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by

H. J. McSkimin

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Measurement of Elastic Constants at Low Temperatures by Means of Ultrasonic Waves—Data for Silicon and Germanium Single Crystals, and for Fused Silica

H. J. McSkimin
Bell Telephone Laboratories, Murray Hill, New Jersey
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Ultrasonic waves (shear or longitudinal) in the 10–30 mc range are transmitted down a fused silica rod, through a polystyrene or silicone one-quarter wavelength seal, and into the solid specimen. Measurement of reflections within the specimen yields values for velocities of propagation and elastic constants.

Data obtained over a temperature range of 78° to 300°K for silicon and germanium single crystals, and 1.6° to 300°K for fused silica are listed. For the latter, a high loss is noted, with an indicated maximum near 30°K.

1. INTRODUCTION

THE advantages of using high-frequency ultrasonic waves for measuring the elastic constants of solids—and in particular single crystals—have been pointed out by numerous investigators.[1–4] In the present paper application of principles outlined in reference 5 will be made to low-temperature measurements in the range −196°C to +25°C. Results for germanium and silicon single crystals will be listed, also data for fused silica. For the latter, a few attenuation measurements made with the use of liquid helium will be described also.

2. METHOD USED

2.1 Single Transducer Technique

Ultrasonic waves in the frequency range 10–30 mc can be transmitted readily down a fused silica rod as shown by Fig. 1. Either longitudinal or shear waves may be used.

The specimen is attached to the lower end of the rod with a plastic seal approximately $\frac{1}{4}$ wavelength in thickness. Details of this seal will be described later.

Only the specimen end need be cooled to the desired temperature; so that at all times the quartz crystal transducer is maintained near room temperature. Failure of the solder bond seal between crystal and rod, with resulting impairment of pulse transmission, is therefore avoided.

Waves entering the specimen through the seal are reflected back and forth, giving rise to a series of transmitted pulses T (Fig. 1), decaying exponentially with time. Because of the impedance transformation properties of the seal, only a small reduction in amplitude occurs for each reflection. Also, near the frequency for which the seal thickness is $\frac{1}{4}$ wavelength, the reflection phase shift error will be small.[5]

2.2 Determining the Number of Wavelengths in the Path-Velocity Calculation

At discrete frequencies, the emerging wave trains will be in phase, so that an observed pattern (envelopes only) occurs as shown by Fig. 2(a). The number of wavelengths in the complete path (for twice the specimen thickness) is given without ambiguity by

$$n_0 = f_0/\Delta f, \tag{2.1}$$

where f_0 is the critical frequency of interest, and Δf is

[1] H. B. Huntington, Phys. Rev. **72**, 321 (1947).
[2] J. K. Galt, Phys. Rev. **73**, 1460–1462 (1948).
[3] D. L. Arenberg, J. Acoust. Soc. Am. **20**, 1 (1948).
[4] W. C. Overton, Jr., and R. T. Swim, Phys. Rev. **84**, 758 (1951).
[5] H. J. McSkimin, J. Acoust. Soc. Am. **22**, 413–418 (1950).

the frequency separation between two consecutive critical frequencies. Accuracy in determining Δf is obtained by determining critical frequencies over a wide range of frequencies.

The velocity of propagation is then given by

$$V_0=\frac{2tf_0}{n_0-(\varphi_0/2\pi)}, \tag{2.2}$$

where t is the specimen thickness and φ_0 is the phase shift per reflection. In general, this phase shift term may be neglected at frequencies near the seal $\lambda/4$ frequency, so that the velocity of propagation is simply

$$V_0=2tf_0/n_0. \tag{2.3}$$

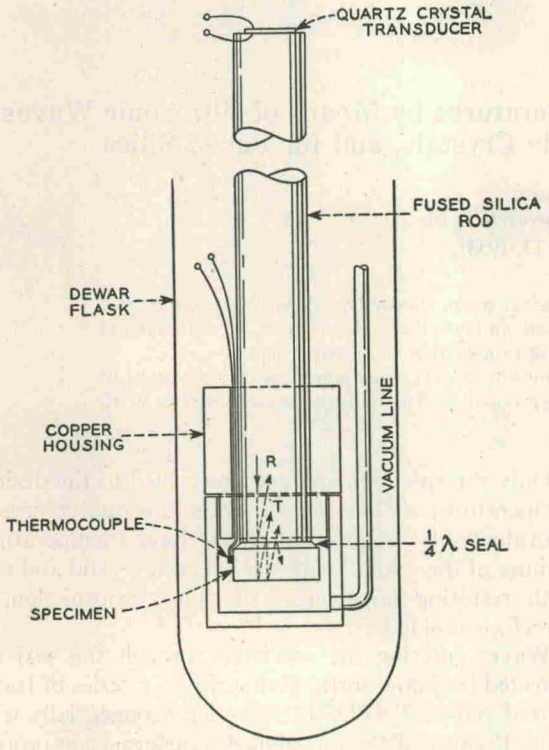


FIG. 1. Apparatus for measuring elastic constants.

Another useful pattern occurs for odd numbers of half-wavelengths as shown by Fig. 2(b).

3. DETAILS OF APPARATUS USED

3.1 Longitudinal Wave Unit

For longitudinal waves the fused silica rod of Fig. 1 was approximately 7.5 in. long by $\frac{7}{8}$ in. diam.[6,7] The ends were carefully aligned parallel and surface finished with No. 600 Carborundum.

[6] Material made by Nieder Company and supplied by Amersil Company, Inc., Hillside, New Jersey. Rods were clear and essentially strain free. Refer also to reference 7.

[7] E. S. Pennell, "Vitreous silica for ultrasonic delay line applications," to be published in Proc. Natl. Electronics Conf. Vol. 8, 1952.

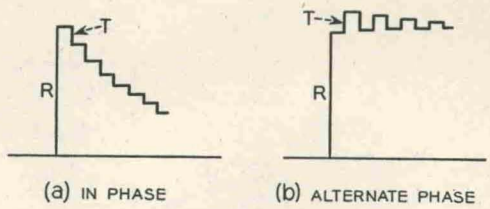


FIG. 2. Oscilloscope patterns for critical frequencies (envelopes).

A 25 mc x-cut quartz crystal was used as the transducer, being fastened to the rod by means of a silver paste-solder technique previously described.[5] Accurate measurements with this unit were limited to frequencies above 20 mc because of spurious "trailing" pulses generated at the rod surface. Additional roughening might have been resorted to for operation at lower frequencies.

3.2 Seals for Longitudinal Waves

For the temperature range between +25°C and −78°C, the most useful seal was found to be a 0.5-mil film of polystyrene with very viscous poly-α-methylstyrene[8,9] used as the binder. A 70°C assembly temperature was used with a pressure of approximately 25 lb/sq in.

Figure 3 shows measured values of R/T, the ratio of reflected to transmitted components (see Fig. 1) with an indicated $\lambda/4$ resonance at about 20 mc.[10,11] As the temperature is lowered, the liquid solidifies, and the polystyrene becomes stiffer so that the $\lambda/4$ point increases to about 23 mc at −78°C.

For the temperature range −78°C to −195°C, it was found that a suitable seal could be made with Dow Corning 200 Fluid of 200 000 cs viscosity (25°C). To provide control of the seal thickness, two tungsten wires 0.001 in. diam were stretched across the end of the fused silica rod. With a moderate pressure, the specimen (with excess of seal liquid and at room temperature) was pressed down until it touched the shims.

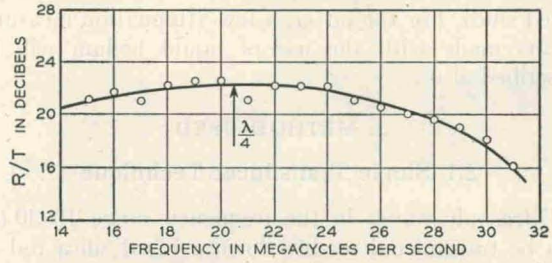


FIG. 3. Ratio of reflected to transmitted components for longitudinal waves along the 110 direction of a silicon crystal. (See text for seal.)

[8] Dow resin 276-V9, Blend 288. For properties, refer to reference 9.

[9] H. J. McSkimin, J. Acoust. Soc. Am. **23**, 429–434 (1951).

[10] A description of measurements of this type is to be found in reference 11.

[11] Anderson Labs. Inc., "Interim report on solid supersonic delay lines," Dec. 20, 1950 to March 30, 1951.

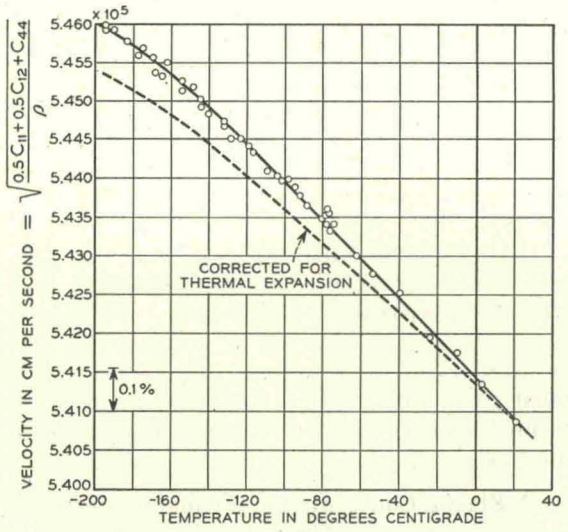


FIG. 4. Velocity of longitudinal waves in germanium single crystal—propagation parallel to 110 direction.

These wires were left in place, and the assembled unit (still in a vertical position) was cooled with dry ice until the seal was rigid enough to allow inverting the unit into a standard Dewar flask for further cooling by liquid nitrogen.

The quarter-wave frequency varied between 18 and 24 mc for the 1 mil shims depending on the temperature. Direct measurement of this frequency should be made from a comparison of R and T (Fig. 1) as previously noted.

3.3 Water Seal for Longitudinal Waves

An excellent low loss $\lambda/4$ seal can be obtained by the shim technique described above, using water or other suitable low viscosity liquid. A light pressure should be maintained on the specimen, and care should be exercised to keep liquid off the free face. Use of this technique in making loss measurements will be described later.

3.4 Shear Wave Unit

A construction similar to that described in Section 3.1 was used. The transducer was a 13-mc y-cut quartz crystal. The direction of the x-axis must be known, for particle motion takes place along this direction.

3.5 Seals for Shear Wave Operation

The same seals described in Section 3.2 were used for shear waves as well as longitudinal. The $\lambda/4$ frequencies were lower, in the range 10–15 mc.

3.6 Chamber for Specimen

In order to prevent moisture from condensing on the specimen, a vacuum-tight chamber was made of copper as shown by Fig. 1. With the cover removed, the end of the fused silica rod was completely accessible. Either a vacuum could be maintained, or the chamber could be filled with dry nitrogen.

Temperature equilibrium was obtained rather quickly because of the good heat conduction of the copper.

3.7 Temperature Measurement and Control

A small thermocouple of constantan and copper was placed on the specimen. Voltages were determined by means of a Leeds and Northrup Company No. 8657-C Double Range Potentiometer Indicator with uncertainties of about $\pm 1°C$.

In practice, the unit was cooled with liquid nitrogen to approximately $-195°C$ and then allowed to warm gradually. Measurements were made over the three- or four-hour period required for the temperature to rise to $-75°C$.

For temperatures between $25°C$ and $-75°C$, the unit was immersed in a dry ice-methanol mixture.

3.8 R.F. Oscillator and Gated Amplifier

The driving source for the transducer was a Measurements Corporation Model 80 Standard Signal Generator. The output was gated by means of a two stage amplifier, and provided pulse durations of from 1–50 microseconds.

Great care was taken to suppress the carrier in the output to minimize undesirable interference effects. Copper shielding was used throughout.

Frequencies were measured to ± 1 kc so that, in general, errors no greater than one part in 10 000 could be attributed to this source.

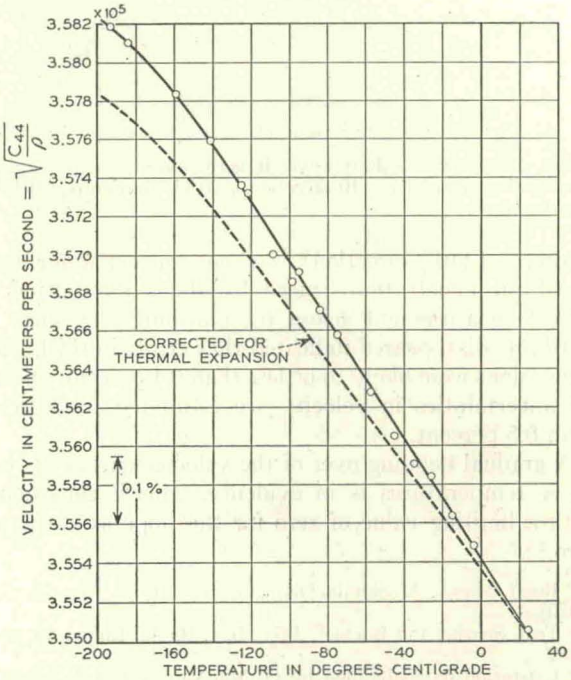


FIG. 5. Velocity of shear waves in germanium single crystal—propagation parallel to 110 direction, particle motion parallel to 001 direction.

3.9 Detection Equipment

A wide-band (4 mc) converter-amplifier was used with an IF frequency of 10 mc. After rectification, the signals were displayed on a DuMont Type 241 Oscilloscope.

4. RESULTS

4.1 Germanium Single Crystal

One of the germanium single crystals previously described[12,13] was measured for velocity of propagation, with results as shown by Figs. 4, 5, and 6. The data shown have been corrected for thickness-temperature changes in accordance with Fig. 7.[14]

Dimensions of the crystal were 1.9×1.3×0.6293 cm. The edge dimensions were left rough in order to scatter energy reaching the outer boundaries. The thickness

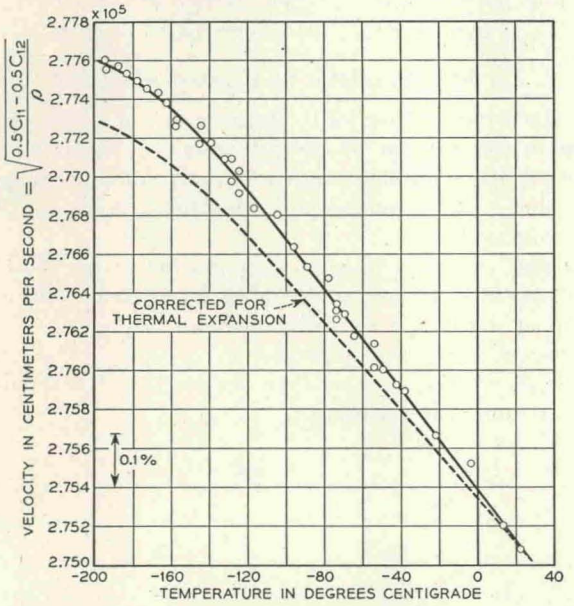


FIG. 6. Velocity of shear waves in germanium single crystal—propagation parallel to 110 direction, particle motion parallel to 110 direction.

(along a [110] direction) was not corrected for the slight pit penetration caused by the surface grind.[15] Direct measurement made by polishing the surface until pits disappeared indicated that errors in thickness dimensions were likely to be less than 0.1 percent. Overall uncertainties in velocity are estimated to be less than 0.5 percent.

A gradual bending over of the velocity curves at the lower temperatures is in evidence. This is consistent with a limiting value of zero for the slope at absolute zero.[2]

[12] Bond, Mason, McSkimin, Olsen, and Teal, Phys. Rev. **78**, 176 (1950).

[13] Teal, Sparks, and Buehler, Proc. Inst. Radio. Engrs. **40**, 906 (1952).

[14] Expansion data obtained by D. MacNair of Bell Telephone Laboratories.

[15] Roughening the surface by wet grinding with No. 600 Carborundum produced much stronger seals than a polished surface.

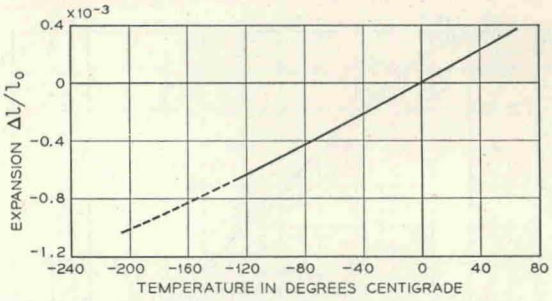


FIG. 7. Thermal expansion of germanium (D. MacNair).

A comparison of velocity data obtained in the present study with that for other germanium crystals measured is shown by Table I. Agreement in general is quite good.

4.2 Elastic Constants for Germanium Single Crystal

The three independent elastic constants for germanium were calculated from the velocities of propagation given by Figs. 4, 5, and 6. Results are shown by Figs. 8, 9, and 10. For these calculations, a density of 5.323 at 25°C was used.[16]

Measurements on single crystals of germanium have also been made by Mr. M. E. Fine with a low frequency (about 50 kc) resonance technique being used.[17,18] His

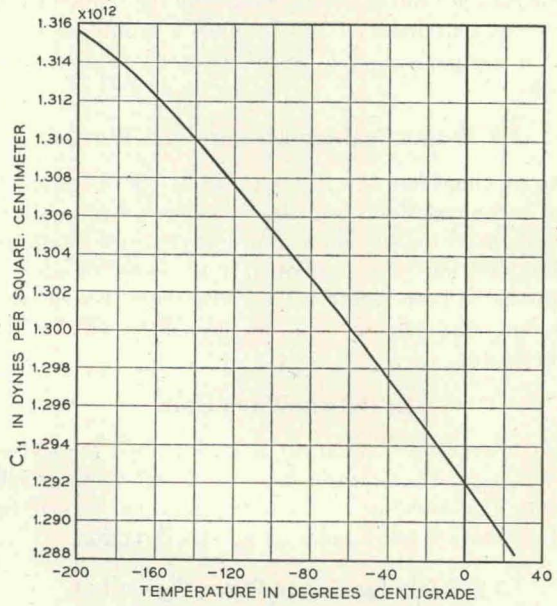


FIG. 8. C_{11} *versus* temperature for germanium.

[16] This value was supplied by Eagle Picher Lead Company. A value of 5.329 was determined with x-rays by W. L. Bond, Bell Telephone Laboratories. The 5.35 value used previously (reference 12) is apparently in error.

[17] M. E. Fine, "Dynamic methods for determining elastic constants and their temperature variation in metals," American Society for Testing Materials, Symposium on Determination of Elastic Constants, June, 1952.

[18] M. E. Fine, "Elasticity and thermal expansion of germanium between −195 and +275°C", submitted for publication in J. Appl. Phys.

TABLE I. Data for germanium single crystals.

Crystal designation	Direction of propagation	Direction of particle motion	Type wave	Temp. (°C)	Approx. freq. (mc)	Velocity (cm/sec)	Notes
B	110	110	Long.	26.4	10	5.410×10^5	Reported in reference 12
B				27	27	5.403	Remeasured
B				25	20	5.408	Present study
A				27	24	5.39	Reported in reference 12
B	110	001	Shear	28.3	10	3.547	Reported in reference 12
B				25	10	3.550	Present study
A				Rm	11	3.54	Reported in reference 12
B	110	$1\bar{1}0$	Shear	26.3	10	2.751	Reported in reference 12
B				25	10	2.751	Present study
A				30	10	2.75	Reported in reference 12
A	100	100	Long.	27	24	4.92	Reported in reference 12
C				25.3	27	4.9148	Imperfections present, *N*-type
D				29	27	4.9123	*N*-type, 1 hr. 900°C in N_2
D				26	14	4.914	
D				27	18	4.9136	$\lambda/4$ water seal used
E				27	17	4.9179	low res. *N*-type
F				27	17	4.9168	high res. *N*
G				27	18	4.9150	low res. *P*
H				27	17	4.9178	high res. *N*
I				30	17	4.9144	low res. *P*. (heat treated 50 min at 900°C in N_2)
A	100	001	Shear	30	7.5	3.54	Reported in reference 12

results are compared with those of the present study on Figs. 11 through 13. Considering that different samples, frequency ranges, and techniques were used, the close agreement is noteworthy.

4.3 Velocities of Propagation and Elastic Constants for Silicon Single Crystals

One of the two crystals reported on previously[19] was measured again with the thought of obtaining data over a temperature range. Detailed measurements over a wide frequency range, however, showed a dispersion effect for longitudinal waves not appreciated before. This particular crystal was approximately of 9 mm square cross section with two accurately parallel edge faces. At the lower frequencies, reflections from these faces caused interference effects with the "apparent" velocity varying as shown by Fig. 14. The use of a larger crystal with irregular edge boundaries was indicated, expecially in view of the large beam spreading due to the high velocity.

TABLE II. Data for silicon single crystals $T=25$°C.

Crystal No.	Direction of propagation	Direction of particle motion	Type mode	Velocity in cm/sec	Velocity-temperature coefficient	Notes
1	110	$1\bar{1}0$	Shear	4.682×10^5	-18×10^{-6}	
2				4.682	−47	(a)
3				4.673	−18.5	
2	110	001	Shear	5.834		
3				5.842	−17.9	$T=29$°C
1	110	110	Long.	9.167	−30	values calc. (b)
2				9.152		$T=30$°C (b)
3				9.129	−27.4	(c)
1	001	110	Shear	5.843	−21	(a)
1	001	001	Long.	8.474	−31	(a), (b)
1				8.420		(c)

Notes: (a) Velocity-Temp. Coeff. corrected in accordance with $\alpha=-3\times10^{-6}$ at 25°C.
(b) Velocity not corrected for geometric dispersion.
(c) Corrected for geometric dispersion.

[19] McSkimin, Bond, Buehler, and Teal, Phys. Rev. **83**, 1080 (1951).

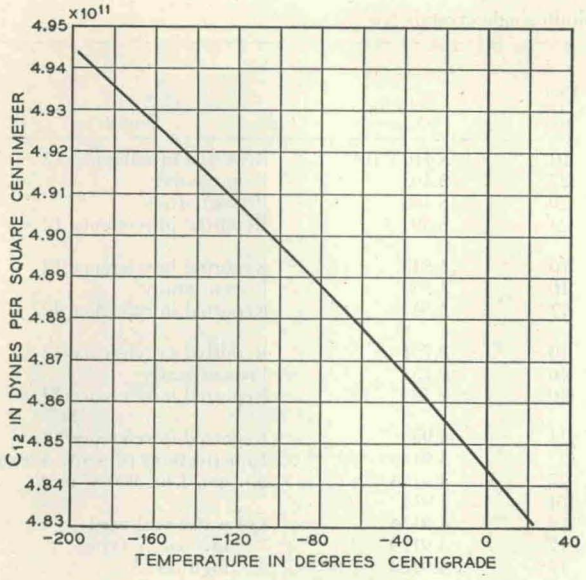


FIG. 9. C_{12} *versus* temperature for germanium.

Figure 15 shows similar data for a larger crystal with a thickness along the [110] direction of 0.9533 cm.[20, 21] The cross dimensions were approximately 2.0×1.3 cm, with the edges quite irregular. It is seen that variations with frequency are quite small.

For shear waves, no significant variation with frequency was noticed.

Figures 16, 17, and 18 list data for velocities of propagation, again corrected for length expansion. The

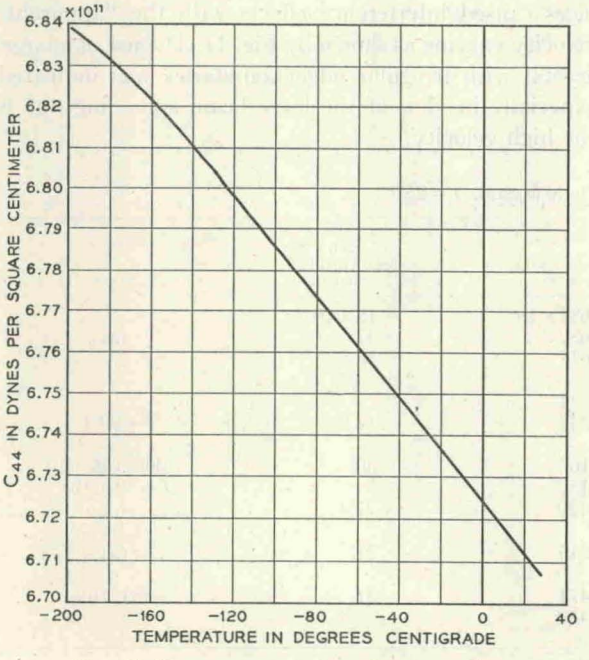


FIG. 10. C_{44} *versus* temperature for germanium.

[20] Crystal provided by E. Buehler and oriented by J. Andrus Refer to reference 17 for method of growing.

[21] G. K. Teal and E. Buehler, Bull. Am. Phys. Soc. **27**, 14 (1952).

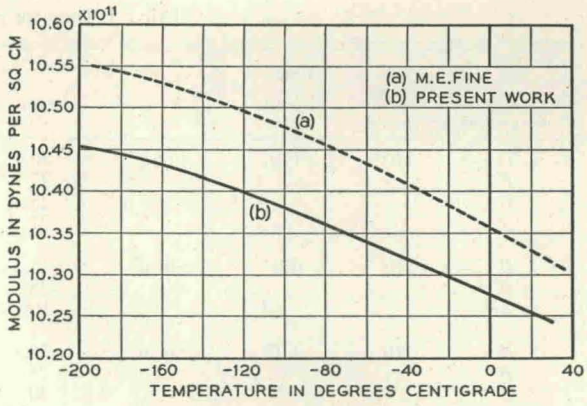


FIG. 11. Young's modulus for 100 direction in germanium.

data of Valentiner and Wallot was used.[22] (See Fig. 19 and reference 22.) The elastic constants are shown by Figs. 20, 21, and 22. A density of 2.331 at 25°C was used.

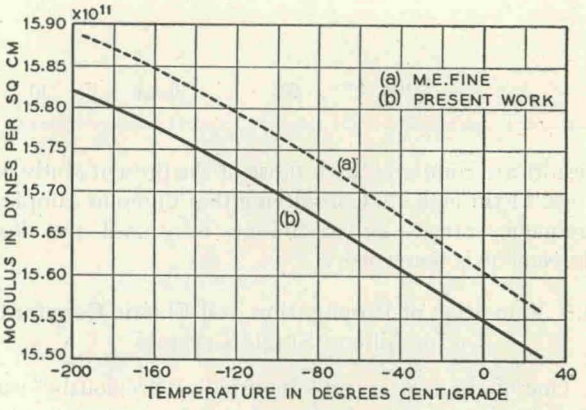


FIG. 12. Young's modulus for 111 direction in germanium.

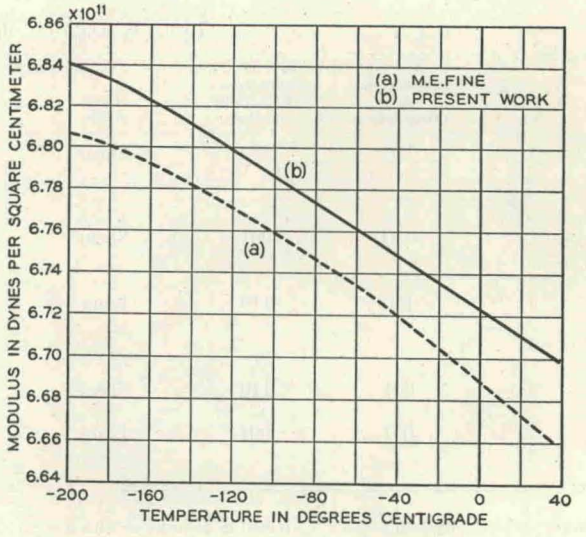


FIG. 13. Shear modulus C_{44} for germanium.

[22] S. Valentiner and J. Wallot, Ann. Physik **46**, 837 (1915).

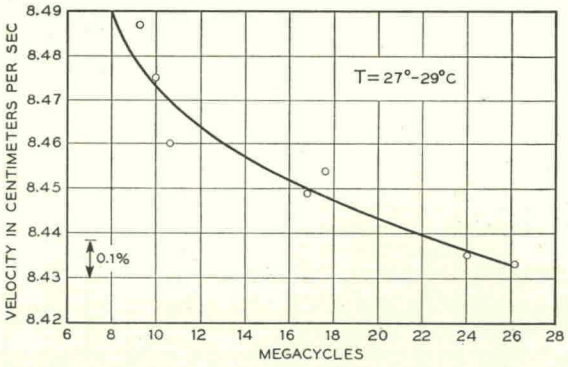


FIG. 14. "Apparent" velocity of longitudinal waves propagated along the 001 direction in silicon (cross dimensions approximately 9×9 mm, thickness 5.971 mm).

4.4 Attenuation Measurements

Because of the small specimen thicknesses used, it was not possible to obtain accurate determinations of attenuation for germanium and silicon over the temperature range of interest. Careful measurements at room temperature with direct evaluation of reflection loss using bayberry wax seals[5] indicated losses for the large silicon crystal tested to be less than 0.05 db per cm at

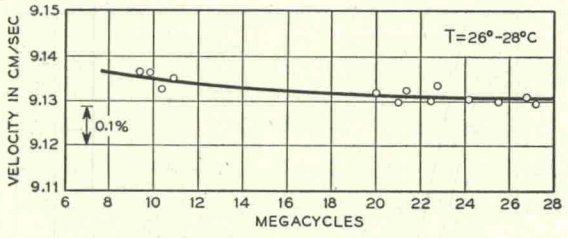


FIG. 15. "Apparent" velocity of longitudinal waves propagated along the 110 direction in silicon (cross dimensions approximately 13×20 mm and irregular, thickness 9.533 mm).

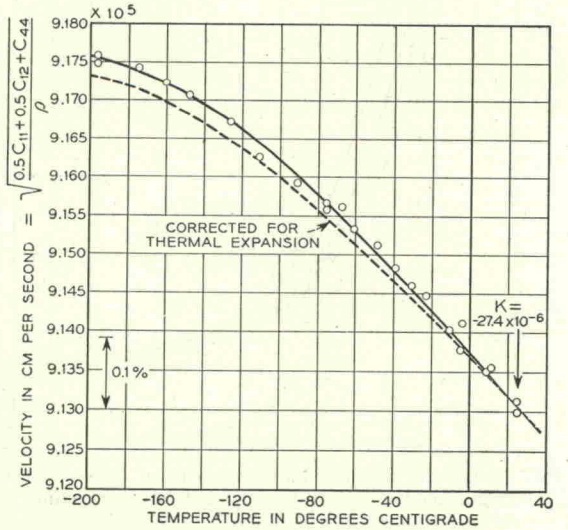


FIG. 16. Velocity of longitudinal waves in silicon single crystal—propagation parallel to 110 direction.

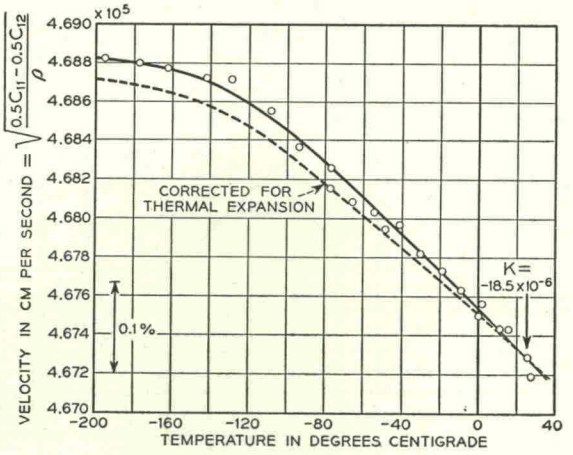


FIG. 17. Velocity of shear waves in silicon single crystal—propagation parallel to 110 direction, particle motion parallel to $\bar{1}10$ direction.

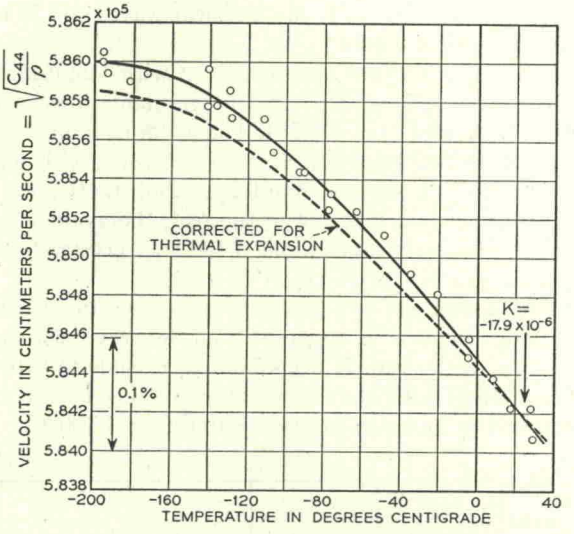


FIG. 18. Velocity of shear waves in silicon single crystal—propagation parallel to 110 direction, particle motion parallel to 001 direction.

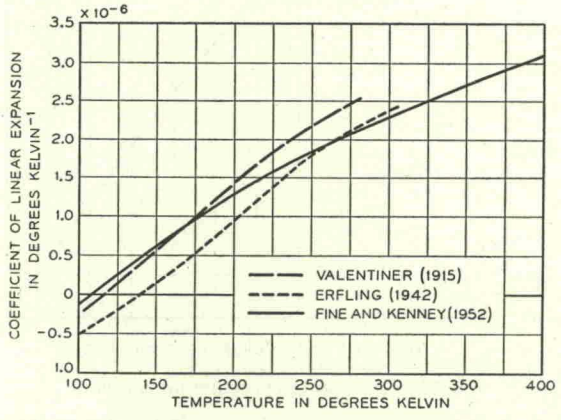


FIG. 19. Coefficient of linear expansion of silicon.

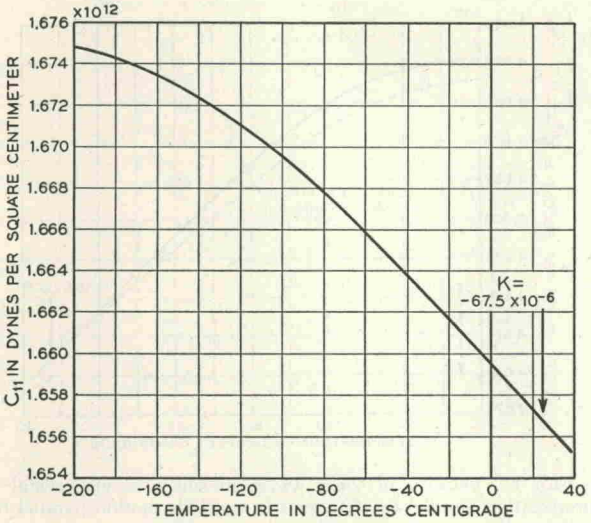


FIG. 20. C_{11} *versus* temperature for silicon.

frequencies as high as 15 mc for shear waves and 25 mc for longitudinal waves.

Room temperature measurements with longitudinal waves were also made for the germanium crystals (*E*, *F*, *G*, *H*, and *I*) of Table I. The water coupling technique described briefly in Sec. 3.3 was used, with total "round-trip" losses less than 0.2 db. Subtracting out a 0.11 db reflection loss due to the seal, the average loss for longitudinal waves along [100] (5 crystals) was approximately 0.06 db/cm at 18 mc.

The advantage of this method over other water coupling schemes[23] is apparent from the very low reflection loss at the seal. It would appear feasible to extend this method with the use of other liquids to cover a temperature range of at least −100°C to +100°C.

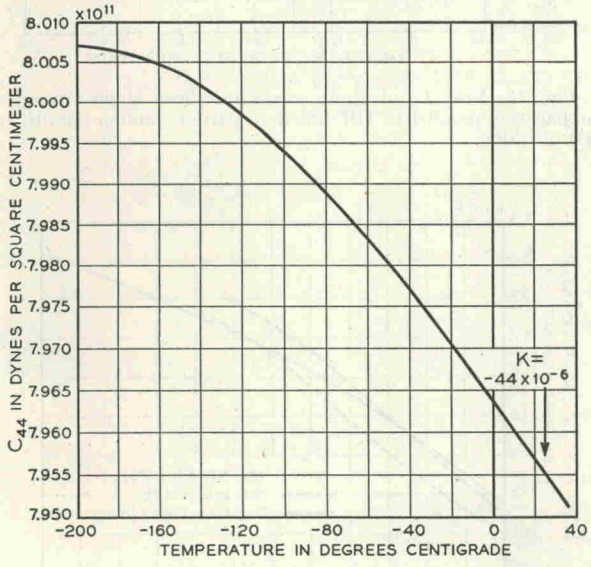


FIG. 21. C_{44} *versus* temperature for silicon.

[23] W. Roth, Quarterly Progress Report, M.I.T. Research Lab. of Electronics, Oct. 15, 1947.

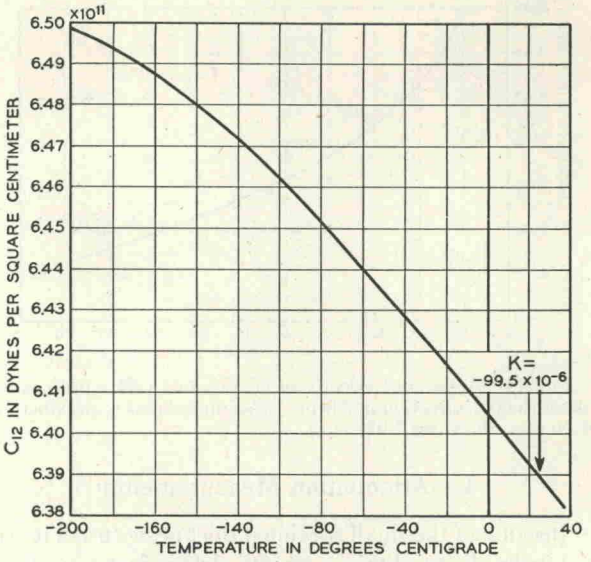


FIG. 22. C_{12} *versus* temperature for silicon.

4.5 Attenuation for Fused Silica

It was noticed that at temperatures below −150°C the response of the units fell off appreciably. With about 6 in. of the longitudinal wave rod[24] encased in a copper

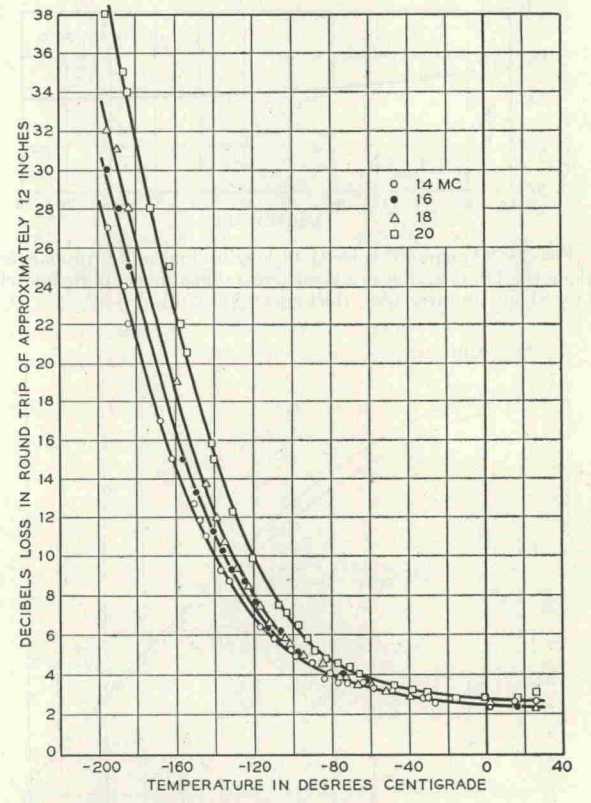


FIG. 23. Loss for longitudinal waves in fused silica rod. (Data include reflection loss at crystal end and beam spreading loss, estimated 2 db total.)

[24] The "effective" length covered was probably slightly greater than 6 in. because of heat conduction within the rod.

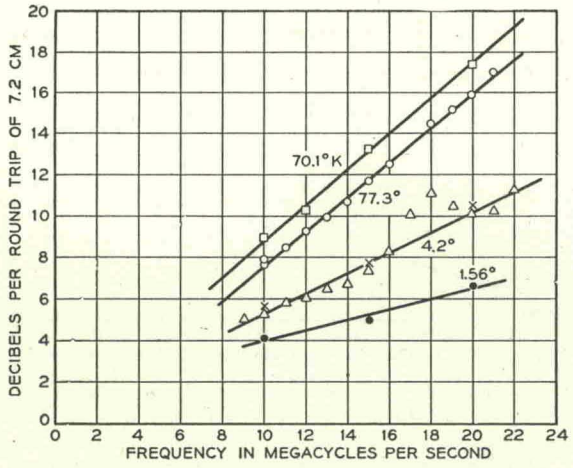


FIG. 24. Loss for shear waves in fused silica rod as a function of frequency and temperature. ($l = 3.60$ cm, diam = 2.25 cm).

sleeve and immersed in liquid nitrogen, the pulse decay rate was measured as a function of frequency with the results shown in Fig. 23. Similar data for shear waves was obtained.

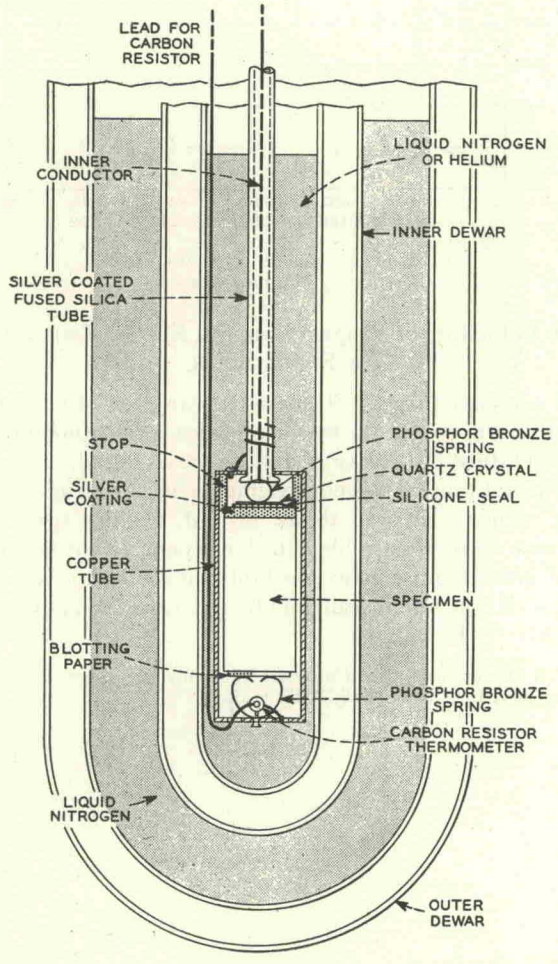


FIG. 25. Apparatus for measuring loss in fused silica at low temperatures.

Additional measurements were made with other samples of fused silica of similar quality (see reference 6). Figure 24 shows shear wave data for one of length 3.60 cm and diameter 2.25 cm. For these measurements the specimen was immersed in either liquid nitrogen or liquid helium, with the experimental arrangement of Fig. 25 being used.

The 18 mc y-cut quartz crystal transducer was attached to the specimen with a very viscous silicone,[25] a pressure of approximately 10 lb per sq in. being used. It was found advisable to roughen the silver coating on the end of the specimen with fine emery paper to increase the strength of the seal. Preparation of this silver coating was the same as described in reference 5.

The temperature was varied over narrow limits by varying the pressure over the liquid nitrogen or helium.

As seen from Fig. 24, the loss is approximately linear

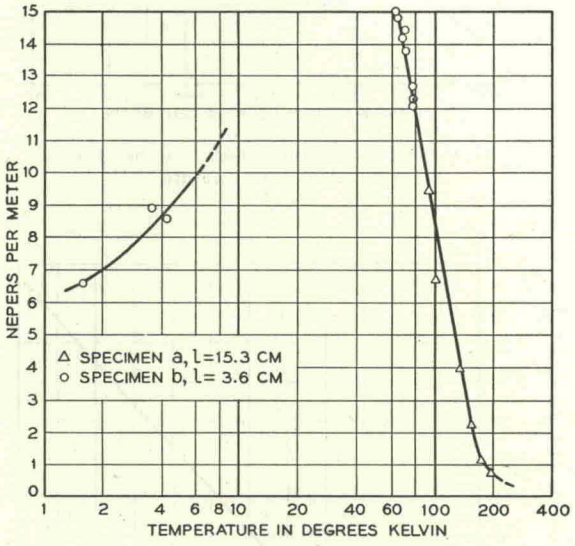


FIG. 26. Attenuation of shear waves in fused silica as a function of temperature (frequency = 10 mc).

with frequency over the two-to-one range used. The hump in the curve for 4.2°K was found to result from loss of energy to the electrical termination near the 18 mc crystal resonance frequency. Lowering the termination minimized this effect as can be seen from the 77.3° data.

Figure 26 shows a plot of shear wave attenuation as a function of temperature for 10 mc. A maximum is indicated near 31°K. From the shape of the loss curve, it would appear that a relaxation process exists. Correlation of data for the two different types of wave motion indicates that whatever this process is, it is primarily sensitive to shear distortion.[26]

[25] Dow Corning 200 Fluid, viscosity 25 000 poises.

[26] The mechanism of this relaxation process will be discussed in a forthcoming paper by O. L. Anderson and H. J. McSkimin.

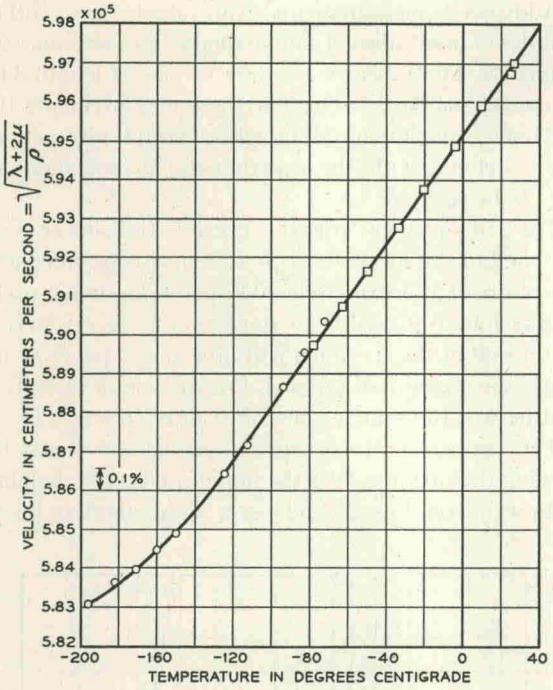


FIG. 27. Velocity of longitudinal waves in fused silica as a function of temperature.

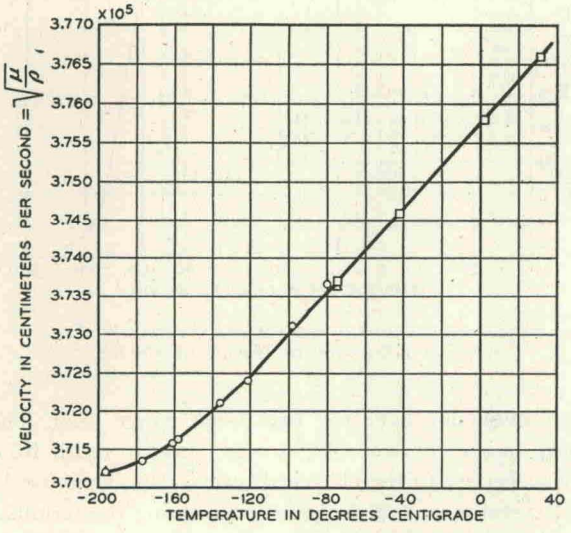


FIG. 28. Velocity of shear waves in fused silica as a function of temperature.

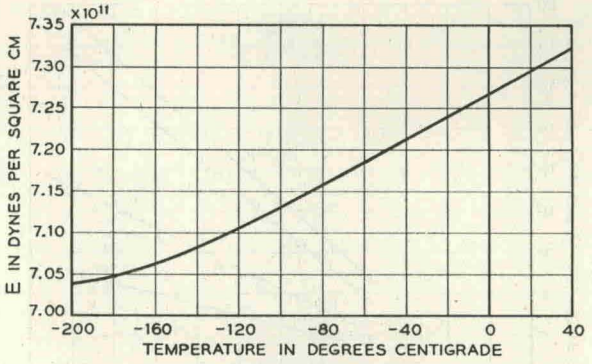


FIG. 29. Young's modulus E for fused silica (frequency = 20 mc, approx).

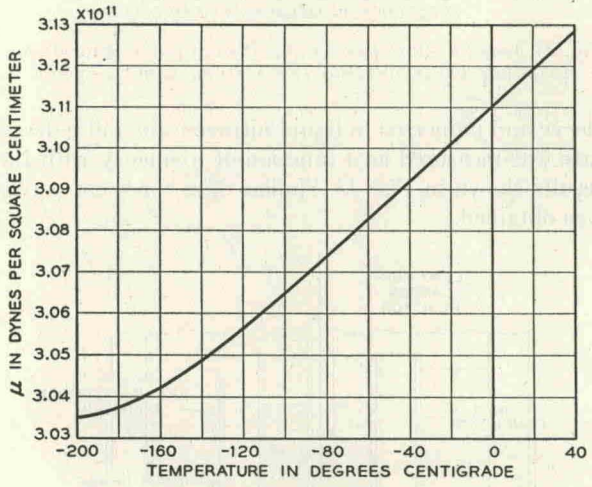


FIG. 30. Shear modulus μ for fused silica (frequency = 12 mc, approx).

4.6 Velocities of Propagation and Elastic Constants for Fused Silica

Figures 27 through 30 show the variation of velocity and elastic constants for fused silica as a function of temperature. A density of 2.203 g/cc was used.[27]

In addition to acknowledgments in the references, the author wishes to thank Mr. M. E. Fine for permission to reproduce his data for expansion coefficients and germanium elastic constants, and also to express appreciation for measurements and calculations made by Mr. T. B. Bateman.

[27] R. B. Sosman, *The Properties of Silica* (Chemical Catalog Company, Inc., New York, 1927) p. 361.

2171: H. J. McSKIMIN

BELL TELEPHONE LABORATORIES, *incorporated*

463 West Street, New York 14, N. Y.