



FIG. 2. Pressure dependences of the elastic constants.

constants are shown in Fig. 2. From Figs. 1 and 2 we see that the elastic properties of  $\text{UO}_2$  appear to exhibit normal pressure dependences with no evidence for any anomalous softening of any elastic constant or for any pressure-induced phase transitions. Within experimental uncertainty the elastic constants vary linearly with pressure, at least up to the 20-kbar limit of the present experiment. The pressure derivatives of the various elastic parameters are listed in Table I with their experimental uncertainties.

The pressure-dependent elastic constants (determined as described above from the modes propagating along [110]) were used to predict the expected pressure derivatives of the  $[f(b)/f_0]^2$  data for the modes propagating along [111]. For the longitudinal mode the agreement between prediction and the actual measurement is within 3%, which is well within the experimental un-

certainties listed in Table I. For the shear mode there is a discrepancy of about 10%, but, again, the data for this mode are not considered as reliable as for the other modes.

#### IV. DISCUSSION

##### A. Elastic constants at ambient conditions and prediction of polycrystalline properties

The values of the elastic constants obtained under ambient conditions obtained in this work are shown in Table I along with the values obtained by Wachtman *et al.*<sup>1</sup> The agreement between these two sets of values is disappointingly poor, especially for  $C_{44}$ , where there is a 7% discrepancy which is well outside the range of the experimental uncertainties. The reason for the disagreement is not known, but there are several possibilities. In the first place, it has been found difficult to obtain consistent and reproducible values for other measured physical properties of  $\text{UO}_2$  such as thermal expansion,<sup>6</sup> and this is apparently due to actual sample-to-sample variations. Thus, even though our crystal was from the same source as those used by Wachtman *et al.*,<sup>1</sup> the measured differences may be real. Wachtman *et al.* obtained a large range of values for the  $C_{ij}$  from their measurements on different samples and with different sound propagation directions. This may be partially due to sample differences. Another possible problem may be related to the fact that Wachtman *et al.* made their transit-time measurements on rectified pulses. Techniques using unrectified pulses (such as pulse superposition or pulse-echo overlap, for example) are generally regarded as significantly more reliable, as systematic errors which may occur when using rectified pulses are quite easily eliminated. A third source of error may be associated with the problem mentioned above of measuring the shear-mode velocity for [111] propagation. Noncolinearity of the acoustic energy flux and the propagation direction can, in some instances, cause distortion of the echoes leading to velocity errors. As Wachtman *et al.* did not measure velocities along high-symmetry directions, this effect could possibly have been a problem.

The single-crystal elastic constants can be used to estimate the bulk elastic properties of polycrystalline  $\text{UO}_2$  by using the method of Hill<sup>7</sup> (Voigt-Reuss-Hill averaging scheme). Anderson<sup>8</sup> has found this method to give reliable values for the polycrystalline properties

TABLE II. Adiabatic elastic moduli of polycrystalline  $\text{UO}_2$ .  $K$ ,  $G$ , and  $E$  in units of kbar.

Modulus $M$	VRH averages			Measured values		$\frac{dM}{dp}$
	This work	Wachtman <i>et al.</i> <sup>a</sup>	Marlowe <sup>b</sup>	Forlano <i>et al.</i> <sup>c</sup>	Igato and Domoto <sup>d</sup>	
$K$	2090	2130	2032	...	...	4.69
$G$	830	870	821	...	...	1.42
$E$	2210	2310	2172	2234	2196	3.90
$\sigma$	0.324	0.319	0.323	...	...	0.08 <sup>e</sup>

<sup>a</sup>Reference 1.

<sup>b</sup>Reference 9.

<sup>c</sup>Reference 10.

<sup>d</sup>Reference 11.

<sup>e</sup>Units of  $10^{-12}$  cm<sup>2</sup>/dyn.

of many materials. Predicted values for the bulk modulus  $K$ , shear modulus  $G$ , Young's modulus  $E$ , and Poisson's ratio  $\sigma$  are shown in Table II for the values of the  $C_{ij}$  obtained by us (first column) and by Wachtman *et al.* (second column). The last three columns show measured values (all extrapolated to zero porosity) as obtained by Marlowe,<sup>9</sup> Forlano *et al.*,<sup>10</sup> and Igata and Domoto.<sup>11</sup> The agreement between the measured values and the values predicted from the  $C_{ij}$  of Wachtman *et al.* is significantly worse. The pressure derivatives of  $K$ ,  $G$ ,  $E$ , and  $\sigma$  (predicted from the pressure dependences of the  $C_{ij}$ ) are shown in the last column of Table II.

Anderson<sup>8</sup> has calculated values of "average" longitudinal and shear sound velocities for many oxides and it is interesting to compare the  $\text{UO}_2$  results with the properties of the other oxides. We find average velocities (longitudinal and shear, respectively) of

$$\bar{v}_l = [(K + \frac{4}{3}G)/\rho]^{1/2} = 5.4 \times 10^5 \text{ cm/sec},$$

and

$$\bar{v}_s = (G/\rho)^{1/2} = 2.8 \times 10^5 \text{ cm/sec}.$$

The pressure derivatives of these velocities are  $d\ln\bar{v}_l/dp = 1.0 \times 10^{-3} \text{ kbar}^{-1}$  and  $d\ln\bar{v}_s/dp = 0.85 \times 10^{-3} \text{ kbar}^{-1}$ . Anderson<sup>8</sup> shows in his Fig. 2 the general trend for materials with a given kind of anion (oxides, fluorides, chlorides, bromides, iodides, and carbides) to have a decreasing value of  $\bar{v}_l/\rho$  as a function of the mean atomic weight  $\bar{M}$  (where  $\bar{M} = M/n$  with  $M$  equal to molecular weight and  $n$  equal to number of atoms in the molecule). For the oxides considered by Anderson,  $\bar{v}_l/\rho$  decreases anomalously rapidly compared to the other substances on the graph and in fact extrapolates to zero at  $\bar{M} \approx 55$ . For  $\text{UO}_2$  we have  $\bar{M} = 90$ , and the value of  $\bar{v}_l/\rho \approx 0.5$  is generally in line with the values for other materials with large values of  $\bar{M}$ , e.g., the iodides. Thus the general trends for the oxides with  $\bar{M} \leq 41$  do not necessarily extrapolate to large values of  $\bar{M}$ . Anderson *et al.*<sup>12</sup> have shown that the elastic properties of many oxides can be parameterized as a function of  $\bar{M}$  and  $\rho$ , but have cautioned that this approach may be too simplistic in general. The present results for  $\text{UO}_2$  appear to justify this caution. For example, the  $\text{UO}_2$  values of  $K$  and  $\rho$  do not fall anywhere near the values for other oxides on a double log plot of  $K$  versus  $\rho$ . (See, for example, Fig. 7 of Ref. 12.)

### B. Separation of "pure" temperature and volume effects

The temperature dependences of the elastic constants  $C_{ij}$  between 4.2 and 300 °K have been measured by Brandt and Walker<sup>13</sup> in their study of the 31 °K anti-ferromagnetic phase transition. From their data we have determined the temperature derivatives of the  $C_{ij}$  at room temperature (296 °K). These derivatives, which are listed in Table I, can be considered as being composed of two separate contributions, namely the "pure volume" contribution (due to the thermal expansion of the sample) and a "pure temperature" contribution (due to anharmonic lattice effects at constant volume). The relation expressing this composition is<sup>14</sup>

$$\left(\frac{\partial \ln C_{ij}}{\partial T}\right)_p = -\frac{3\alpha}{\kappa_V} \left(\frac{\partial \ln C_{ij}}{\partial p}\right)_T + \left(\frac{\partial \ln C_{ij}}{\partial T}\right)_V, \quad (4)$$

TABLE III. Separation of "pure" temperature and volume contributions to the isobaric temperature derivatives of the elastic constants. Units are  $10^{-1}/^\circ\text{K}$ .

$C_{ij}$	$\left(\frac{\partial \ln C_{ij}}{\partial T}\right)_p$	=	$-\frac{3\alpha}{\kappa_V} \left(\frac{\partial \ln C_{ij}}{\partial p}\right)_T$	+	$\left(\frac{\partial \ln C_{ij}}{\partial T}\right)_V$
$C_{11}$	-1.32	=	-0.65	-	0.67
$C_{12}$	-1.88	=	-1.72	-	0.16
$C_{44}$	+1.70	=	-1.27	+	2.97

where the first term on the right-hand side is the "pure volume" contribution with  $\alpha$  the linear thermal expansion, and the second term is the "pure temperature" effect. For  $\alpha$  we use the value  $\alpha = 7.5 \times 10^{-6}/^\circ\text{K}$  which we obtained as a typical experimental value from data shown by Winslow.<sup>6</sup> The separation described by Eq. (4) is shown for the  $C_{ij}$  in Table III. For  $C_{11}$  and  $C_{12}$  both the "pure volume" and "pure temperature" effects are negative, with the volume effect dominating for  $C_{12}$ . For  $C_{44}$  the pure temperature effect is positive and dominates the isobaric temperature effect causing  $C_{44}$  to increase with increasing temperature. This anomalous temperature effect is due to the low-temperature phase transition, which has been discussed previously in the literature.<sup>15</sup> The softening of  $C_{44}$  as the 31 °K transition is approached is due to the coupling of the  $xz$  strain to the low-lying electronic states of the  $\text{UO}_2$  ions (cooperative Jahn-Teller effect). It is the large temperature effect of this coupling which is responsible for the large and positive "pure temperature" effect for  $C_{44}$  shown in Table III.

### C. Adiabatic-isothermal corrections

All of the elastic properties discussed so far have been adiabatic properties. For some applications it is desirable to have isothermal values of the various elastic moduli. The transformation between adiabatic and isothermal compliances ( $S_{ij}^S$  and  $S_{ij}^T$ , respectively) is given by the following equations:

$$S_{11}^T = S_{11}^S + \frac{\alpha^2 T}{\rho C_p},$$

$$S_{12}^T = S_{12}^S + \frac{\alpha^2 T}{\rho C_p}, \quad (5)$$

$$S_{44}^T = S_{44}^S,$$

where  $C_p$  is the specific heat at constant pressure, for which we take the value<sup>16</sup> 15.3 cal/°K mol. Note that the following hold:

$$S_{11}^S - S_{12}^S = S_{11}^T - S_{12}^T,$$

$$C_{11}^S - C_{12}^S = C_{11}^T - C_{12}^T, \quad (6)$$

$$C_{44}^S = C_{44}^T.$$

We will discuss the adiabatic-isothermal correction only for the moduli  $K$ ,  $G$ ,  $E$ , and  $\sigma$ . For the bulk modulus we obtain from Eqs. (5) the result

$$\frac{1}{K^T} = \frac{1}{K^S} + \frac{9\alpha^2 T}{\rho C_p}, \quad (7)$$