

ions. On the other hand, for an impurity semiconductor, the resistivity due to lattice scattering generally decreases with decreasing temperature because of the T^{-1} dependence of the mean free path.⁵ Hence, the im-

portance of the impurity ion scattering resistivity in determining total resistivity increases as temperature decreases.⁶

⁵ A. Sommerfeld and H. Bethe, *Handbuch der Physik XXIV* (1933), Vol. 12, p. 560.

⁶ K. Lark-Horovitz and V. A. Johnson, *Phys. Rev.* **69**, 258 (1946). K. Lark-Horovitz, Contractor's Final Report, NDRC 14-585 (November, 1945), pp. 36-41.

Evaluation of the Stiffness Coefficients for Beryllium from Ultrasonic Measurements in Polycrystalline and Single Crystal Specimens*

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The pulsed ultrasonic method has been applied to the determination of the stiffness coefficients for beryllium. The constants $c_{11}=30.8 \times 10^{11}$ dynes/cm², $c_{33}=35.7$ were evaluated from compressional wave velocities in single crystals by extrapolating a plot of the effective stiffness coefficient *versus* $\sin^2\theta$ (θ being the angle between the hexagonal axis and the direction of wave propagation) to the points $\theta=\pi/2$ and 0. The values $c_{12}=-5.8$, $c_{44}=11.0$ were derived from an analysis relating the average effective stiffness coefficients for compressional and shear waves with the shear modulus and Lamé's constant. The latter data were calculated from measurements of longitudinal and transverse body wave velocities in polycrystalline metal. To find

the coefficient $c_{13}=0.87$, the established values for the other constants were employed in the general relation for the effective stiffness coefficient of the form $C_l=f(c_{ijk}, s, \theta)$.

Several criteria have been used to assess the validity of the c_{ijk} data: (1) The ratio of c_{11}/c_{33} is in accord with the c/a ratio for the hexagonal close-packed structure of beryllium; (2) the compressional and shear wave anisotropy factors of $c_{33}/c_{11}=1.16$ and $c_{44}/\frac{1}{2}(c_{11}-c_{12})=1.68$, respectively are in harmony with the observed transmission properties of polycrystalline beryllium; and (3) the experimental and theoretical curves for the directional variation of the effective compressional stiffness coefficient agree quite well.

1. INTRODUCTION

THE literature contains the stiffness coefficients of only three hexagonal metals, these being magnesium, zinc, and cadmium.¹ Some recent work on the preparation of large beryllium crystals has made available several adequate-sized single crystals of beryllium for ultrasonic velocity measurements from which the c_{ijk} constants were determined.²

It was found that essentially all of the crystal specimens were so oriented that measurements along ideal directions were virtually precluded. This condition eliminated any hope of obtaining the best possible accuracy, and, therefore, redetermination would be warranted when better crystals could be had. Nevertheless, the values for the c_{ijk} 's of beryllium are determinable to the order of accuracy common to the other hexagonal metals.

The method employed for evaluating the stiffness coefficients of beryllium is unique and has not been reported previously. It is based upon the following experimental data:

(1) Compressional and shear wave velocities in polycrystalline metal.

(2) Compressional wave velocities in single crystal

specimens having their crystallographic axes differently oriented with respect to the direction of propagation. Deriving the coefficients from this information requires the conditions, (1) the crystal belongs to classes 21-27 of Voigt's designation, thus having five independent constants, (2) the crystal is not too anisotropic.

The first of these conditions permits one to considerably simplify the expressions for the various wave velocities;³ the functions $v=f(\alpha, \beta, \gamma, c_{ijk}, s, \rho)$ can be reduced to $v=F(\theta, c_{ijk}, s, \rho)$ where θ , the angle between the hexagonal axis and the direction of wave propagation, takes the place of the three direction cosines α , β , and γ . The second condition makes possible certain extrapolation and approximations which will be described in detail. If the crystal is too anisotropic it becomes very difficult to obtain velocity data for polycrystalline specimens because of the poor multiple echo patterns.⁴ Beryllium exhibited excellent patterns, so it appeared reasonable at the outset to infer that it was not a highly anisotropic crystal. The significance of this feature will be accounted for later.

2. EXPERIMENTAL ASPECTS

Apparatus for the pulsed-ultrasonic measurements was of the nature already described in a number of

* This paper is based on work performed at the Metallurgical Project, Massachusetts Institute of Technology, under Contract No. W-7405-eng-175 for the AEC.

¹ R. F. S. Hearmon, *Rev. Mod. Phys.* **18**, 409 (1946).

² L. Gold, *Rev. Sci. Inst.* **20**, 115 (1949).

³ H. E. Mueller (private communication).

⁴ W. P. Mason and H. J. McSkimin, *J. Acous. Soc. Am.* **19**, 464 (1947). W. Roth, *J. App. Phys.* **19**, 901 (1947).

publications.⁵ The data were taken at room temperature with microsecond pulses at 10 mc. It was found that the optimum procedure for obtaining good velocity data required, (1) the use of salol films both for the longitudinal and transverse modes, (2) recording range readings on the scope pattern at the first discontinuity in the linear sweep produced by an echo. The oil film coupling between transducer and specimen gave rise to relatively large fluctuations in the echo intervals, principally because of its tendency to distort the pulses and make readings difficult. Apparently, better reproducibility of the echo intervals is achieved by reading to the very front edge of the pulse rather than a fixed db down from the bottom of the pulse.

Two possible ways of arriving at an average value for the range intervals were employed. For the polycrystalline specimens, where a number of good echoes could be obtained, it was convenient to plot the range readings *versus* the echo number and then to compute the average echo interval from the slope. This procedure is not practical where a large number of echoes are observed, whence for the single crystals differences in range for the various echoes were averaged numerically.

Velocity measurements for the single crystals were limited to compressional waves because of uncertainty in interpreting the multiple echo patterns for the shear waves; since two shear modes are excited simultaneously, it is difficult to resolve the pattern into the shear components, particularly when the velocities of propagation are not widely divergent.*

The orientation of the beryllium crystals was determined by the well-known back-reflection Laue technique, followed by stereographic projection. The angle between the hexagonal axis and the axis of the specimen is accurate to about 1–2°, a value which is sufficient for the over-all accuracy of the final data.

3. RESULTS FOR POLYCRYSTALLINE BERYLLIUM

Data was taken on a wide variety of samples of extruded flake, vacuum-cast lump, etc. There did not appear to be any significant divergence of results, in spite of the fact that preferred orientation was undoubtedly present in some of the specimens. This is substantial evidence for the relative isotropy of beryllium. In general, better patterns were manifest for longitudinal vibration than for transverse vibration; pulse distortion was more pronounced for the shear waves, a condition which makes the shear velocity measurement of lower accuracy.

Some rough estimates of the attenuation for compressional and shear oscillations, indicated that the latter was somewhat larger. If one interprets this as "scattering" losses at the crystal boundaries, then it can be inferred that beryllium has a higher degree of

shear anisotropy than compressional anisotropy.⁶ This conclusion is a useful one for checking the c_{jk} values as will be demonstrated.

Table I summarizes all the data one can obtain from ultrasonic propagation measurements in an isotropic substance. The compressional velocity is seen to be in excellent accord with the Sawyer-Kjellgren reported value;⁷ the manner in which S-K obtained this value is not clear, but presumably it was based upon the composite oscillator technique. Quite recently Squire *et al.* have reported ultrasonic velocity measurements in beryllium;⁸ their values agree very well with the table values.

The elastic constants were computed by means of the standard relations of elasticity theory.⁹ Young's modulus for the static stress-strain method agrees very well with the dynamic value. The compressibility value is in fair agreement with those obtained by the high pressure technique.¹⁰ Considering the differences in experimental approach, the agreement is much better than anticipated; very likely, the result obtained by the ultrasonic method is more reliable.

The values for Poisson's ratio is surprisingly low. By combining the literature values for the compressional velocity and the compressibility, the comparative figures listed were derived from the relation

$$\nu = (3 - v_l^2 \beta \rho) / (3 + v_l^2 \beta \rho), \quad (3)$$

where v_l is the compressional velocity, β the compressibility and ρ the density of beryllium. Thus, it is reasonably certain that the Poisson ratio for beryllium is the lowest for any of the known metals and alloys.

As an item of general interest, it was thought worthwhile to calculate the theoretical value for the characteristic temperature of beryllium for comparison with the value derived from specific heat measurements. The relation used is the classical Einstein-Debye equation

$$\nu_{\max} = \left\{ \frac{9}{4\pi} \frac{N}{V} \frac{1}{(1/v_l^3) + (2/v_t^3)} \right\}^{\frac{1}{3}} \quad (3.1)$$

where $\nu_{\max}$, the characteristic frequency of the crystal lattice, is related to the characteristic temperature Θ by the relation $\Theta = (h/k)\nu_{\max}$. The various symbols defined and evaluated are

N —atoms per cell = 2

V —volume of unit cell = 16.0×10^{-24} cm³

v_l —longitudinal wave velocity = 1.26×10^6 cm/sec.

v_t —transverse wave velocity = 0.888×10^6 cm/sec.

h —Planck's constant = 6.64×10^{-27} erg-sec.

k —Boltzmann's constant = 1.37×10^{-16} erg/°K.

⁶ W. P. Mason and H. J. McSkimin, *J. App. Phys.* **19**, 940 (1947).

⁷ C. B. Sawyer and B. J. Kjellgren, *Ind. Eng. Chem.* **30**, 501 (1938).

⁸ Rice Institute Progress Report N6onr-224 Task Order No. 3, October 1, 1948.

⁹ A. E. H. Love, *Mathematical Theory of Elasticity* (Dover Publications, New York, 1944).

¹⁰ P. W. Bridgman, *Proc. Am. Acad.* **68**, 27 (1933). Richards, Hall, and Mair, *J. Am. Chem. Soc.* **50**, 3304 (1928).

⁵ J. R. Pellam and J. K. Galt, *J. Chem. Phys.* **14**, 608 (1946). H. B. Huntington, *Phys. Rev.* **72**, 321 (1947).

* Mode separation is facilitated when the crystal constants have been established previously.

TABLE I. Data for polycrystalline beryllium.

For extruded flake metal	
Compressional velocity	1.265×10^6 cm/sec.
S and K value (method not reported)	1.26×10^6 cm/sec.
Shear velocity	0.888×10^6 cm/sec.
Young's modulus	2.965×10^{12} dynes/cm ²
	$(4.300 \times 10^7 \text{ lb./in.}^2)$
Lit. value (stress-strain method)	$4.26 \times 10^7 \text{ lb./in.}^2)$
Shear or rigidity modulus	1.465×10^{12} dynes/cm ²
Bulk modulus	1.014×10^{12} dynes/cm ²
Compressibility	0.985×10^{-12} cm ² /dyne
Bridgman value (high pressure tech.)	0.874×10^{-12}
Richard <i>et al.</i> (high pressure tech.)	0.95×10^{-12}
Poisson's ratio	0.0122
Based on Bridgman value	0.0754
Based on Richards value	0.035
Lamé's constant	0.038×10^{12} dynes/cm ²
Characteristic temperature	
From Debye-Einstein rel'n	1430°K
From specific heat data	1000°K

Calculation gives $v_{\max} = 2.96 \times 10^{13}$ /sec. and $\Theta = 1430^\circ\text{K}$.
The specific heat value is 1000°K .

4. RESULTS FOR SINGLE CRYSTALS

Four single crystals with dimensions of the order of 1 in. diameter and 1–2 in. in length were employed for the compressional velocity measurements. Data for three of the specimens are included in Table II.

It is evident that the velocity is comparatively insensitive to crystal orientation; the values listed were computed from the relation

$$v = 1.670 \times 10^6 (l/2\Delta y) \quad (4)$$

which converts the radar scope range readings to velocity values, l being the specimen length and Δy the range interval. The results for the fourth specimen are omitted since they were found subsequently to be questionable when the data were used in arriving at the c_{jk} 's.

5. BASIC STIFFNESS COEFFICIENT RELATIONS AND THE DETERMINATION OF c_{11} AND c_{33}

The body wave velocities in a hexagonal crystal of classification D_{6h}^4 can be expressed as follows:

$$v_1 = \left(\frac{c_l}{\rho} \right)^{\frac{1}{2}}, \quad v_{t1} = \left(\frac{c_{t1}}{\rho} \right)^{\frac{1}{2}}, \quad v_{t2} = \left(\frac{c_{t2}}{\rho} \right)^{\frac{1}{2}}, \quad (5.1)$$

where

$$\begin{aligned} c_{l1} &= \frac{1}{2}(c_{11} - c_{12}) \sin^2\theta + c_{44} \cos^2\theta \\ c_{t2} &= \frac{1}{2}[(c_{11} + c_{44}) \sin^2\theta + (c_{33} + c_{44}) \cos^2\theta - \varphi(c_{jk}, \theta)] \\ c_l &= \frac{1}{2}[(c_{11} + c_{44}) \sin^2\theta + (c_{33} + c_{44}) \cos^2\theta + \varphi(c_{jk}, \theta)]. \end{aligned} \quad (5.2)$$

The angle between the direction of wave propagation and the hexagonal axis is θ . For the function $\varphi(c_{jk}, \theta)$ one has

$$\begin{aligned} \varphi(c_{jk}, \theta) &= \{ (c_{11} - c_{44})^2 \sin^4\theta + (c_{33} - c_{44})^2 \cos^4\theta \\ &\quad + 2 \sin^2\theta \cos^2\theta [(c_{11} - c_{44})(c_{44} - c_{33}) \\ &\quad + 2(c_{13} + c_{44})^2] \}^{\frac{1}{2}}. \end{aligned} \quad (5.3)$$

It is evident that a plot of c_l versus θ should permit extrapolation to $\theta = \pi/2$ and 0 where $c_l = c_{11}$ and c_{33} , respectively. Since only three reliable points were available, some misgiving as to the reliability of such a solution for c_{11} and c_{33} was at first manifest; however, several considerations established a modicum of confidence in this approach.

A review of the results for the metals cadmium, zinc, and magnesium indicated that extrapolation is apt to be more accurate if one plots c_l versus $\sin^2\theta$. Moreover, since beryllium is comparatively isotropic c_{11} should not be too different from c_{33} and also the extrapolation at the end points should be gradual. Figure 1 shows the c_l versus $\sin^2\theta$ plot with the extrapolation values for c_{11} and c_{33} identified.

If one interprets the significance of the c_{jk} constants along the c and a axes of a hexagonal crystal, additional confirmation of the derived values for beryllium is possible. Effectively, c_{11} and c_{33} are measures of the bonding strength along the a and c axes, respectively. Hence, in hexagonal crystals of similar electronic configuration, it is apparent that the ratio c_{11}/c_{33} should have some correlation with regard to the axial ratio c/a . Figure 2 is what may be conveniently termed an anisotropy plot for hexagonal metals. It is surprising how closely the four points lie on a straight line. For the ratio $c/a = 1.63$, corresponding to the axial ratio for the ideal hexagonal close-packed structure, $c_{11}/c_{33} = 1$. This is in accord with the idea that the cohesive forces along the $[001]$ and $[210]$ directions should be the same when the H.C.P. structure is truly attained; where the c/a ratio is less than 1.63, c_{11} should be less than c_{33} which is the state of affairs for beryllium.

Thus, the inference can be made that the greater the deviation from the ideal c/a ratio for close-packing the more anisotropic will the metal be with regard to body wave propagation. The predicted position for cadmium not being in very good agreement with the experimental value might indicate errors in the determination of c_{11} and c_{33} ; it would be of interest to redetermine these values.

6. DETERMINATION OF c_{12} , c_{13} , AND c_{44}

In principle, the cross constants should be determinable from Eqs. (5.2) and (5.3). By selecting points from the curve of c_l versus $\sin^2\theta$ in Fig. 1, one might attempt to evaluate the cross constants c_{12} , c_{13} , and c_{44} . This approach, however, is not practicable because of the transcendental nature of the equations involved.

TABLE II. Data for single crystals of beryllium.

Specimen	Length (inches)	Range interval (yards)	$v_l \times 10^6$ cm/sec.	$c_n \times 10^{12}$ dynes/cm ²	θ
(1)	1.714	1100	1.30	3.14	52°
(2)	1.283	800	1.34	3.33	33°
(3)	1.533	990	1.29	3.09	67°

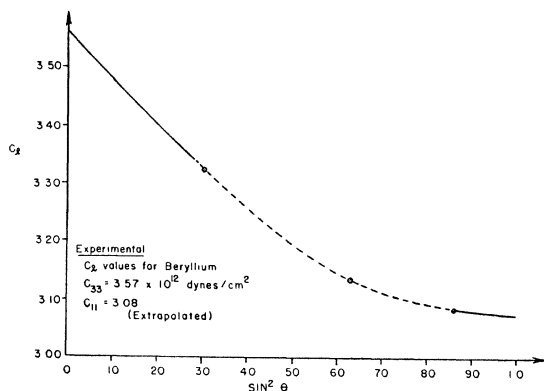


FIG. 1. Variation of the values of c_l for beryllium with $\sin^2\theta$ (experimental).

Now for the polycrystalline data there are the relations

$$\bar{c}_l = 2\mu + \lambda, \quad \bar{c}_t = \mu, \quad (6)$$

where μ is the shear modulus and λ Lamé's constant. These average values are related to the c_{jk} constants as clearly

$$\bar{c}_l = \frac{1}{2} \frac{2}{\pi} \int_0^{\pi/2} (c_{11} + c_{44}) \sin^2\theta + (c_{33} + c_{44}) \cos^2\theta d\theta + \frac{1}{2} \frac{2}{\pi} \int_0^{\pi/2} \varphi(c_{jk}, \theta) d\theta \quad (6.1)$$

$$\bar{c}_{t1} = - \frac{2}{\pi} \int_0^{\pi/2} [\frac{1}{2}(c_{11} - c_{12}) \sin^2\theta + c_{44} \cos^2\theta] d\theta, \quad (6.2)$$

$\bar{c}_{t2}$ is essentially (6.1), but with a minus sign in front of the second integral.

Making use of the fact that beryllium is at least moderately isotropic, we assume that $\bar{v}_{t1} = \bar{v}_{t2}$ so that we can write

$$\bar{c}_{t1} = \bar{c}_{t2} = \bar{c}_t. \quad (6.3)$$

This assumption is vital in the procedure for finding expressions for $\bar{c}_l$ and $\bar{c}_t$ in terms of the stiffness coefficients. Several criteria form the basis of latter checking the soundness of (5.6), as well as the entire line of attack. These are:

(1) The theoretical curve for c_l based upon the c_{jk} values should agree with the experimental curve of Fig. 1.

(2) The cross constants c_{12} , c_{44} , c_{13} must be small compared to c_{11} and c_{33} because Poisson's ratio is low.

(3) The transverse velocities must be comparable when evaluated from the c_{jk} data.

Proceeding then with the analysis

$$\bar{c}_{t1} = \frac{1}{2} [\frac{1}{2}(c_{11} - c_{12}) + c_{44}] \quad (6.4)$$

and

$$\frac{1}{2} [\frac{1}{2}(c_{11} - c_{12}) + c_{44}] = - \frac{1}{\pi} \int_0^{\pi/2} [(c_{11} + c_{44}) \sin^2\theta + (c_{33} + c_{44}) \cos^2\theta] d\theta - \frac{1}{\pi} \int_0^{\pi/2} \varphi(c_{jk}, \theta) d\theta, \quad (6-5)$$

from which one obtains

$$\begin{aligned} \frac{1}{\pi} \int_0^{\pi/2} \varphi(c_{jk}, \theta) d\theta &= \frac{1}{4}(c_{11} + c_{13} + 2c_{44}) - \frac{1}{2} [\frac{1}{2}(c_{11} - c_{12}) + c_{44}] \\ &= \frac{1}{4}(c_{33} + c_{12}). \end{aligned} \quad (6.6)$$

The integral in (6.6) would be quite impossible to evaluate by direct integration. Clearly, relation (6.3) circumvents this barrier and permits ready solution of $\bar{c}_l$. The relation for $\bar{c}_l$ is accordingly

$$\bar{c}_l = \frac{1}{4}[c_{11} + c_{12} + 2(c_{33} + c_{44})]. \quad (6.7)$$

From relations (6), (6.4), and (6.7) one can write down the simultaneous equations

$$\begin{cases} c_{11} + c_{12} + 2(c_{33} + c_{44}) = 4(2\mu + \lambda) \\ \frac{1}{2}(c_{11} - c_{12}) + c_{44} = 2\mu. \end{cases} \quad (6.8)$$

Putting in the values for c_{11} , c_{33} , μ and λ these become

$$\begin{cases} 2c_{44} + c_{12} = 1.62 \\ 2c_{44} - c_{12} = 2.78 \end{cases} \quad (6.9)$$

which give the solutions

$$c_{44} = 1.10, \quad c_{12} = -0.58. \quad (6.10)$$

The remaining constant c_{13} can next be calculated from (5.2) and (5.3), using the values for the identified c_{jk} 's and selecting some value for c_l and θ . The result is

$$c_{13} = 0.87.$$

7. DISCUSSION OF DERIVED c_{jk} VALUES FOR BERYLLIUM

Table III is a comparison of the stiffness coefficients for beryllium with those of magnesium, zinc, and cadmium. The data of Wright, Bridgman, and Gruen-eisen-Goens were the result of the static measurements

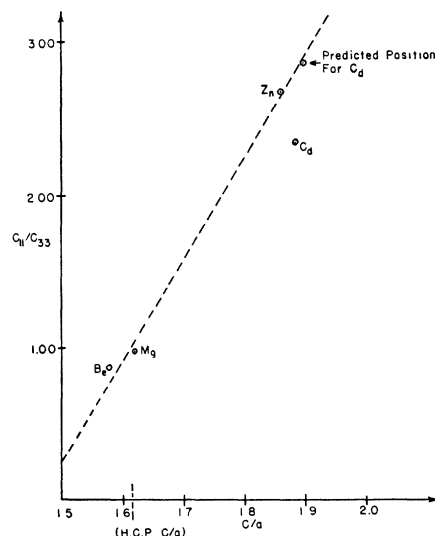
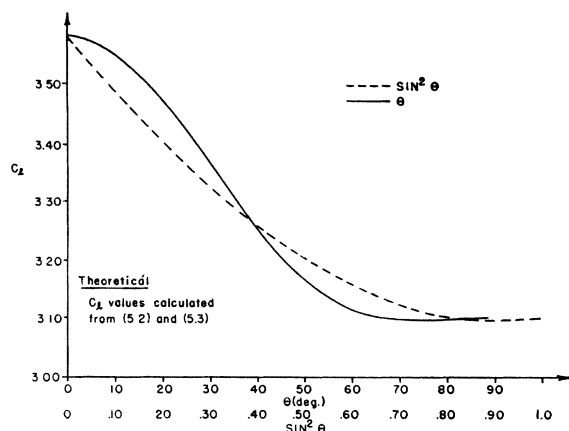


FIG. 2. Anisotropy plot for hexagonal metals showing bonding strength variation.

FIG. 3. Variation of c_1 for beryllium with $\sin^2\theta$ (theoretical).

on many crystals; it is evident that the differences between the various sets is generally much greater for the cross constants. This would seem to indicate greater likelihood of error in c_{44} , c_{12} , and c_{13} , and is apt to be the case for the beryllium values. As a rough assessment of the over-all accuracy of the beryllium constants, it would be reasonable to believe that they are of the same order of accuracy as the other data in Table III.

Confirmation of the general correctness of the stiffness coefficients is revealed in Fig. 3 which gives the theoretical c_1 plot calculated from the listed values. The $\sin^2\theta$ plot if compared with Fig. 1 will be seen to fit the experimental curve quite gratifyingly; the end points would, of course, have to match, but the fact that the entire curve is in accord indicates the validity of the calculations. The c_1 versus θ curve demonstrates why a better extrapolation for the c_{11} and c_{33} constants is possible with $\sin^2\theta$ as the abscissa. If the former had been used, the c_{33} value would have been found to be somewhat higher.

Recalling that beryllium is relatively more isotropic for compressional waves than shear waves, we now compare the ratios c_{33}/c_{11} and $1/2(c_{11}-c_{12})c_{44}$ which are a measure of the degree of anisotropy—being unity for complete isotropy. Thus

$$c_{33}/c_{11} = 1.16, \quad \frac{c_{44}}{\frac{1}{2}(c_{11}-c_{12})} = 1.68 \quad (7)$$

TABLE III. Stiffness coefficients for hexagonal metals (c_{jk} values $\times 10^{11}$ dynes/cm²).

Metal	c_{11}	c_{33}	c_{44}	c_{12}	c_{13}	Source
Mg	5.65	5.87	1.68	2.32	1.81	Wright
	5.94	5.94	1.14	2.03	2.03	Bridgman
Zn	16.1	5.42	4.00	4.32	4.37	Grueneisen-Goens
	15.9	6.21	4.00	3.23	4.82	Bridgman
Cd	12.1	5.13	1.85	4.81	4.42	Grueneisen-Goens
	10.9	4.60	1.56	3.98	3.75	Bridgman
Be	30.8	35.7	11.0	-5.8	8.7	

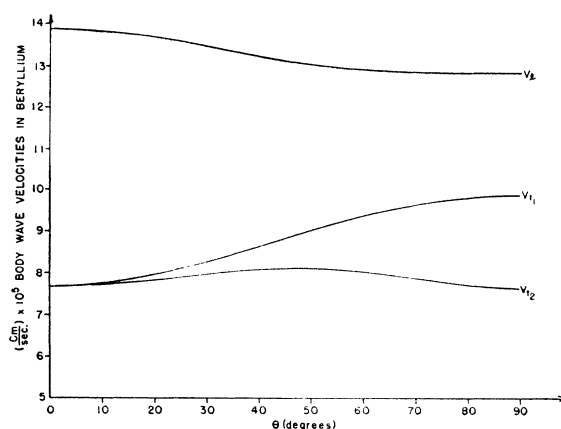


FIG. 4. Variation of body wave velocity with orientation.

which corroborates the observed transmission properties of polycrystalline beryllium.

Finally, Fig. 4 shows how the body wave velocities vary with orientation. The compressional velocity curve is quite flat as compared to the two shear velocity curves. Although the shear waves have velocities which differ as much as approximately 20 percent for propagation along the a axis, the average velocities agree to within roughly 10 percent.

8. CONCLUSION AND ACKNOWLEDGMENT

The stiffness coefficients for beryllium have been evaluated in a manner which necessitated cross checking of all sorts. It has been shown that the results are in conformity with a number of experimental facts and basic principles. The need for accurate measurement of the coefficients for beryllium is certainly unquestionable, but the same may be said for the other hexagonal metals.

The author is indebted to a number of individuals for helpful discussions and services rendered. The single crystals of beryllium were the result of a crystal growing research project sponsored by Professors Cohen and Kaufmann of the Massachusetts Institute of Technology Metallurgy Department. The equipment used for the ultrasonic velocity measurements was furnished by the Massachusetts Institute of Technology Research Laboratory of Electronics, thanks to Dr. J. K. Galt. The advice of Mr. D. L. Arenberg in regard to the technique of ultrasonic measurements was invaluable.

Professor H. E. Mueller was kind enough to outline the simplification of the hexagonal relations for the body wave velocities. The essential details are given in the Appendix.

APPENDIX

The relation for the body wave velocities in crystals has been derived by Christoffel.¹¹ Solutions of the cubic equation

$$C^3 - I_1 C^2 + I_2 C - I_3 = 0 \quad (8)$$

¹¹ K. B. Christoffel, Ann. di Matematica (2) 8, 193 (1877).

define the compressional and two shear velocities. I_1 , I_2 and I_3 are the invariants

$$\begin{aligned} I_1 &= k_{11} + k_{22} + k_{33} \\ I_2 &= k_{11}k_{22} + k_{22}k_{33} + k_{11}k_{33} - (k_{12}^2 + k_{23}^2 + k_{13}^2) \\ I_3 &= k_{11}k_{22}k_{33} + 2k_{12}k_{13}k_{23} - (k_{12}^2k_{33} + k_{13}^2k_{22} + k_{23}^2k_{11}). \end{aligned} \quad (9)$$

For the Voigt classes 21-27, the c_{ijk} 's are

$$\begin{aligned} c_{11} &= c_{22}, \quad c_{23} = c_{13}, \quad c_{44} = c_{55} \\ c_{66} &= \frac{1}{2}(c_{11} - c_{12}) \end{aligned} \quad (10)$$

with all other stiffness coefficients but c_{33} zero. The k 's are then

$$\begin{aligned} k_{11} &= c_{11}(\alpha^2 + \beta^2/2) - c_{12}(\beta^2/2) + c_{44}\gamma^2 \\ k_{22} &= c_{11}(\alpha^2/2 + \beta^2) - c_{12}(\alpha^2/2) + c_{44}\gamma^2 \\ k_{33} &= c_{44}(\alpha^2 + \beta^2) + c_{33}\gamma^2 \\ k_{12} &= \frac{1}{2}(c_{11} + c_{12})\alpha\beta \\ k_{13} &= (c_{13} + c_{44})\alpha\gamma \\ k_{23} &= (c_{13} + c_{44})\beta\gamma, \end{aligned} \quad (11)$$

where α , β , and γ are the direction cosines for the angles between the direction of wave propagation and the orthogonal axes corresponding to the direction [001], [120], and [100] in the hexagonal system.

Solution of Eq. (1) at this point looks hopeless. If we transform (11) to Eulerian angles, it can be shown that the invariants will not contain the azimuthal angle, and that, therefore, the roots of (8) will only contain the angle between the hexagonal axis and

the direction of wave propagation. Making the substitutions

$$\begin{aligned} \alpha &= \cos\varphi \sin\theta \\ \beta &= \sin\varphi \sin\theta \\ \gamma &= \cos\theta \end{aligned} \quad (12)$$

the k 's can be written as

$$\begin{aligned} k_{11} &= [A + B \cos^2\varphi] \sin^2\theta + c_{44} \cos^2\theta \\ k_{22} &= [A + B \sin^2\varphi] \sin^2\theta + c_{44} \cos^2\theta \\ k_{33} &= c_{44} \sin^2\theta + c_{33} \cos^2\theta \\ k_{12} &= B \cos\varphi \sin\varphi \sin^2\theta \\ k_{13} &= (c_{13} + c_{44}) \cos\varphi \cos\theta \sin\theta \\ k_{23} &= (c_{13} + c_{44}) \sin\varphi \cos\theta \sin\theta, \end{aligned} \quad (13)$$

where

$$A = \frac{1}{2}(c_{11} - c_{12}), \quad B = \frac{1}{2}(c_{11} + c_{12}).$$

Using relations (13) in (9) one has

$$\begin{aligned} I_1 &= 2A \sin^2\theta + B(\cos^2\varphi + \sin^2\varphi) + 2c_{44} \cos^2\theta + c_{44} \sin^2\theta + c_{33} \cos^2\theta; \\ I_2 &= \langle \sin^4\theta \rangle [A^2 + AB + \langle B^2 \sin^2\varphi \cos^2\varphi \rangle] + c_{44} \cos^4\theta \\ &\quad + (2A + B)c_{44} \cos^2\theta \sin^2\theta + (c_{44} \sin^2\theta + c_{33} \cos^2\theta) \\ &\quad \times [2c_{44} \cos^2\theta + (2A + B) \sin^2\theta] - \langle B^2 \sin^4\theta \cos^2\varphi \sin^2\varphi \rangle \\ &\quad + (c_{13} + c_{44})^2 \cos^2\theta \sin^2\theta; \end{aligned} \quad (14)$$

$$\begin{aligned} I_3 &= \langle (c_{44} \sin^2\theta + c_{33} \cos^2\theta) [B^2 \sin^4\theta \sin^2\varphi \cos^2\varphi + \dots] \rangle + \dots \\ &\quad + \langle (c_{13} + c_{44})^2 B \cos^2\theta \sin^4\theta \cos^2\varphi \sin^2\varphi \rangle \\ &\quad - \langle (c_{44} \sin^2\theta + c_{33} \cos^2\theta) B^2 \sin^4\theta \cos^2\varphi \sin^2\varphi \rangle \\ &\quad - \langle (c_{13} + c_{44})^2 \cos^2\theta \sin^2\theta [2B \sin^2\theta \sin^2\varphi \cos^2\varphi + \dots] \rangle, \end{aligned} \quad (15)$$

where the terms in $\langle \rangle$ cancel, eliminating the φ terms. Relations (5.2) and (5.3) follow directly as the solutions of Eq. (8).