

TABLE 7. Isothermal First Pressure Derivatives of the Effective Elastic Constants at 25°C

$c_{\mu\nu}$	Specimen	$\vec{N}$	$\vec{U}$	$[\partial(\rho_0 W^2)/\partial P]_0$	$(\partial c_{\mu\nu}^S/\partial P)_0$	Weighted Average
$c_{11}$	3	[100]	[100]	9.86	11.08 ± 0.06	11.04 ± 0.06
	1	[100]	[100]	9.72	10.94 ± 0.09	
$c_{22}$	1	[010]	[010]	9.07	9.27 ± 0.07	9.19 ± 0.08
	4	[010]	[010]	8.90	9.11 ± 0.07	
$c_{33}$	1	[001]	[001]	15.69	16.40 ± 0.06	16.42 ± 0.04
	1	[001]	[001]	15.72	16.44 ± 0.06	
$c_{44}$	1	[010]	[001]	2.25	2.35 ± 0.01	2.38 ± 0.03
	4	[010]	[001]	2.36	2.46 ± 0.01	
	1	[001]	[010]	2.08	2.36 ± 0.01	
	1*	[001]	[010]	2.12	2.40 ± 0.02	
$c_{55}$	1	[100]	[001]	2.58	2.98 ± 0.01	2.92 ± 0.04
	3	[100]	[001]	2.45	2.85 ± 0.01	
	1	[001]	[100]	2.71	2.97 ± 0.02	
$c_{66}$	1	[100]	[010]	2.36	2.77 ± 0.01	2.75 ± 0.01
	3*	[100]	[010]	2.35	2.77 ± 0.01	
	1	[010]	[100]	2.61	2.71 ± 0.02	
	4	[010]	[100]	2.61	2.71 ± 0.02	
$c_{12}$	2	[ $Lm0$ ]	[ $m\bar{L}0$ ]	1.66	6.97 ± 0.14	6.97 ± 0.10
	2*			1.66	6.97 ± 0.14	
$c_{13}$	4*	[ $L0n$ ]	[ $n0\bar{L}$ ]	2.21	9.11 ± 0.14	9.09 ± 0.10
	4*			2.19	9.07 ± 0.14	
$c_{23}$	3	[ $0nm$ ]	[ $0m\bar{n}$ ]	1.64	8.69 ± 0.10	8.73 ± 0.10
	3*			1.57	8.83 ± 0.15	

\*Run made with Arenberg PSP AFC ultrasonic equipment. All other data were taken with MRL PSP AFC equipment.

culated from the isothermal elastic compliances [Graham, 1969; Barsch and Frisillo, 1973]. The computed cross checks  $c_{33}' = 8.72$  and  $c_{33}'' = 16.53$  are in excellent agreement with their corresponding values in Table 7. The agreement of the check on  $c_{33}'$  illustrates the self-consistency of the data, since knowledge of  $c_{44}$  and  $c_{22}$  and of their first pressure derivatives is required for the calculation.

To test the possibility of inherent systematic error in the MRL PSP AFC ultrasonic equipment used to obtain most of these data, several pressure runs were made with a different ultrasonic unit (Arenberg PSP AFS). The agreement of the data obtained by using the two ultrasonic units demonstrates that systematic errors from the electronic system are very small.

The errors shown in Table 7 for  $(\partial c_{\mu\nu}/\partial P)_0$  are based on the standard deviations of the least-squares curve fit of  $(\rho W^2)_0'$ . Because the major source of error in  $(\rho W^2)_0'$  arises from  $(\rho W^2)_0'$ ,

the standard deviation of the curve fitted to the raw data can be considered as a reasonable estimate of the probable error for each run. The error given for the cross-coupling moduli was determined from the errors of  $(\rho_0 W^2)_0'$ , of the pressure coefficient of the on-diagonal moduli, and of the direction cosines by means of the Gaussian error propagation law. In several cases the differences between the value of  $(\partial c_{\mu\nu}^S/\partial P)_0$  obtained from different modes are larger than the standard errors of the individual runs. Therefore the 'weighted average' values  $\langle V \rangle$  were determined by

$$V = \frac{\sum_{i=1}^n W_i V_i}{\sum_{i=1}^n W_i} \quad (7)$$

where  $W_i = 1/(\text{s.d.})^2$  for the individual runs and  $V_i$  are the corresponding values of  $(\partial c_{\mu\nu}^S/\partial P)_0$  to be averaged. The errors for the weighted average values were estimated according to

$$\Delta = \left[ \sum_{i=1}^n W_i (V_i - \langle V \rangle)^2 + \sigma_i^2 / n \sum_{i=1}^n W_i \right]^{1/2} \quad (8)$$

where  $\sigma_i$  is the standard error of each value  $V_i$  and  $n$  is the number of modes to be averaged. (This formula has been suggested to the authors by H. H. Demarest, Jr.) This formula is a useful extension of the Gaussian error propagation law to which it reduces in the case of perfect consistency ( $V_i = \langle V \rangle$  for all  $i$ ). Its validity is restricted to the case of good consistency ( $(V_i - \langle V \rangle)^2 < \sigma_i^2$ ). For 'inconsistent' data ( $(V_i - \langle V \rangle)^2 > \sigma_i^2$ ) the factor  $n$  in the denominator has to be replaced by the value  $(n - 1)$ , and in the limit  $(V_i - \langle V \rangle)^2 \ll \sigma_i^2$  the revised formula reduces to the regular expression for the standard errors of the average  $\langle V \rangle$  obtained from  $n$  independent single measurements of  $V_i$ . For the data in Tables 7 and 8 the consistency is good, and the use of (8) is therefore justified.

*Second pressure derivatives of effective second-order elastic constants.* For calculating the second pressure derivatives, the isothermal first

pressure derivative of the isothermal single-crystal bulk modulus is required. This derivative is found by using the general relation [Thurston, 1967]

$$(\partial K_0^S / \partial P)_T = (K_0^S)^2 (S_{ppij}^S \beta_{ijkl}^S S_{klmm}^S) \quad (9)$$

to determine the isothermal derivative of the adiabatic bulk modulus  $(K_0^S)' = 9.63$  and then converting this value to the purely isothermal derivative  $(K_0^T)' = 9.42$  by using Barsch's [1967] equation 5. The quantities  $\beta_{ijkl}^S$  appearing in (9) are the thermodynamic pressure derivatives of the single-crystal adiabatic elastic constants. The equations necessary to convert the measured effective derivatives to thermodynamic quantities have been given by Thurston [1965]. By using the equations of Barsch and Frisillo [1973], the second pressure derivatives of the effective elastic constants have been computed (Table 8). It should be noted that the quantities  $c_{44}''$ ,  $c_{55}''$ , and  $c_{66}''$  are negative but that the second derivatives  $c_{12}''$ ,  $c_{13}''$ , and  $c_{23}''$  of the cross-coupling moduli are positive. These positive values result from a change in sign when the negative values of  $(\rho_0 W^2)''$  are subtracted in determining  $(\rho V^2)''$ , used in com-

TABLE 8. Isothermal Second Pressure Derivatives of the Adiabatic Effective Elastic Constants at 25°C

$c_{\mu\nu}$	Specimen	$\vec{N}$	$\vec{U}$	$[\partial^2(\rho_0 W^2) / \partial P^2]_0$ , Mb <sup>-1</sup>	$[\partial^2 c_{\mu\nu}^S / \partial P^2]_0$ , Mb <sup>-1</sup>	Weighted Average, Mb <sup>-1</sup>
$c_{44}$	1	[010]	[001]	-30.0 ± 1.8	-31.5	-28.1 ± 2.5
	4	[010]	[001]	-33.6 ± 2.3	-35.1	
	1	[001]	[010]	-24.3 ± 1.6	-23.4	
	1*	[001]	[010]	-26.3 ± 2.4	-25.2	
$c_{55}$	1	[100]	[001]	-61.5 ± 1.6	-62.3	-59.5 ± 2.2
	3	[100]	[001]	-54.1 ± 2.2	-55.0	
	1	[001]	[100]	-59.1 ± 3.0	-57.8	
$c_{66}$	1	[100]	[010]	-17.0 ± 1.4	-18.1	-17.3 ± 1.2
	3*	[100]	[010]	-13.4 ± 2.4	-14.7	
	1	[010]	[100]	-17.2 ± 3.8	-18.6	
	4	[010]	[100]	-15.9 ± 1.9	-17.2	
$c_{12}$	2	[ $\bar{2}m0$ ]	[ $m\bar{2}0$ ]	-23.4 ± 2.2	49.3	(50.7)†
	2*	[ $\bar{2}m0$ ]	[ $m\bar{2}0$ ]	-25.1 ± 1.6	51.4	
$c_{13}$	4*	[ $20n$ ]	[ $n0\bar{2}$ ]	-42.4 ± 4.7	64.4	(66.3)†
	4*	[ $20n$ ]	[ $n0\bar{2}$ ]	-44.2 ± 5.5	68.8	
$c_{23}$	3	[ $0nm$ ]	[ $0\bar{n}m$ ]	-30.8 ± 3.0	64.4	(62.0)†
	3*	[ $0nm$ ]	[ $0\bar{n}m$ ]	-30.0 ± 5.1	68.8	

\*Test made with Arenberg PSP AFC ultrasonic equipment. All other data taken with MRL PSP AFC equipment.

†Calculated by assuming  $c_{11}''$ ,  $c_{22}''$ , and  $c_{33}''$  to be zero.