

## Hydrostatic Pressure Derivatives of the Single-Crystal Elastic Moduli of Zirconium

E. S. FISHER

Argonne National Laboratory, Argonne, Illinois 60439

AND

M. H. MANGHANI\* AND T. J. SOKOLOWSKI†

University of Hawaii, Honolulu, Hawaii 96825

(Received 14 January 1970)

The adiabatic elastic moduli of single-crystal Zr vary linearly with hydrostatic pressures up to 4.7 kbar. The pressure derivatives are  $dC_{11}/dP=3.93$ ,  $dC_{33}/dP=5.49$ ,  $dC_{44}/dP=-0.22$ ,  $dC_{66}/dP=0.26$ ,  $dC_{12}/dP=3.42$ , and  $dC_{13}/dP=4.25$ . The average high-temperature Gruneisen mode  $\bar{\gamma}_H$  calculated from this data is in wide disagreement with that calculated from the volume thermal expansion coefficient. It is proposed that this disagreement arises because the negative  $dC_{44}/dP$  is caused by the change with pressure in the  $c/a$  ratio, rather than the volume change.

### INTRODUCTION

The metallic crystals formed by the Group IVA elements of the periodic table Ti, Zr, and Hf are of great interest in the study of phase transformations in the solid state. At atmospheric pressures the low-temperature crystal structures, simple hcp with  $c/a$  ratio  $<1.6$ , transform to the simple bcc ( $\beta$ ) structures at temperatures  $T_c$  of 1135°, 1155°, and near 2000°K, respectively. This transformation occurs in several other metals at temperatures near the melting points. The hcp $\rightarrow$ bcc ( $\alpha\rightarrow\beta$ ) transformations in Ti and Zr are somewhat unique in that they occur at nearly one-half the respective melting temperature and involve a small but clear increase in density, i.e.,  $dT_c/dP < 0$ .<sup>1</sup>

The measurements of the temperature dependence of the shear moduli  $C_{44}$  and  $C_{66}$  in single crystals of Ti and Zr show some unusual features which suggest that the ( $\alpha\rightarrow\beta$ ) transformation may be either closely associated with or the result of phonon interactions that occur during heating of the hcp crystals.<sup>2</sup> The  $C_{66}$  moduli have very large negative temperature coefficients,  $d \ln C_{66}/dT$ , and  $C_{66}$  becomes very small, but not zero, at the respective transformation temperatures. The  $C_{66}$  shear is precisely the kind of homogeneous shear that is required for the crystal structure change.<sup>3</sup> The other important feature, related to the present work, is that  $d^2C_{66}/dT^2$  in both metals and  $d^2C_{44}/dT^2$  in Zr become positive at  $T > 400^\circ\text{K}$ . Expressing  $dC_{66}/dT$  as functions of temperature and thermal expansion,

$$dC_{66}/dT = (\partial C_{66}/\partial T)_V - (\alpha_V/\beta_V) (\partial C_{66}/\partial P)_T, \quad (1)$$

where  $\alpha_V$  and  $\beta_V$  are volume thermal expansion coefficient and isothermal compressibility, respectively, and  $P$  is hydrostatic pressure, we note that a positive  $d^2C_{66}/dT^2$  could arise from the volume expansion if  $(\partial C_{66}/\partial T)_V$  remains a nearly constant negative term, while  $(\partial C_{66}/\partial P)_T$  decreases with increasing temperature. Since  $\alpha_V$  is known to increase to exceptionally large values during heating of Zr and Ti,<sup>4,5</sup> the second term of Eq. (1) could indeed be a deciding factor if  $dC_{66}/dP$  is negative. In the present work the measure-

ments of the pressure derivatives of all five stiffness moduli for Zr at 298°K are reported.

The possible importance of the pressure derivatives of the stiffness moduli to the phase transformation comes about if it is assumed that the vibrational entropy difference of the atoms within the  $\alpha$  and  $\beta$  phases supplies the driving force for the structural change.<sup>6</sup> Equating the entropy to the vibrational amplitude and, thus, to the inverse of the vibrational frequency  $\omega$  we conclude that the  $\alpha\rightarrow\beta$  transformation must involve a decreasing average vibrational frequency. It is known, however, that the  $\beta$  phase has the smaller volume, so we are left with the implication that the Gruneisen coefficients ( $\gamma_i = -d \ln \omega_i / d \ln V$ ) for some modes of vibration are negative in the  $\alpha$  phase at the transformation temperature. The  $\gamma_i$  for the low-frequency modes can be closely approximated from hydrostatic pressure derivatives of the stiffness moduli,<sup>7</sup> and Gerlich<sup>8</sup> has shown that the average  $\bar{\gamma}_i$  for all modes in several hcp crystals agree remarkably well with  $\gamma$  obtained from high-temperature thermal-expansion data. Thus, measurements of the pressure derivatives may be quite useful in understanding the temperature derivatives of the elastic moduli, as well as precursory phenomena leading to the first-order phase transformations in Zr and Ti.

In addition to the thermally induced structural change, it has also been found that hcp Ti and Zr will transform under pressures of 55–60 kbar to a structure that is similar to the omega phase found in certain Ti and Zr alloys.<sup>9</sup> It may be possible to observe precursory phenomenon leading to this phase change from measurements of the elastic moduli in the 0–4 kbar pressure range.

### SPECIMENS

Two  $\alpha$ -Zr single crystals were prepared for velocity measurements in the specific crystallographic directions for determining the elastic moduli. Specimen No. 1 was used for wave propagation in directions parallel and perpendicular to the hexagonal ( $c$ ) axis. Specimen No. 2 was used for wave propagation in a



TABLE I. Basic frequency data used to compute wave-propagation velocities and related elastic parameters of single-crystal zirconium at 1 bar and 25°C.

Crystal specimen	Length (cm)	Direction of propagation	Direction of vibration	Mode	Mode no.	Pulse repetition frequency (cycles/sec)	Velocity (km/sec)	Velocity notation	Elastic coefficient determined
1	0.48142	[100]	[100]	longit.	1	488 115	4.6998	$v_1$	$C_{11} = \rho v_1^2$
	0.48132	[001]	[001]	longit.	2	523 456	5.0390	$v_2$	$C_{33} = \rho v_2^2$
	0.48132	[001]	any	shear	3	230 893	2.2227	$v_3$	$C_{44} = \rho v_3^2$
	0.48142	[100]	[010]	shear	4	242 000	2.3301	$v_4$	$C_{66} = \frac{1}{2}(C_{11} - C_{12}) = \rho v_4^2$
2	0.30546	45° to [001] and [100]	~45° to [001] and [100]	longit.	5	766 387	4.6820	$v_5$	$C_{RS}^a$

$$^a C_{RS} = \rho v_5^2 = \frac{1}{4} [C_{11} + C_{33} + 2C_{44} + (C_{11} - C_{33})^2 + 4(C_{12} + C_{44})^2]^{1/2}$$

direction 45° to the  $c$  axis. The modes of wave-propagation velocity measurements made on the two specimens at the ambient conditions and at high pressures are listed in Table I.

#### EXPERIMENTAL METHODS

The ultrasonic pulse superposition method<sup>10</sup> was used to measure the wave-propagation velocities at pressures of 1 bar–4.7 kbar at 25°C. In this method an rf pulse is applied to a transducer, attached to one of the two parallel faces of the specimen, at a time interval  $t$  ( $t = 1/f_r$ ) which is equal to the one round-trip delay time in the specimen. 30 MHz  $X$ -cut and  $Y$ -cut quartz transducers, 0.25 in. in diameter, were used to generate compressional and shear waves, respectively, in the specimen. Dow Corning resin 276-V9 was used for bonding the transducers to the specimen.

The pressure apparatus consisted of a pressure vessel, a two-stage compressing system, a manganin coil, a Carey-Foster pressure measuring bridge, and a Harwood dead-weight tester. The latter was used for calibrating the Carey-Foster bridge. The accuracy of pressure measurements is believed to be within  $\pm 0.2\%$  of the values. A minimum time interval of 15 min was allowed between change of pressure and the measurement. The temperature of the test specimen in the pressure vessel was maintained at  $25^\circ \pm 0.1^\circ\text{C}$  during all the measurements by circulating water in a constant temperature bath around the vessel.

#### DATA REDUCTION

The velocities were computed from the relationship,  $v = 2lf_r$ , where  $l$  is length of the specimen and  $f_r$  is the pulse repetition frequency (prf); the correction for phase angle in the bond was ignored. The basic measurements of prf and the calculated velocities and the elastic coefficients are listed in Table I. Table II shows a comparison of the values of the elastic constants deter-

mined in this study and those reported previously.<sup>11</sup> A good agreement (within  $\pm 1\%$ ) is found.

The prf measurements were made at intervals of 0.276 kbar in increasing and decreasing pressure cycles. Figure 1 shows the plots of frequency ratio ( $f_r/f_{r0}$ ) versus pressure for the modes of propagation explained in Table I; the zero subscript is for a 1 bar value. The least-squares fit equations for these plots are

$$v_1, \quad (f_1/f_{01}) = 1.0000 + 1.2088P, \quad r = 0.9995,$$

$$v_2, \quad (f_2/f_{02}) = 1.0000 + 1.4477P, \quad r = 0.9997,$$

$$v_3, \quad (f_3/f_{03}) = 1.0000 - 0.5542P, \quad r = 0.9989,$$

$$v_4, \quad (f_4/f_{04}) = 1.0000 + 0.2038P, \quad r = 0.9946,$$

$$v_5, \quad (f_5/f_{05}) = 1.0000 + 1.3200P, \quad r = 0.9998,$$

where  $P$  is pressure in megabars and  $r$  is the coefficient of correlation.

The elastic constants at pressure were calculated after correcting for changes in length and density of the specimen under pressure by adopting an approximation to Cook's method.<sup>12,13</sup> The general relationship is

$$(C_{ij}) = (C_{ij})_0 (f_r/f_{r0})^2 (l/l_0)^2 (\rho/\rho_0), \quad (2)$$

TABLE II. Comparison of the values of elastic constants obtained in this investigation and those previously determined. Values are given in kilobars.

Elastic constant	Value (this study)	Value (Fisher and Renken) <sup>11</sup>
$C_{11}$	1436.8	1434
$C_{33}$	1651.7	1648
$C_{44}$	321.4	320
$C_{66}$	353.2	353
$C_{12}$	730.4	728
$C_{13}$	658.8	653



where  $C_{ij}$ ,  $f_r$ ,  $l$ , and  $\rho$  are, respectively elastic stiffness constant, pulse repetition frequency, length, and density; zero subscripts are, again, for 1 bar values. The parameters were computed at pressure intervals of 0.267 kbar; the volume compressibility,  $\beta_v$ , and the linear compressibilities,  $\beta_{||}$  and  $\beta_{\perp}$ , were assumed invariant within these pressure intervals.

## RESULTS

### Single-Crystal Data

Figure 2 shows the plots of  $C_{ij}$  versus pressure. The relationships are linear within the experimental error. The values of the pressure derivatives  $dC_{ij}/dP$  shown in parentheses were calculated from the least-squares analysis of the data. It should be noted that  $dC_{44}/dP$

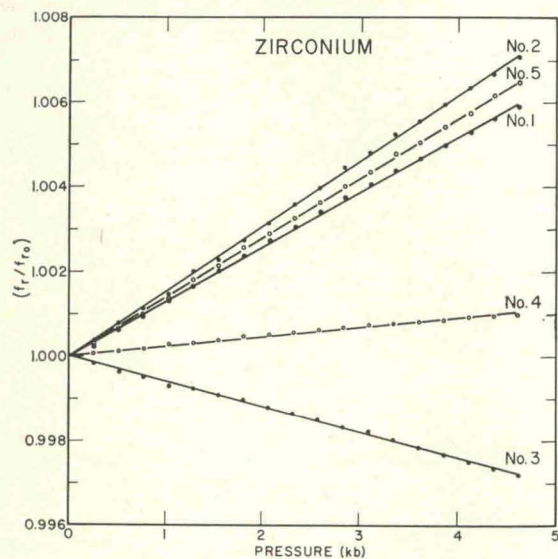


FIG. 1. Frequency ratio versus pressure for the five modes of wave propagation (see Table I for explanation of the modes).

is negative ( $-0.22$ ) and that  $dC_{66}/dP$  is remarkably small ( $0.26$ ) compared to the pressure derivatives of  $C_{66}$  in other hcp metals.

The adiabatic values for  $\beta_{||}$ ,  $\beta_{\perp}$ , and  $\beta_v$  at various pressures were derived from the  $C_{ij}$  values. The isothermal values were obtained from the adiabatic-isothermal relationship.  $\beta_T = \beta_s(1 + \alpha\gamma T)$ , where  $\alpha$ ,  $\gamma$ , and  $T$ , respectively, are the volumetric coefficient of thermal expansion, average Gruneisen parameter, and temperature. The values of  $\alpha = 1.733 \times 10^{-5}/\text{deg}$  and  $\gamma = 1.01$  were used in these computations.<sup>4</sup>

The isothermal compressibility values versus pressure are shown in Fig. 3. The initial pressure derivatives of the isothermal compressibilities are:

$$d\beta_{||}/dP = -1.9/(\text{Mbar})^2,$$

$$d\beta_{\perp}/dP = -1.3/(\text{Mbar})^2,$$

and

$$d\beta_v/dP = -4.4/(\text{Mbar})^2.$$

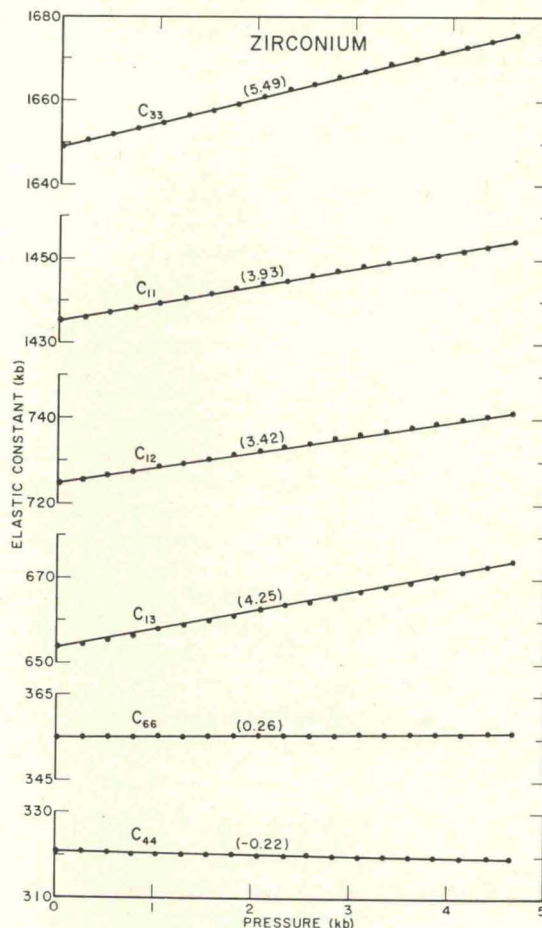


FIG. 2.  $C_{ij}$  versus pressure. The  $dC_{ij}/dP$  values are shown in parentheses.

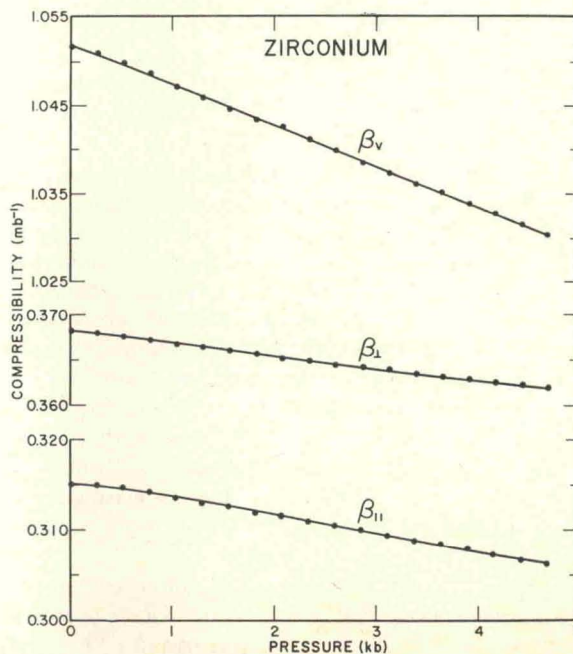


FIG. 3. Isothermal compressibilities versus pressure.



TABLE III. Isotropic elastic parameters of zirconium and their pressure derivatives.

Elastic parameter, $X$	Value	$(dX/dP)$
Adiabatic bulk modulus, $K_s$	953.1 kbar	4.08
Shear modulus, $\mu_H$	361.3 kbar	0.02
Compressional-wave velocity, $v_p$	4.697 km/sec	$4.23 \times 10^{-3}$ km/sec/kbar
Shear-wave velocity, $v_s$	2.357 km/sec	$-1.27 \times 10^{-4}$ km/sec/kbar
Poisson's ratio, $\sigma_s$	0.3317	$6.2 \times 10^{-4}$ /kbar
Density, $\rho$	6.505 g/cm <sup>3</sup>	$6.8 \times 10^{-3}$ g/cm <sup>3</sup> /kbar

### Pressure Dependence of Isotropic Elastic Parameters

The isotropic elastic moduli for zirconium were computed from the Voight-Reuss-Hill<sup>14</sup> approximation. The values of the various isotropic elastic parameters at ambient conditions and their initial pressure derivatives are given in Table III. The pressure dependence of the bulk modulus  $K$ , shear modulus  $\mu$ , Poisson's ratio  $\sigma$ , and density  $\rho$  are shown in Fig. 4. The change with pressure of the shear modulus is irregular. The value of  $d\mu/dP$  is small but, in general, positive (0.06) to about 3 kbar and it becomes negative at higher pressures. It should be noted that this unusual phenomenon may be related to the pressure-induced phase change at  $\sim 60$  kbar.<sup>9</sup>

## DISCUSSION

### Calculation of Intrinsic Temperature Coefficients of the $C_{ij}$

The pressure coefficients of the  $C_{ij}$  are related to the temperature derivatives through the following variation of Eq. (1)

$$C_{ij}^{-1}(dC_{ij}/dT) = C_{ij}^{-1}(\partial C_{ij}/\partial T)_V - (\alpha_V/\beta_V C_{ij})(\partial C_{ij}/\partial P)_T, \quad (3)$$

where the first term on the right side of the equation represents the intrinsic temperature dependence of the elastic modulus, and the second term is the temperature dependence caused by volume change (thermal expansion). For a quasiharmonic solid the lattice frequencies are not an intrinsic function of temperature and  $dC_{ij}/dT$  is dependent only on volume. In real solids the vibrational energy will vary with applied stress and the change with temperature of this effect contributes to the intrinsic term, along with possible intrinsic effects of electron excitation. In those fcc metals where  $(\partial C_{ij}/\partial P)_T$  has been measured the volume change effect generally accounts for at least  $\frac{1}{3}$  of the total temperature coefficient.<sup>15</sup>

The two unusual features in the observed temperature dependence of the elastic moduli of Zr are mentioned in the introduction to this paper. The total

temperature coefficients for Zr, at 298°K, the calculated volume dependent terms, and the intrinsic terms that remain are listed in Table IV. It is clear that  $dC_{66}/dT$  and  $dC_{44}/dT$  at 298°K are derived almost completely from the intrinsic contribution and only about  $\frac{1}{7}$  of  $dC_{11}/dT$  is due to the volume change during thermal expansion. In contrast, about 86% of  $dK_s/dT$  is derived from the volume change.

The very evident changes<sup>2</sup> in the total temperature derivatives of the elastic moduli at temperatures above 400°K could, however, be a consequence of the in-

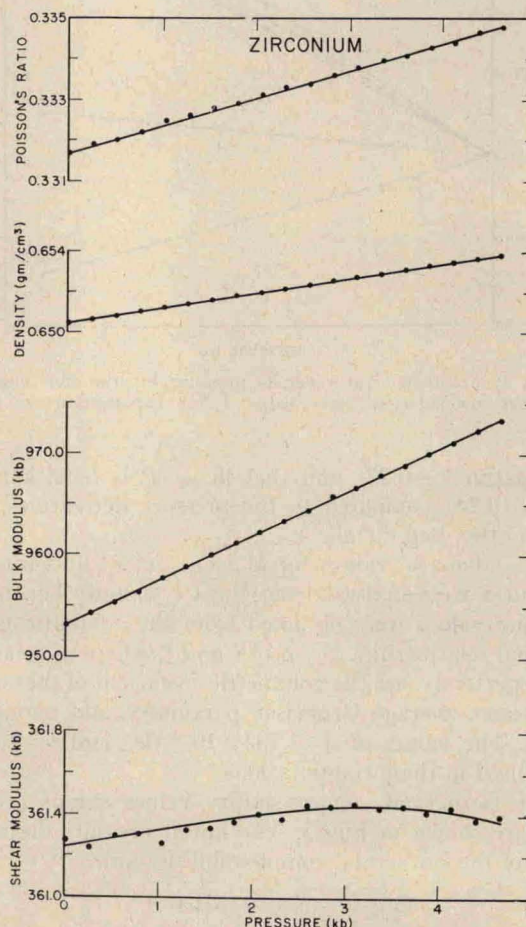


FIG. 4. Isotropic bulk and shear moduli, Poisson's ratio and density versus pressure.



TABLE IV. Intrinsic temperature dependence of elastic moduli for Zr at 298°K (units of 10<sup>-4</sup>/°K).

Modulus	$C_{ij}^{-1}(dC_{ij}/dT)$	$-(\alpha_V/\beta_V C_{ij})(\partial C_{ij}/\partial P)_T$	$(C_{ij})^{-1}(dC_{ij}/dT)_V$
$C_{44}$	-5.02	+0.114	-5.13
$C_{66}$	-10.00	-0.125	-9.88
$C_{11}$	-3.49	-0.45	-3.03
$C_{33}$	-1.94	-0.54	-1.40
$K_s = \beta_V^{-1}$	-0.76	-0.66	-0.10

creasing thermal-expansion coefficient and increasingly negative pressure coefficients for the shear moduli. This would require rather large effects of temperature on the pressure coefficients. It is also conceivable that it is not the volume change but the change in  $c/a$  ratio with thermal expansion that contributes most to the temperature derivatives of the shear moduli. This cannot be evaluated from hydrostatic pressure data alone but would require measurements of the dependence of  $C_{44}$  and  $C_{66}$  on uniaxial elastic stresses. The analysis of the Gruneisen parameters in the following discussion indicates that the change in  $c/a$  ratio is indeed an important factor.

#### Computation of the Gruneisen Mode $\gamma$ 's

The procedure for computing the volume dependence of the individual mode frequencies for hexagonal symmetry has been derived by Gerlich.<sup>8</sup> The basic definition of the mode gamma is

$$\gamma_{jk}^p(q) = -[\partial \ln \omega_p(q)] / \partial n_{jk}, \quad (4)$$

where  $q$  is the direction of wave mode propagation,  $p$  is the polarization index,  $n_{jk}$  denotes the Lagrangian strain component, and  $\omega_p(q)$  is the frequency of the lattice vibration corresponding to the mode  $p, q$ . For strains derived from hydrostatic pressure the strain indices are confined to  $j=k=1, 2$  or  $3$ , corresponding

TABLE V. Comparison of  $\bar{\gamma}$ , calculated from pressure dependence of elastic constant data, with  $\bar{\gamma}(\alpha_V)$ , obtained from thermal-expansion measurements.

	$\bar{\gamma}_L$	$\gamma_L(\alpha_V)$	$\bar{\gamma}_H$	$\gamma_H(\alpha_V)$
Mg	1.45 <sup>a</sup>	1.40 <sup>d</sup>	1.52 <sup>a</sup>	1.50 <sup>d</sup>
Cd	2.16 <sup>b</sup>	2.10 <sup>e</sup>	2.06 <sup>b</sup>	1.86 <sup>e</sup>
Gd	0.138 <sup>c</sup>	0.2 <sup>f</sup>	0.34 <sup>c</sup>	0.4 <sup>h</sup>
Zr	0.018	0.3 <sup>g</sup>	0.37	1.01 <sup>i</sup>

<sup>a</sup> Reference 16.<sup>b</sup> Reference 17.<sup>c</sup> Reference 18.<sup>d</sup> Reference 19.<sup>e</sup> Reference 20.<sup>f</sup> K. Andres, Phys. Rev. Lett. 10, 223 (1963).<sup>g</sup> Reference 22.<sup>h</sup> Reference 21.<sup>i</sup> Reference 4.

to compressions along the principal Cartesian axes of the hexagonal cell. We can compute only an average  $\gamma^p(q)$  that is a function of the individual  $\gamma_1^p(q)$  and  $\gamma_3^p(q)$ , where subscripts 1 and 3 correspond to the strains perpendicular and parallel to the  $c$  axis, respectively,

$$\begin{aligned} \beta_V^{-1} \cdot [\partial \ln \omega_p(q) / \partial P] \\ = \gamma^p(q) \\ = (2\beta_{\perp} / \beta_V) \gamma_1^p(q) + (\beta_{\parallel} / \beta_V) \gamma_3^p(q). \quad (5) \end{aligned}$$

To compute  $\partial \omega_p(q) / \partial P$  from the  $(\partial C_p(q) / \partial P)_T$ , where  $C_p(q)$  is the elastic modulus corresponding to the wave mode  $p, q$ , it is necessary to neglect dispersion and assume  $\omega_p(q)$  is directly related to the ultrasonic wave velocity corresponding to the  $p, q$  mode. We then obtain

$$\begin{aligned} \gamma^p(q) = (\beta_{\perp} / \beta_V) (1 - n^2) + (\beta_{\parallel} / \beta_V) n^2 \\ - \frac{1}{2} \{ 1 - \beta_V^{-1} [\partial \ln C_p(q) / \partial P] \}_T, \quad (6) \end{aligned}$$

where  $n$  is the cosine of the angle between the  $q$  direction and the  $c$  axis. The average  $\gamma^p(q) = \bar{\gamma}$ , which is to be compared with the Gruneisen  $\gamma$  derived from thermal expansion data, is, at high temperatures, obtained by computing  $\gamma^p(q)$  for  $N=300$  different  $q$  directions, with  $n$  varying from 0→1, and averaging to give

$$\bar{\gamma}_H = (3N)^{-1} \sum_1^{3N} \gamma^p(q). \quad (7)$$

For low temperatures

$$\bar{\gamma}_L = \sum_1^{3N} C_p(q)^{-3/2} \gamma^p(q) / \sum_1^{3N} C_p(q)^{-3/2}, \quad (8)$$

where the  $C_p(q)$  are the 4°K values of the elastic moduli for the  $p, q$  mode. This weighting process is necessary to take into account the differences in contributions to the heat capacity at low temperatures by the individual lattice modes.

The values of  $\bar{\gamma}_H$  and  $\bar{\gamma}_L$  for Zr as computed from Gerlich's computer program<sup>8</sup> are given in Table V. Included for comparison are the  $\bar{\gamma}_H$  and  $\bar{\gamma}_L$  for Mg, Cd, and Gd, as computed from the same program. In all cases the pressure coefficients<sup>16-18</sup> were measured at temperatures above 273°K, so the  $\bar{\gamma}_L$  values represent an assumption that the pressure coefficients at 4°K are



TABLE VI. Differences in linear compressibilities and linear expansion coefficients for Mg, Cd, and Zr.

	$\beta_V^{-1}(\beta_{  }-\beta_{\perp})$	$\alpha_V^{-1}(\alpha_{  }-\alpha_{\perp})$
Mg	0.013	0.019
Cd	0.660	0.361
Zr	-0.049	0.136

the same as measured. Also included in Table V are the Gruenisen coefficients computed from volume thermal-expansion measurements:

$$\gamma(\alpha_V) = (V/C_V)\alpha_V\beta_V, \quad (9)$$

where  $C_V$  is the lattice heat capacity at constant volume and  $C_V/V$  represents the thermal pressure causing the thermal expansion. For Mg, Cd, and Gd the agreement between the computations from the elasticity data and thermal-expansion data<sup>4,19,20,21</sup> are very good, with the Mg values giving excellent agreement. For Zr the  $\tilde{\gamma}_H$  value is far below, (1/3), the  $\gamma_H(\alpha_V)$  value. The apparent disagreement between  $\tilde{\gamma}_L$  and  $\gamma_L(\alpha_V)$  for Zr may be a result of the difficulties encountered in obtaining reproducible values from polycrystalline thermal-expansion data.<sup>22</sup> The near zero value for  $\tilde{\gamma}_L$  is consistent with the lack of significant change in lattice constants between 50° and 4°K in the x-ray diffraction data.<sup>4</sup>

The very low value for  $\tilde{\gamma}_H$  in Zr is evidently created by giving equal weight to the  $\gamma^p(q)$  values computed from the negative  $dC_{44}/dP$ . Nevertheless, in view of the good agreement in the cases of Mg and Cd, and in several cubic crystal cases,<sup>7</sup> it would appear that the  $\gamma_H(\alpha_V)$  should also reflect the presence of negative  $\gamma^p(q)$  and thereby give better agreement to  $\tilde{\gamma}_H$ . One possible explanation for this dilemma is that the effect of the change in the  $c/a$  ratio on the vibrational frequency spectrum is neglected in comparing the hydrostatic pressure effects to thermal expansion. If the  $c/a$  change is assumed to have an intrinsic effect the  $\gamma^p(q)$  should be composed of two parts:

$$\gamma^p(q) = [\gamma^p(q)]_{c/a} - \left( \frac{\partial \ln \omega_p(q)}{\partial \ln(c/a)} \right)_V \frac{d \ln(c/a)}{d \ln V}, \quad (10)$$

where  $[\gamma^p(q)]_{c/a}$  and  $\partial \ln \omega_p(q)/d \ln(c/a)$  are intrinsic properties, but the  $d(c/a)/dV$  term will depend on experimental conditions. For thermal expansion,

$$\frac{d \ln(c/a)}{d \ln V} = \frac{V}{c/a} \left[ \frac{d(c/a)}{dT} \cdot \frac{dT}{dV} \right] = \frac{\alpha_{||} - \alpha_{\perp}}{\alpha_V}, \quad (11)$$

whereas for hydrostatic pressure,

$$\frac{d \ln(c/a)}{d \ln V} = \frac{V}{c/a} \left[ \frac{d(c/a)}{dP} \cdot \frac{dP}{dV} \right] = \frac{\beta_{||} - \beta_{\perp}}{\beta_V}. \quad (12)$$

The  $\gamma^p(q)$  contributing to  $\gamma(\alpha_V)$  will be the same as those evaluated from Eq. (6) only when Eqs. (11) and

(12) are numerically equal or when  $[\partial \ln \omega_p(q)/\partial \ln c/a]_V$  vanishes. Table VI lists the differences between axial thermal-expansion and compressibility coefficients, respectively, for Mg, Cd, and Zr. It can be seen that Zr is somewhat unusual in that  $\alpha_{||} > \alpha_{\perp}$  but  $\beta_{||} < \beta_{\perp}$ . Assuming  $\partial \ln \omega_p(q)/d \ln c/a$  to be negative, the effect of the  $c/a$  change will enhance the total  $\gamma^p(q)$  during thermal expansion but have the reverse effect during hydrostatic compression. This would be consistent with the differences between the observed  $\tilde{\gamma}_H$  and  $\gamma(\alpha_V)$  for Zr. For Mg there would be no significant difference, as is observed. For Cd the  $c/a$  change under hydrostatic pressures would have about twice the effect on a given mode  $\omega_p(q)$  as the  $c/a$  change during thermal expansion. Assuming the average  $(\partial \ln \omega_p(q)/d \ln c/a)_V$  to be negative,  $\tilde{\gamma}_H$  should be greater than  $\gamma_H(\alpha_V)$ , as is observed.

The same kind of analysis for the  $C_{44}$  mode of Zr suggests that the negative  $dC_{44}/dP$  could be entirely due to the  $c/a$  change under hydrostatic pressure. Separating the volume change and  $c/a$  change effects we obtain

$$\frac{dC_{44}}{dP} = -\beta_V V \left( \frac{\partial C_{44}}{\partial V} \right)_{c/a} + \frac{c}{a} (\beta_{\perp} - \beta_{||}) \left( \frac{\partial C_{44}}{\partial(c/a)} \right)_V. \quad (13)$$

If we assume that  $(\partial C_{44}/\partial V)_V$  has a negative value as is normally found in cubic metals, the anomalous negative pressure derivative could arise entirely from a relatively large and negative  $(\partial C_{44}/\partial c/a)_V$ .

Assuming the above interpretation of the  $\tilde{\gamma}_H$  to  $\tilde{\gamma}_H(\alpha_V)$  difference is correct, the phenomenon should be of fundamental interest as a means for detecting wide departures from the quasiharmonic approximation, which assumes that the change in lattice frequencies are determined only by the volume change. If  $(\partial C_{44}/\partial a_0)_V$  is positive while  $(\partial C_{44}/\partial c_0)_V$  is negative or normal in sign, the implication is that there is a strong coupling in Zr between the  $C_{44}$  and  $C_{11}$  phonon modes.

Another possible cause of the  $\tilde{\gamma}_H$  to  $\gamma_H(\alpha_V)$  disagreement is that at high frequencies the  $C_{44}$  phonons frequencies have a normal pressure dependence and that the negative  $dC_{44}/dP$  is characteristic only of the ultrasonic frequency part of the spectrum. This would also imply a strong anharmonic coupling between the  $C_{44}$  and other modes, with the coupling strength being frequency dependent. There is some evidence<sup>23</sup> from neutron inelastic scattering studies of Zr that something like this mechanism is indeed occurring for  $C_{44}$ . This data shows frequencies at the long wavelength part of the spectrum that are considerably higher than expected from the ultrasonic  $C_{44}$ . Since these wavelengths are still shorter than in the ultrasonic range they could represent the uncoupled  $C_{44}$  phonons that in turn contribute to the thermal expansion. We know, however, that this is not true at 4°K since the Debye temperature,  $\theta_D$ , computed from the ultrasonic velocities at this temperature agrees extremely well with that determined from accurate low-temperature heat-capacity data.<sup>24</sup>



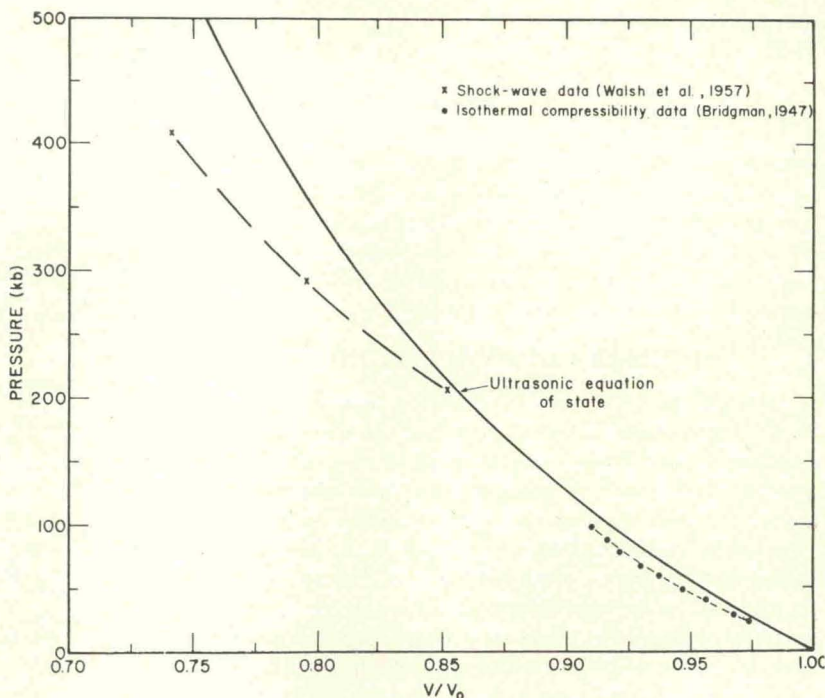


FIG. 5. Comparison of compression data for Zr as obtained from measurements of isothermal compressibility, ultrasonic-wave velocities and shock-wave velocities.

Thus, the interaction between the ultrasonic waves and other lattice waves must come into existence at higher temperatures and perhaps increases in degree as the transformation from hcp to bcc is approached. Measurements of the pressure coefficients of the elastic moduli at high temperatures are needed to look further into this question.

One can also calculate  $\bar{\gamma}_H$  and  $\bar{\gamma}_L$  values from the isotropic elastic moduli and pressure derivatives. The equations are given in Ref. 7. These relations give  $\bar{\gamma}_H$

$$\bar{\gamma}_H(ISO) = 0.59, \bar{\gamma}_L(ISO) = 0.34.$$

Here, again,  $\bar{\gamma}_H$  is considerably below  $\bar{\gamma}_H(\alpha_V)$  from polycrystalline thermal expansion because of the negative pressure coefficient for the shear modulus  $\mu_H$  calculated from the single-crystal data.

TABLE VII. Values of the parameters in Eqs. (15) and (16) used for computing  $(\partial K_T/\partial P)_T$  at 298°K.

Parameter	Value	Unit
$K_s$	953.1	kbar
$K_T$	948.44	kbar
$(\partial K_s/\partial P)_T$	4.08	
$\alpha_V$	$17.35 \times 10^{-6}$	deg <sup>-1</sup>
$(\partial \alpha_V/\partial T)$	$1.0 \times 10^{-8}$	deg <sup>-2</sup>
$C_p$	$2.82 \times 10^6$	erg/g/deg
$\gamma$	0.95	
$(1 + \alpha_V \partial T)$	1.005	
$(\partial K_s/\partial T)_P$	$-9.35 \times 10^{-2}$	kbar/deg
$(\partial K_T/\partial T)_P$	$-11.1 \times 10^{-2}$	kbar/jeg
$T$	298°K	deg
$(\partial K_T/\partial P)_T$	4.11	

#### Estimation of Compression of Zr to Higher Pressures

Anderson<sup>25</sup> has shown that the low-pressure ultrasonic data can be used to estimate compression of solid at high pressures below the phase-transition pressure by means of Murnaghan's equation of state

$$V/V_0 = [1 + (\partial K_T/\partial P)_T (P/K_T)]^{-1/(\partial K_T/\partial P)_T}, \quad (14)$$

where  $V$  and  $V_0$  are volumes at a given pressure and at zero pressure, respectively, and  $K_T$  is the isothermal bulk modulus. For zirconium,  $K_T$  was calculated from the relationship  $K_T = K_s(1 + \alpha_V T)^{-1}$  to be 950.1 kbar. To calculate  $(\partial K_T/\partial P)_T$  from  $(\partial K_s/\partial P)_T$ , Overton's<sup>26</sup> relationships were used:

$$\begin{aligned} \left(\frac{\partial K_T}{\partial P}\right)_T = & \left(\frac{\partial K_s}{\partial P}\right)_T + T\alpha_V\gamma \left(\frac{C_p}{C_p}\right) \left[\frac{-2}{\alpha_V K_T} \left(\frac{\partial K_T}{\partial T}\right)_P \right. \\ & \left. - 2 \left(\frac{\partial K_s}{\partial T}\right)_P\right] + \left[T\alpha_V\gamma \left(\frac{C_p}{C_p}\right)\right]^2 \left[\left(\frac{\partial K_s}{\partial P}\right)_T \right. \\ & \left. - \frac{1}{\alpha_V^2} \left(\frac{\partial \alpha}{\partial T}\right)_P - 1\right], \quad (15) \end{aligned}$$

and

$$\begin{aligned} \left(\frac{\partial K_T}{\partial T}\right)_P = & \left(\frac{\partial K_s}{\partial T}\right)_P (1 + T\alpha_V\gamma)^{-1} \\ & - \frac{K_s\gamma}{(1 + T\alpha_V\gamma)^2} \left[\alpha_V + T \left(\frac{\partial \alpha}{\partial T}\right)_P\right]. \quad (16) \end{aligned}$$

Table VII shows the values of various parameters in Eqs. (15) and (16) used for deriving the values of  $(\partial K_T/\partial P)_T$  which is 4.11. Thus the compression equa-



tion for zirconium is

$$V/V_0 = [1 + 0.00433P]^{-0.243} \quad (17)$$

In Fig. 5, a comparison of the ultrasonic equation of state (17) is made with the shock-wave data,<sup>27</sup> and Bridgman's isothermal compressibility data.<sup>28</sup> There is a poor agreement between Bridgman's data to 98 kbar and our results. This is partially explained by the phase transformation in Zr.<sup>9</sup> At higher pressures (760 kbar) the ultrasonic equation of state certainly cannot be used to estimate compression.

### SUMMARY OF CONCLUSIONS

Attempts to correlate volume thermal expansion in Zr with the temperature and hydrostatic pressure derivatives of the elastic moduli lead to the conclusion that the elastic shear moduli and the transverse phonon modes are more dependent on the  $c/a$  ratio in this hcp structure than on the volume changes. In Zr, where the anisotropy in linear compressibility is the inverse of the anisotropy in linear thermal expansion, the strong coupling of the shear mode frequencies to the  $c/a$  ratio leads to a wide deviation between the high-temperature Gruneisen  $\bar{\gamma}_H$  determined from the hydrostatic pressure derivatives of the elastic moduli and the Gruneisen parameter calculated from thermal-expansion data. Measurements of the elastic modulus changes under uniaxial stresses are needed to answer the questions raised in this study. Measurements of the high-temperature hydrostatic pressure derivatives should be helpful in deciding whether volume changes, rather than relative axial expansion, produced the effects on the lattice vibrations that lead to the hcp to bcc transformation. The pressure-induced phase change in Zr<sup>9</sup> at 60 kbar may be a result of the negative pressure derivative of the  $C_{44}$  shear modulus in Zr.

### ACKNOWLEDGMENTS

The authors are indebted to Mr. D. Dever for his assistance in crystal preparation and to Dr. D. Gerlich

for the "Gammacal" computer program. Parts of this work was carried out under the auspices of the United States Atomic Energy Commission and NAS-NRC Residencship at AFCRL, Bedford.

\* Hawaii Institute of Geophysics, Honolulu, Haw.

† Associated with the Environmental Sciences Services Administration, Pacific Oceanographic Laboratories, Honolulu, Haw.

<sup>1</sup> A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, *Phys. Rev.* **131**, 644 (1963).

<sup>2</sup> E. S. Fisher and C. J. Renken, *Phys. Rev.* **135**, A482 (1964).

<sup>3</sup> W. G. Burger, *Physica* **1**, 561 (1934).

<sup>4</sup> J. Goldak, L. T. Lloyd, and C. S. Barrett, *Phys. Rev.* **144**, 478 (1966).

<sup>5</sup> J. Goldak and L. T. Lloyd, measurements of thermal expansion in Ti from 4° to 1153°K (unpublished), L. T. Lloyd, Argonne National Laboratory, Argonne, Ill. (private communication).

<sup>6</sup> C. Zener, *Elasticity and Anelasticity of Metals* (The University of Chicago Press, Chicago, 1948).

<sup>7</sup> D. E. Schuelle and C. S. Smith, *J. Phys. Chem. Solids* **25**, 8d (1964).

<sup>8</sup> D. Gerlich, *J. Phys. Chem. Solids* **30**, 1638 (1969).

<sup>9</sup> J. C. Jameson, *Science* **140**, 72 (1963).

<sup>10</sup> H. J. McSkimin, *J. Acoust. Soc. Amer.* **33**, 12 (1961).

<sup>11</sup> E. S. Fisher and C. J. Renken, *J. Nucl. Mat.* **4**, 311 (1961).

<sup>12</sup> R. K. Cook, *J. Acoust. Soc. Amer.* **29**, 445 (1957).

<sup>13</sup> M. H. Manghnani, *J. Geophys. Res.* **74**, 4317 (1969).

<sup>14</sup> R. Hill, *Proc. Phys. Soc. (London)* **A65**, 349 (1952).

<sup>15</sup> D. Gerlich and E. S. Fisher, *J. Phys. Chem. Solids* **30**, 1197 (1969).

<sup>16</sup> R. E. Schmunk and C. S. Smith, *J. Phys. Chem. Solids* **9**, 100 (1959).

<sup>17</sup> J. A. Corll, ONR Tech. Rep. No. 6 (1962).

<sup>18</sup> E. S. Fisher, M. H. Manghnani, W. M. Benzing, and G. M. Goodman, *Proc. Int. Colloq. Phys. Properties Solids High Pressures*, Grenoble, 1969 (unpublished).

<sup>19</sup> J. G. Collins and G. K. White, *Progr. Low Temperature Phys.* **4**, 450 (1964).

<sup>20</sup> N. Madaiah and G. M. Graham, *Can. J. Phys.* **42**, 221 (1964).

<sup>21</sup> R. M. Bozorth and F. Wakiyama, *J. Phys. Soc. Japan* **18**, 97 (1963).

<sup>22</sup> J. A. Cowan, A. T. Pawlowicz, and G. K. White, *Cryogenics* **8**, 155 (1968).

<sup>23</sup> R. E. Schmunk (private communication).

<sup>24</sup> G. D. Kneip, J. O. Betterton, Jr., and J. A. Scarborough, *Phys. Rev.* **130**, 1687 (1963).

<sup>25</sup> O. L. Anderson, *J. Phys. Chem. Solids* **27**, 547 (1966).

<sup>26</sup> W. C. Overton, Jr., *J. Chem. Phys.* **37**, 116 (1962).

<sup>27</sup> J. M. Walsh, M. H. Rice, R. G. McQueen, and F. L. Yarger, *Phys. Rev.* **108**, 196 (1957).

<sup>28</sup> P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.* **76**, 55 (1948).