4.67	3.70	4.53
200	7.06	8.44	7.35	1.78	4.85	2.78	4.76	3.76	4.61
190	7.33	8.69	7.59	1.83	5.08	2.92	4.92	3.89	4.66
180	7.60	8.95	7.81	1.89	5.31	3.04	5.07	3.94	4.66
170	7.88	9.26	8.01	1.95	5.53	3.18	5.08	3.85	4.80

ELASTIC CONSTANTS (C$_{ij}$)

C_{22}

C_{33}

C_{11}

C_{55}

C_{66}

C_{44}

ELASTIC CONSTANTS (DYNES PER CM^2 x 10^{-10})

TEMPERATURE °K

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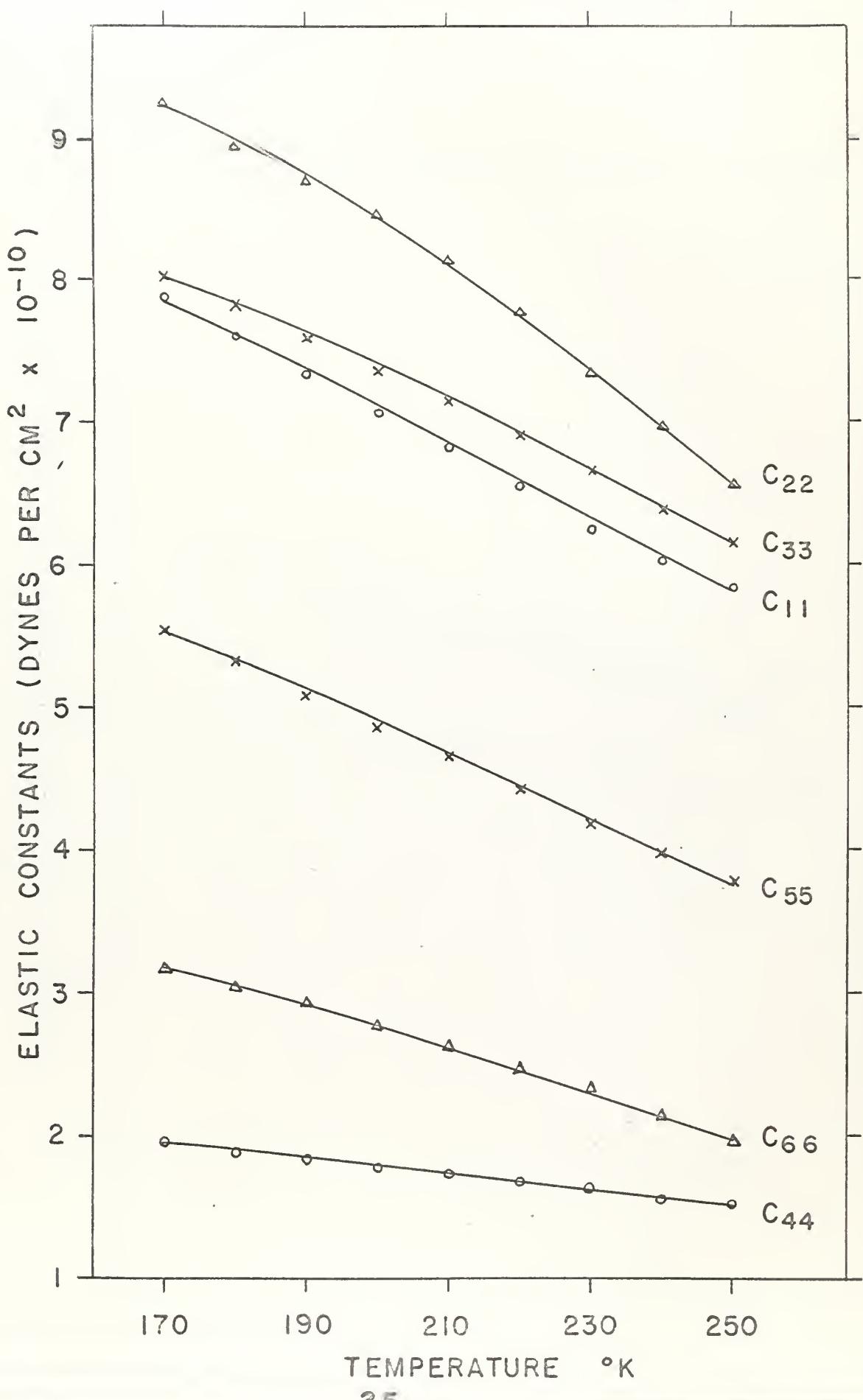
ELASTIC CONSTANTS (C_{ij})
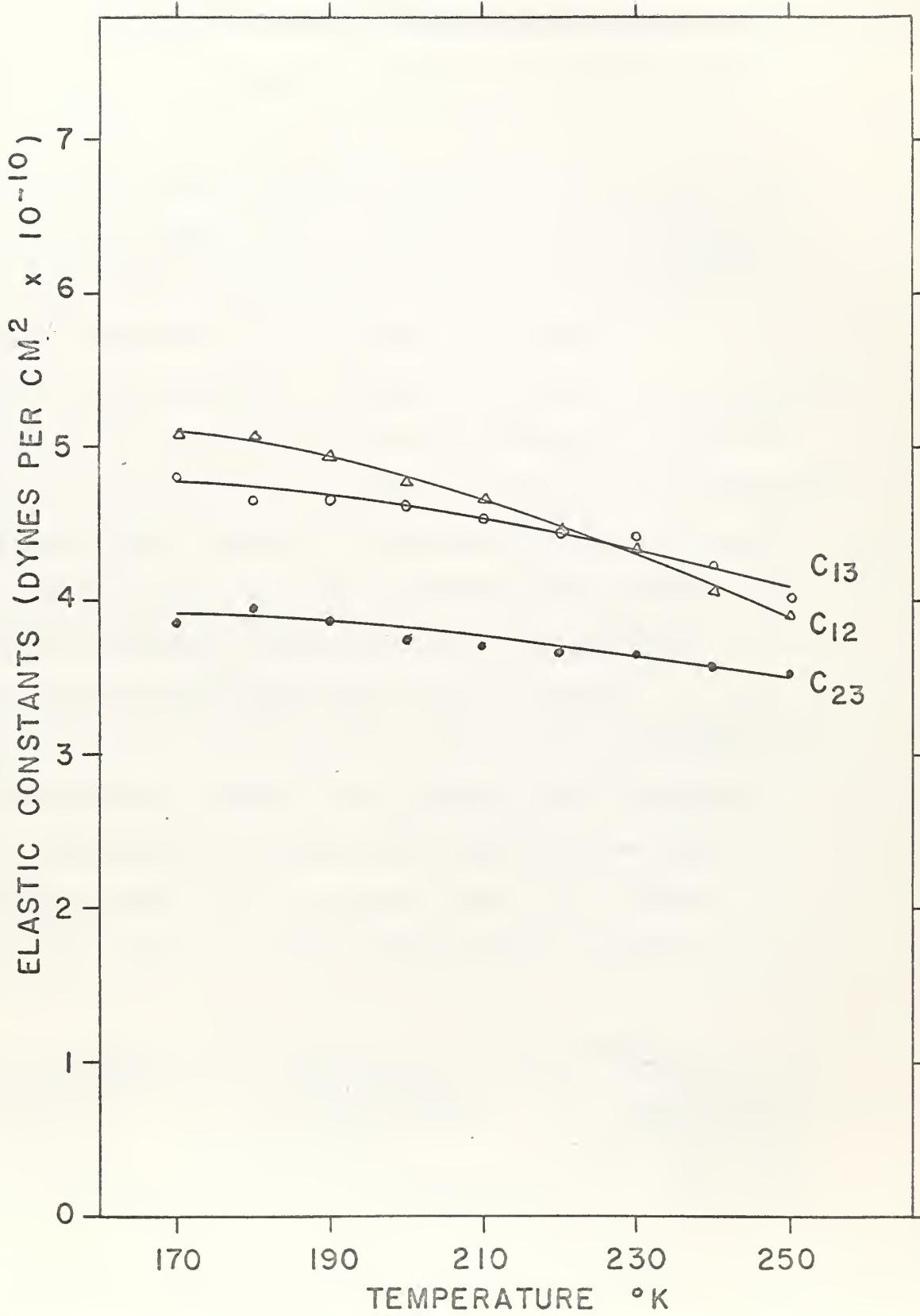
For the crystals not aligned on a major axis, a further source of error was introduced by the anisotropic thermal contraction, which produced a continual minor change of alignment throughout the temperature range. Because of other larger sources of error present in the determination of the off-diagonal constants, no correction was made for this error.

The specific volume of benzene was considered to be 0.9425 cc/gm for the temperature range 250°K to 170°K, based on data summarized in Andrew and Eades (8). Possible errors in this data were considered negligible in comparison with the other errors present.

Since it was not possible to measure any alignment errors present, an estimate of the accuracy was obtained by comparison of velocities which determine the same elastic constant. For the constants determined by longitudinal axial velocities, the error was estimated at less than 2%, based on velocities obtained from different crystal samples. For the constants determined by shear velocities, the comparative velocities obtained also differed by no greater than 2%.

The values of the diagonal elastic constants (C_{ii}) determined from axial velocities were required in the solution of the off-diagonal elastic constants (C_{ij}); thus, any error present in these values was unavoidably included in the off-diagonal values. This resulted in a possible overall error in the off-diagonal elastic constants of up to 10%.

Table of Estimated Error in Elastic Constants

Elastic Constants	Velocities Used	Error
C_{11}, C_{22}, C_{33}	Longitudinal, Axial	less than 2%
C_{44}, C_{55}, C_{66}	Shear, Axial	approximately 2%
C_{12}, C_{13}, C_{23}	Longitudinal, Non-axial	up to 10%

MEASUREMENT OF ABSORPTION

Although measurement of absorption was not the primary objective, the method used to pulse crystals to obtain velocity data was readily adaptable to providing absorption data.

Absorption measurements were, therefore, made in conjunction with velocity measurements by comparing the amplitude of successive pulse echoes. The comparison was made by matching the leading echo to the output of the time marker generator displayed on the second channel of the oscilloscope. The time marker generator output was fed through an attenuator which permitted an adjustment of amplitude in steps of one decibel.

In measuring the attenuation of successive echoes, the time marker was matched to the leading echo and the attenuator then adjusted until the time marker amplitude was the same as that of the succeeding echo. The attenuation between echoes was, therefore, given directly as the attenuator setting in decibels. These measurements were repeated for as many echoes as appeared in a given pulse train.

All absorption measurements were made at a frequency of 10 megacycles per second using 0.50 inch diameter quartz crystal transducers. The accuracy of the measurement was extended to within one half of one decibel by logarithmic interpolation of the superimposed waveforms.

DETERMINATION OF ABSORPTION

The average of the attenuator settings was then converted to absorption in nepers per centimeter by a calculation based on the measured length of the crystal:

$$\text{Absorption (nepers/cm)} = \frac{\text{attenuation (db)}}{2 \times l_c \text{ (cm)}} \times 8.68 \frac{\text{nepers}}{\text{db}}$$

The ultrasonic absorption computed from the measurements of
pulse attenuation has been presented graphically on page 30 and in
tabular form on page 31.

All of this data was based on the attenuation between first and
second echoes only, thus involving a total path length of six centi-
meters in the crystal. For this length of path, the effects of
diffraction were small and within the errors of the actual measure-
ments, thus no correction was made for attenuation due to diffraction.

The absorption computed varied from greater than 0.6 nepers per
cm. to less than 0.1 nepers per cm. the variation being a definite
function of crystal alignment in relation to the direction of ultra-
sonic wave propagation. The absorption for all waves propagating
along the c axis was significantly less than for waves propagating
perpendicular to this direction.

Some variation of absorption with temperature was observed for
certain of the crystal directions. In general this variation showed
a decrease in absorption with a decrease in temperature.

ULTRASONIC ABSORPTION
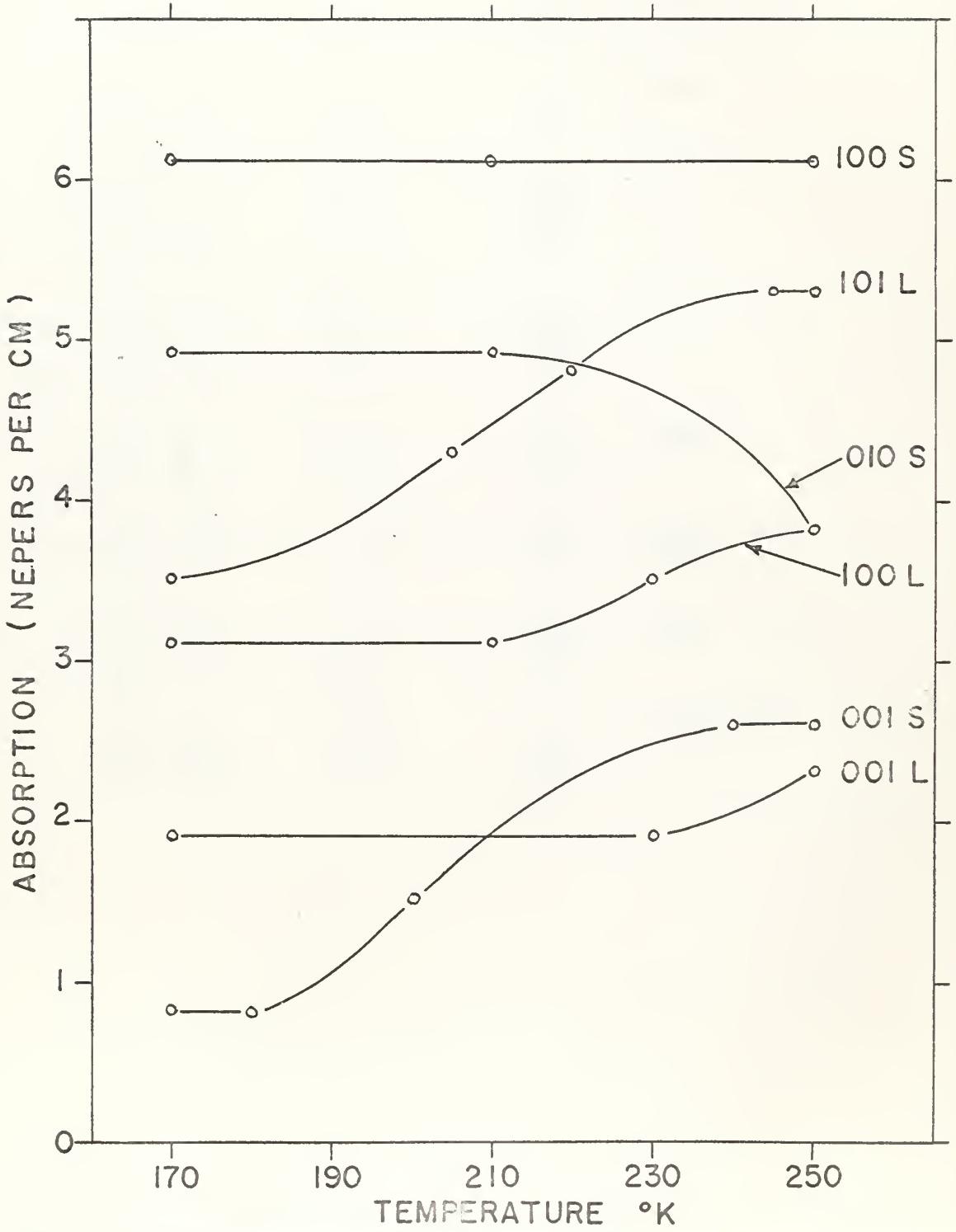
ULTRASONIC ABSORPTION IN BENZENE

Direction of Propagation	Temperature Range °K	Attenuation db/cm.	Absorption nepers per cm.	Mode
100	250 - 170	5.3	0.61	Shear (001)
010	250 - 230	3.3	0.38	Shear (001)
	230 - 170	4.3	0.49	
110	250 - 230	6.0	0.70	Long.
	230 - 170	3.5	0.40	
101	240 - 225	4.7	0.54	Long.
	225 - 210	4.2	0.48	
	210 - 195	3.5	0.40	
	195 - 170	3.0	0.35	
010	250 - 230	4.6	0.53	Long.
	230 - 210	4.2	0.48	
	210 - 200	3.7	0.43	
	200 - 170	3.0	0.35	
100	250 - 240	3.3	0.38	Long.
	240 - 220	3.0	0.35	
	220 - 170	2.7	0.31	
001	250 - 240	2.0	0.23	Long.
	240 - 170	1.7	0.19	
011	250 - 215	1.7	0.20	Long.
	215 - 205	1.5	0.17	
	205 - 170	1.3	0.15	
001	250 - 210	2.3	0.26	Shear (010)
	210 - 190	1.3	0.15	
	190 - 170	0.7	0.08	

APPENDIX I

The method developed by J. R. Neighbours (7) for the determination

of elastic constants is based on velocity measurements of irrotational

plane waves propagated along a specified reference axis (X'), where the

reference axes are oriented so that the Y' axis lies in the 001 (XY)

plane of the crystal.

Using the measured velocity data, the elastic constants are

determined from the solution of the secular equation:

$$\begin{vmatrix} (C'_{11} - \rho V^2) & C'_{16} & C'_{15} \\ C'_{16} & (C'_{66} - \rho V^2) & C'_{56} \\ C'_{15} & C'_{56} & (C'_{55} - \rho V^2) \end{vmatrix} = 0$$

where the primed constants are defined in terms of the crystal elastic

constants by:

$$C'_{11} = \ell^4 C_{11} + 2\ell^2 m^2 C_{12} + 2\ell^2 n^2 C_{13} + m^4 C_{22} + 2m^2 n^2 C_{23} + n^4 C_{33}$$
$$+ 4m^2 n^2 C_{44} + 4\ell^2 n^2 C_{55} + 4\ell^2 m^2 C_{66}$$

$$C'_{66} = \ell^2 m^2 a^{-2} C_{11} - 2\ell^2 m^2 a^{-2} C_{12} + \ell^2 m^2 a^{-2} C_{22} + \ell^2 n^2 a^{-2} C_{44}$$
$$+ m^2 n^2 a^{-2} C_{55} + (\ell^2 - m^2)^2 a^{-2} C_{66}$$

$$C'_{55} = \ell^4 n^2 a^{-2} C_{11} - 2\ell^2 m^2 n^2 a^{-2} C_{12} - 2\ell^2 n^2 C_{13} + m^4 n^2 a^{-2} C_{22} - 2m^2 n^2 C_{23}$$
$$+ n^2 a^2 C_{33} + m^2 a^{-2}(a^2-n^2)^2 C_{44} + \ell^2 a^{-2}(a^2-n^2)^2 C_{55} + 4\ell^2 m^2 n^2 a^{-2} C_{66}$$

$$C'_{15} = -\ell^4 n a^{-1} C_{11} - 2\ell^2 m^2 n a^{-1} C_{12} - \ell^2 n a^{-1}(a^2-n^2) C_{13} - m^4 n a^{-1} C_{22}$$
$$+ m^2 n a^{-1}(a^2-n^2) C_{23} + n^3 a C_{33} + 2m^2 n a^{-1}(a^2-n^2) C_{44} + 2\ell^2 n a^{-1}(a^2-n^2) C_{55}$$
$$- 4\ell^2 m^2 n a^{-1} C_{66}$$

$$C'_{16} = -\ell^3 m a^{-1} C_{11} + \ell m a^{-1}(\ell^2-m^2) C_{12} - \ell m n^2 a^{-1} C_{13} + \ell m^3 a^{-1} C_{22}$$
$$+ \ell m n^2 a^{-1} C_{23} + 2\ell m n^2 a^{-1} C_{44} - \ell m n^2 a^{-1} C_{55} + 2\ell m a^{-1}(\ell^2-m^2) C_{66}$$

$$C'_{56} = \ell^3 m n a^{-2} C_{11} - \ell m n a^{-2}(\ell^2-m^2) C_{12} - \ell m n C_{13} - \ell m^3 n a^{-2} C_{22}$$
$$+ \ell m n C_{23} + \ell m n a^{-2}(a^2-n^2) C_{44} - \ell m n a^{-2}(a^2-n^2) C_{55} - 2\ell m n a^{-2}(\ell^2-m^2) C_{66}$$

where $a^2 = \ell^2 + m^2$

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and the ℓ, m, and n terms are the direction cosines relating the X$'$ direction to the crystallographic axes (a,b,c).

For a wave propagating along a crystallographic axis, the direction cosines become one or zero, which results in:

$$C_{ij}' = 0$$
$$C_{ii}' = C_{ii}$$

so that the solution is in terms of

$$\rho V^2 = C_{ii}.$$

Example: for $\ell = 1$ $C_{11}' = C_{11} = \rho V^2_{aa}$

$\qquad m = n = 0$ $C_{55}' = C_{55} = \rho V^2_{ab}$

$\qquad\qquad\qquad C_{66}' = C_{66} = \rho V^2_{ac}$

For a wave propagating in an axial plane at 45 degrees to two crystallographic axes, the direction cosines become zero or $\sqrt{2}/2$. For the 110 case, where the wave is propagating at 45 degrees to the a and b axes, and perpendicular to the c axis:

$\ell = m = \sqrt{2}/2$ $C_{11}' = \frac{1}{4}(C_{11} + C_{22} + 4C_{66} + 2C_{12})$

$\quad n = 0$ $C_{66}' = \frac{1}{4}(C_{11} + C_{22} - 2C_{12})$

$\quad a = 1$ $C_{55}' = \frac{1}{2}(C_{44} + C_{55})$

$\qquad\qquad C_{16}' = \frac{1}{4}(C_{22} - C_{11})$

$\qquad\qquad C_{15}' = C_{56}' = 0$

thus the determinant becomes:

$$\begin{vmatrix} C_{11}' - \rho V^2) & C_{16}' & 0 \\ C_{16}' & (C_{66}' - \rho V^2) & 0 \\ 0 & 0 & (C_{55}' - \rho V^2) \end{vmatrix} = 0$$

or $(C_{55}' - \rho V^2)\left[(C_{11}' - \rho V^2)(C_{66}' - \rho V^2) - C_{16}'^2\right] = 0$

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which has solutions:

(a) $\rho V^2 = C_{55}' = \frac{1}{2}(C_{44} + C_{55})$

(b) $\rho V^2 = \frac{1}{2}(C_{11}' + C_{66}') \pm \left[\frac{1}{4}(C_{11}' - C_{66}')^2 + C_{16}'^2\right]^{\frac{1}{2}}$

The solution for the longitudinal velocity (V_{ℓ}) is:

$$\rho V_{\ell}^2 = \frac{1}{2}(C_{11}' + C_{66}') + \left[\frac{1}{4}(C_{11}' - C_{66}')^2 + C_{16}'^2\right]^{\frac{1}{2}}$$

$$= \frac{1}{4}(C_{11} + C_{22} + 2C_{66}) + \frac{1}{2}\left[(C_{12} + C_{66})^2 + \frac{1}{4}(C_{22} - C_{11})^2\right]^{\frac{1}{2}}.$$

Separating the off-diagonal elastic constant

$$C_{12} = \left\{\left[2\rho V_{\ell}^2 - \frac{1}{2}(C_{11} + C_{22} + 2C_{66})\right]^2 - \frac{1}{4}(C_{22} - C_{11})^2\right\}^{\frac{1}{2}} - C_{66}$$

results in a solution for the off-diagonal constant in terms of the
longitudinal velocity and the previously determined diagonal constants.

The solutions for the other off-diagonal constants are analagous:

for the 101 Case $\quad C_{13} = \left\{\left[2\rho V_{\ell}^2 - \frac{1}{2}(C_{11} + C_{33} + 2C_{55})\right]^2 - \frac{1}{4}(C_{33} - C_{11})^2\right\}^{\frac{1}{2}} - C_{55}$

for the 011 Case $\quad C_{23} = \left\{\left[2\rho V_{\ell}^2 - \frac{1}{2}(C_{22} + C_{33} + 2C_{55})\right]^2 - \frac{1}{4}(C_{33} - C_{22})^2\right\}^{\frac{1}{2}} - C_{44}$

It may be noted that since the solution is of the form:

$$(C_{ij} + C_{kk}) = \text{a known positive constant } (k^2),$$

this allows for the possibility of two solutions:

$$C_{ij} = k - C_{kk}$$

$$\text{or} \quad C_{ij} = -(k + C_{kk})$$

The choice between solutions was made on the basis of the stability
requirements for a crystal of orthorhombic symmetry. From Neighbours (9),
this requires that the principal minors of the matrix must all be
positive. The matrix was therefore expanded into terms of the principal

minors, and the following four inequalities obtained:

$$c_{11}c_{22} > c_{12}^2$$

$$c_{11}c_{33} > c_{13}^2$$

$$c_{22}c_{33} > c_{23}^2$$

$$c_{11}(c_{22}c_{33} - c_{23}^2) + 2c_{12}c_{23}c_{13} > c_{12}^2c_{33} + c_{13}^2c_{22}$$

These inequalities were then used to show that the solution giving a

large negative value was not acceptable.

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