FRISILLO AND BARSCH

Associated Elastic Constant	Sample	Ň	Direction Cosine	Angle	Pure-Mode Relation	Calculated ρV^2 , Mb	Measured pV ² , Mb
<i>a</i> 13	4	[20n]	l = 0.8332 n = 0.5529	33°34' 56°26'	$\frac{l^2 c_{56} + n^2 c_{44}}{p_0 V_{S2}^2}$	0.7910	0.7960
c12	2	[Zm0]	l = 0.7437 m = 0.6685	41°57' 48°03'	$\frac{l^2c_{55} + m^2c_{44}}{= \rho_0 V_{53}^2}$	0.7828	0.7874
c23	3	[Omm]	m = 0.7590 n = 0.6510	40°37' 49°23'	$m^{2}c_{66} + n^{2}c_{55} = \rho_{0}V_{S1}^{2}$	0.7673	0.7664

TABLE 4. Calculated Propagation Directions for Cross-Coupling Constants and Associated Pure-Mode Checks

The known experimental errors occurring for the elastic-constant measurements are 0.02% for specimen thickness, 0.003% for specimen orientation, and 0.06% for specimen density. Because many of the moduli were measured on two sets of ultrasonic units that gave results identical to those in Table 3, systematic errors resulting from the ultrasonic equipment are considered negligible. Adding the known experimental errors gives a total probable error of 0.083%. Although this estimate of the known experimental error is a generous one, it does not completely account for the experimentally observed deviations in the values of the elastic constants. This fact, however, is not surprising, since four different specimens of slightly different compositions were used in this study. Because an appropriate compositional correction is not known, possible errors occurring in the measurements owing to compositional variations cannot be accounted for. In addition, because

slight inhomogeneities are known to occur for most natural specimens, a second possible unknown correction term must be ignored. Consequently, a comprehensive estimate of the probable error in the experimental determination of the elastic constants is not possible. As a result, the scatter in the values obtained from the various modes and the cross checks for the on-diagonal moduli are taken to be indicative of the probable error in their measurements.

Because the equations used for calculating the cross-coupling moduli depend on other ondiagonal moduli, on the direction cosines, and on the measured values of ρV^2 , it is apparent that their associated probable errors are considerably larger than those for the on-diagonal moduli. A reasonable estimate of the probable errors for the cross-coupling moduli may be determined from the Gaussian error propagation law. In this manner the probable errors given in Table 5 were obtained from the errors

TABLE 5. Velocities of Quasi-Modes and Calculated Values of the Adiabatic Cross-Coupling Elastic Constants at 25°C

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	Elastic Constant	Sample	Ň	Thickness d, mm	Velocity, km/sec	c _{μν} , Mb
	c23	3	[0mm]	8.641	V_{QS} = 4.515 V_{Qp} = 7.624	0.460 ± 0.002
	c ₁₃	4	[l0n]	5.054	$V_{QS} = 4.914$ $V_{Qp} = 8.055$	0.548 ± 0.002
1	Cl3	2	[2m0]	6.588	$V_{QS} = 4.245$ $V_{Qp} = 8.014$	0.710 ± 0.002

of the on-diagonal moduli, ρV^2 , and the direction cosines.

Pressure dependence of effective second-order elastic constants. The basic data necessary to determine the isothermal pressure derivatives of the effective second-order adiabatic elastic constants are the transit time of the ultrasonic wave at elevated pressure t_r and the specimen thickness at zero pressure d_m . From these data the natural wave velocity W [Thurston and Brugger, 1964] can be calculated at each experimental pressure by using $W = 2d_o/t_r$. The pressure dependence of the quantity $\rho_0 W^2$ can be expressed by the first N expansion terms of the Taylor series:

$$\rho_0 W^2 = \rho_0 \sum_{n=0}^N A_n^N (P^n/n!) \qquad (1a)$$

$$W^{2} = \rho_{0}W_{0}^{2} + (\rho_{0}W^{2})'P$$

+ $(\rho_{0}W^{2})''P^{2}/2 + \cdots$

p

The first term on the right-hand side of (1b) represents the zero pressure value of the respective on-diagonal elastic constant, or the quantities $\rho_0 V_{0s}^2$ or $\rho_0 V_{0p}^2$ used in computing the off-diagonal moduli. The remaining two quantities, $(\rho_0 W^2)'$ and $(\rho_0 W^2)''/2$, are, according to the equations of Graham [1969] and Barsch and Frisillo [1972], related to the first and second pressure derivatives of the elastic constants, respectively.

In this study all data were fitted to first-, second-, and third-order polynomials, and the resulting coefficients and standard deviations were examined for best fit. On the basis of the criteria discussed in the appendix, the data for the longitudinal modes are found to fit the firstorder polynomial best in all cases. The data for the shear and quasi-shear modes, however, required a second-order fit, and thus a statistically significant nonlinearity was indicated. As is shown in the appendix, a fit to a third-order



(1b)

Fig. 2. Experimental data of $(t_o/t_r)^2$ as a function of pressure for the on-diagonal moduli c_{n1} , c_{22} , and c_{33} . Solid and open circles, solid triangles, and open squares indicate specimen 1; open triangles, specimen 3; solid squares, specimen 4.