

## EFFECTS OF CHANGES IN VOLUME AND $c/a$ RATIO ON THE PRESSURE DERIVATIVES OF THE ELASTIC MODULI OF H.C.P. Ti AND Zr\*

E. S. FISHER

Argonne National Laboratory, Argonne, Ill. 60439, U.S.A.

and

M. H. MANGHNANI

University of Hawaii, Hawaii Institute of Geophysics,† Honolulu, Hawaii 96822, U.S.A.

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**Abstract**—The hydrostatic pressure derivatives of the single crystal elastic moduli of Ti have been measured to 5.5 Kbar. The pressure derivatives are  $dC_{11}/dP = 5.01$ ,  $dC_{33}/dP = 4.88$ ,  $dC_{44}/dP = 0.52$ ,  $dC_{66}/dP = 0.45$ ,  $dC_{12} = 4.11$ , and  $dC_{13}/dP = 4.05$ . The positive value for  $dC_{44}/dP$  is in sharp contrast to  $dC_{44}/dP < 0$  for Zr. This difference is assumed to arise from the difference between  $d(c/a)/dP$  in the two h.c.p. crystals and quantitative values of  $dC_{ij}/dV$  and  $dC_{ij}/d(c/a)$  are calculated. It is then shown that the large differences between the average Grüneisen mode  $\gamma_H$  calculated from  $dC_{ij}/dP$  and that obtained from thermal expansion data for both Ti and Zr can be explained by the differences between  $d(c/a)/dV$  under hydrostatic pressure and during thermal expansion, respectively. The relatively large negative value for  $dC_{44}/d(c/a)$  is quantitatively consistent with Cousins' calculations of the dependence of the electrostatic contribution to  $C_{44}$  on the  $c/a$  ratio in any h.c.p. metal lattice.

### 1. INTRODUCTION

IN A RECENT paper [1] we presented measurements of the hydrostatic pressure coefficients of the single crystal elastic moduli of h.c.p. Zr. It was then shown that the shear modulus  $C_{44}$  decreases with increasing hydrostatic pressure and that this negative pressure coefficient causes a severe difference between the high temperature Grüneisen  $\gamma$ ,  $\bar{\gamma}_H$ , calculated from an averaging of the mode  $\gamma$ 's, and the Grüneisen  $\gamma$  calculated from the measurements of volume thermal expansion,  $\gamma_H(\alpha_V)$ . This wide difference was deemed significant in view of the fact that the same method of computing and averaging the mode  $\gamma$ 's from the hydrostatic pressure derivatives of the elastic moduli of Mg, Cd, and Gd produced exceptionally good agreement with the volume thermal expansion data [2]. It was

proposed that the failure to agree in the case of Zr is due to a significant dependence of the elastic moduli on the  $c/a$  ratio and the fact that  $d(c/a)/dV$  derived from hydrostatic pressure at constant temperature differs in algebraic sign from  $d(c/a)/dV$  during thermal expansion at constant pressure:

$$\left(\frac{\partial \ln(c/a)}{\partial \ln V}\right)_T \neq \left(\frac{\partial \ln(c/a)}{\partial \ln V}\right)_P \quad (1)$$

or

$$\frac{\beta_{\parallel} - \beta}{\beta_V} \neq \frac{\alpha_{\parallel} - \alpha_{\perp}}{\alpha_V} \quad (2)$$

where  $\beta$  and  $\alpha$  are compressibility and thermal expansion coefficients, respectively, and the subscripts refer to the axial coefficients parallel ( $\beta_{\parallel}$ ,  $\alpha_{\parallel}$ ) and perpendicular ( $\beta_{\perp}$ ,  $\alpha_{\perp}$ ) to the hexagonal axis and to the volume coefficients ( $\beta_V$  and  $\alpha_V$ ). The important conclusion from this work is that the transverse phonon frequencies and the elastic moduli are strongly dependent on the  $c/a$  ratio in h.c.p. Zr.

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The most direct method of verifying the proposed effect of the change in  $c/a$  ratio on the elastic moduli would be via uniaxial pressure effects. In the case of Zr, however, there appeared to be a unique opportunity to check the  $c/a$  effect by measuring the pressure derivatives of the elastic moduli of h.c.p. Ti. Zr and Ti are remarkably similar in electronic and thermal properties. Both are Group IV transition metals with 2 electrons in an unfilled d electron shell. The thermally induced h.c.p.  $\rightarrow$  b.c.c. structural transformations occur in both metals at nearly the same temperatures (i.e., 1135°K for Zr and 1156°K for Ti). The second order elastic properties contain some very marked similarities[3]: (1) the value of the  $C_{66}$  shear moduli and the  $\beta_{\parallel}$  values for Ti and Zr are the same to within 5 per cent at any given temperature and (2) the temperature derivatives of the  $C_{11}$ ,  $C_{33}$ , and  $C_{66}$  stiffness moduli and the bulk moduli,  $K$ , are very nearly the same for Ti and Zr at all temperatures. The two important differences between the elastic properties are as follows: (1) the anisotropy in linear compressibilities as defined in equation (2) is negative for Zr, ( $\beta_{\perp} > \beta_{\parallel}$ ), but positive for Ti, and (2) the  $C_{44}$  shear modulus for Ti is about 40 per cent greater than in Zr, in contrast to almost identical  $C_{66}$  values mentioned above and the  $\sim 10$  per cent and  $\sim 15$  per cent differences in  $C_{33}$  and  $C_{11}$ , respectively. If we ascribe the negative  $dC_{44}/dP$  in Zr to the increase in  $c/a$  ratio with increasing hydrostatic pressure, because of  $\beta_{\perp} > \beta_{\parallel}$ , then, on the basis of the otherwise strong similarities between the metals, we should find that  $dC_{44}/dP$  for Ti is positive. The measurement of  $dC_{44}/dP$  for Ti is then a qualitative test of the conclusions reached in the Zr work. By making certain reasonable assumptions regarding other similarities in the two metals we can arrive at a quantitative test of the conclusion that the average mode  $\gamma$ ,  $\bar{\gamma}_H$ , computed from the pressure dependence of the elastic moduli in an anisotropic crystal will agree with the Grüneisen  $\gamma$  deduced from thermal expansion

if

$$(\partial \ln(c/a)/\partial V)_T = (\partial \ln(c/a)/\partial V)_P.$$

## 2. EXPERIMENTAL PROCEDURES

The Ti single crystals were obtained by zone melting a rod of crystal bar iodide Ti. The experimental procedure for measuring the changes in ultrasonic wave velocities in Ti as a function of pressure was the same as that for Zr[1]. Nitrogen gas was the pressure medium. The changes in the compressional moduli  $C_{11}$  and  $C_{33}$  with pressure at  $25^\circ \pm 0.1^\circ\text{C}$  were determined from the changes in critical pulse repetition rate frequency[4],  $f_r$ , for longitudinal waves propagated perpendicular and parallel, respectively, to the  $c$  axis of a Ti single crystal. The change in the shear modulus  $C_{66} = \frac{1}{2}(C_{11} - C_{12})$  was determined from the change in  $f_r$  of a transverse wave propagated and polarized perpendicular to  $c$  axis, whereas the change in the  $C_{44}$  shear modulus was determined from the transverse wave mode propagated parallel to the  $c$  axis. The change in  $C_{13}$  with pressure was derived from the change in  $f_r$  for the longitudinal wave propagated  $45^\circ \pm \frac{1}{4}^\circ$  to the  $c$  axis. The basic data,  $f_r/f_{r0}$ , where  $f_{r0}$  corresponds to  $f_r$  at 1 bar, are plotted in Fig. 1. Mode numbers 1 through 5 correspond respectively to the  $C_{11}$ ,  $C_{33}$ ,  $C_{44}$ ,  $C_{66}$  and the  $45^\circ$  quasi-longitudinal modes. Except for mode # 3,  $C_{44}$ , the  $f_r/f_{r0}$  vs. pressure lines are straight, within experimental error, to 5.516 Kb. For the  $C_{44}$  mode the data suggests that a relatively abrupt change in slope occurs at approximately 2.5 Kb.

The changes with pressure of the thickness of the crystal parallel to the ultrasonic wave path and the volume change, that are necessary for computing the modulus change, were computed from the isothermal linear compressibilities calculated at 1 bar and at intervals of 0.0276 Kb from the stiffness moduli[1]. For the adiabatic to isothermal compressibility calculation the following volume thermal expansion coefficient,  $\alpha_V$ , and the Grüneisen constant,  $\gamma_H(\alpha_V)$ , were used:  $\alpha_V = 2.4 \times 10^{-5}/^\circ\text{K}$  and  $\gamma_H(\alpha_V) = 1.10$  (Ref. [5]).

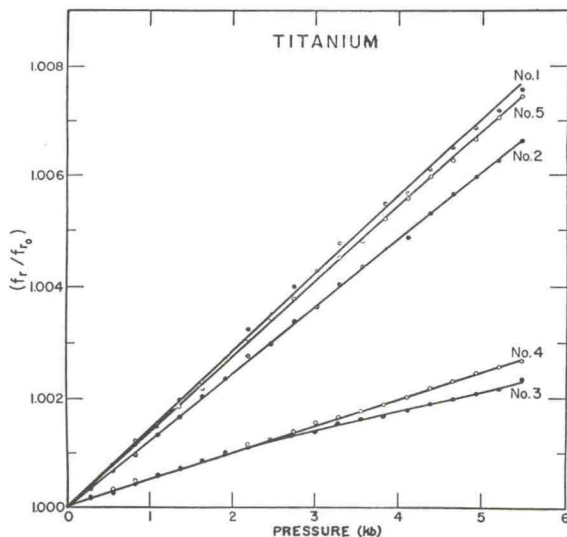


Fig. 1. Frequency ratio vs. pressure for the following 5 modes of wave propagation in Ti crystals: (1) and (2) are longitudinal modes perpendicular and parallel, respectively, to  $c$  axis, (3) shear mode propagated parallel to  $c$  axis, (4) shear mode with propagation and polarization vectors in basal plane and (5) longitudinal mode propagated  $45^\circ$  to  $c$  axis.

### 3. RESULTS

#### (a) Single crystal data

The values of the stiffness moduli as evaluated at intervals of 0.276 Kb (4,000 psi) are plotted against pressure in Fig. 2. The values of the pressure derivatives as derived from the best straight line through the plotted points are shown in parentheses. It should be noted that the small change in slope indicated in the  $f_r/f_{r_0}$  data for  $C_{44}$  (Fig. 1) is not distinguishable in Fig. 2 because of the difference in scales along the ordinates. It is clear, however, that  $dC_{44}/dP > 0$  at any given pressure up to 5.516 Kbar, whereas for Zr,  $dC_{44}/dP$  is constant and less than zero between 1 bar and 4.7 Kb pressures [1].

The variations with pressure of the adiabatic and isothermal compressibilities are shown in Fig. 3. Within the error of the calculations,  $d\beta_{||}/dP \approx d\beta_{\perp}/dP$  and the isothermal values give  $d\beta_{||}/dP = -1.3 (\text{mb})^{-2}$  and  $d\beta_{\perp}/dP = -3.8 (\text{mb})^{-2}$ . Since the pressure derivatives for  $\beta_{||}$  and  $\beta_{\perp}$  are constant over the 5.5 Kb

pressure range, the variation of the  $c/a$  ratio with pressure,

$$\frac{d(c/a)}{dP} = \frac{c}{a} (\beta_{\perp} - \beta_{||}) \quad (3)$$

is negative for Ti and decreases in magnitude with increasing pressure.

#### (b) Pressure dependence of isotropic elastic parameters

The variations with pressure of several bulk properties, as calculated from the present data through the Voigt-Reuss-Hill approximation [6], are plotted in Fig. 4. The pressure derivatives for several parameters are given in Table 1. In contrast to Zr, the isotropic Poisson's ratio of Ti has a very small pressure derivative. The isotropic shear modulus varies linearly with pressure.

The variation of density with pressure,

$$d\rho/dP = \rho\beta_v, \quad (4)$$



Table 1. Isotropic elastic parameters of titanium and their pressure derivatives

Elastic parameter, $X$	Value at	
	1 Bar, 25°C	( $dX/dP$ )
Adiabatic bulk modulus, $K_s$	1072.7 Kb	4.31
Isothermal bulk modulus, $K_t$	1063.4 Kb	4.35
Shear modulus, $\mu_H$	433.6 Kb	0.47
Compressional-wave velocity, $V_p$	6.05 km/sec	$6.1 \times 10^{-3}$ km/sec/kb
Shear-wave velocity, $V_s$	3.10 km/sec	$2.6 \times 10^{-3}$ km/sec/kb
Poisson's ratio, $\sigma_s$	0.322	$2.5 \times 10^{-3}$ kb $^{-1}$
Density, $\rho$	4.5063 gm/cm $^3$	$4.1 \times 10^{-3}$ gm/cm $^3$ /kb

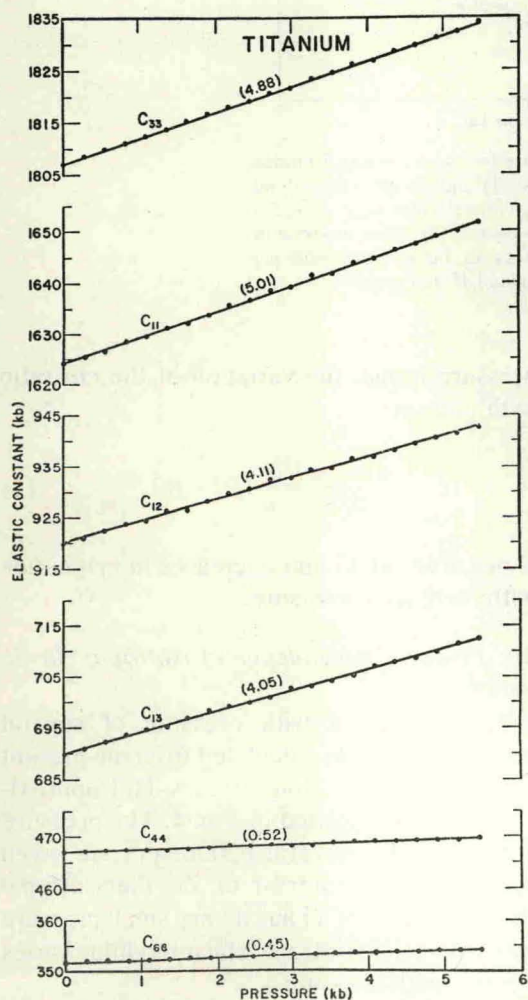


Fig. 2. Elastic stiffness moduli vs. pressure for Ti. Numbers indicate values of pressure derivatives assuming linear relation.

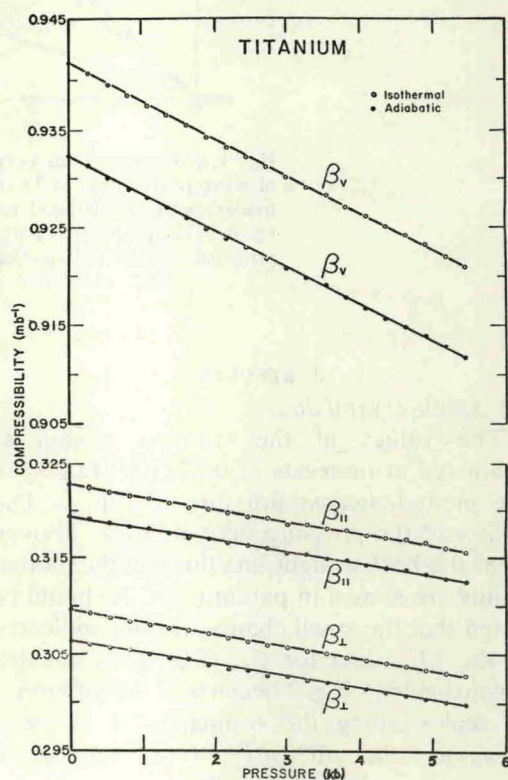


Fig. 3. Linear and volume compressibilities vs. pressure for Ti.

over the initial 5.5 Kb applied pressure is considerably smaller for Ti as compared to the value for Zr. The value of  $dK_s/dP$ , where  $K_s$  is the adiabatic bulk modulus, is about 8 per cent higher for Ti than for Zr, i.e., 4.39 vs. 4.08.

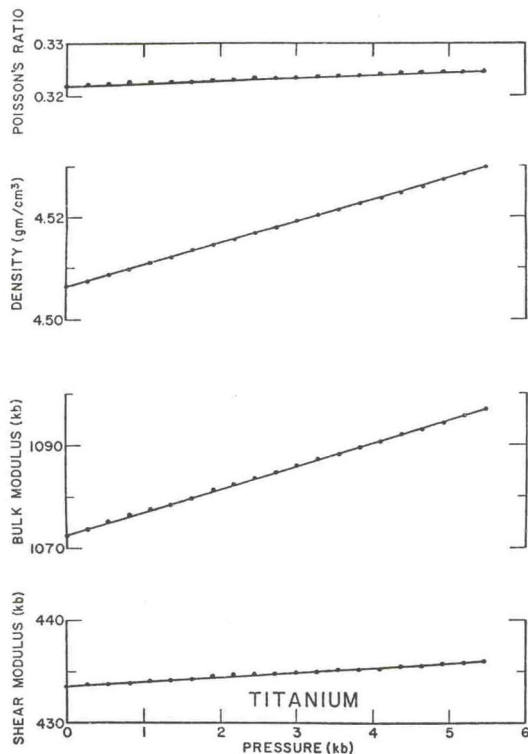


Fig. 4. Shear modulus, Poisson's ratio and bulk modulus vs. pressure as computed from Voigt-Ruess-Hill approximation for polycrystalline Ti with random grain orientation. The density vs. pressure data are obtained from the isothermal volume compressibility data given in Fig. 3.

Anderson[7] has successfully extrapolated the low pressure ultrasonic data to estimate compression of various solids to high pressure. The basic assumptions, given by Murnaghan [8], are that the  $(\partial K_T/\partial P)_{P \rightarrow 0}$ , where  $K_T$  is the isothermal bulk modulus, is a constant quantity in this range of extrapolation. The Murnaghan equation of state can be written[4] as

$$V/V_0 = \left[ 1 + \left( \frac{\partial K_T}{\partial P} \right)_T \left( \frac{P}{K_T} \right) \right]^{-1/(\partial K_T/\partial P)_T} \quad (5)$$

where  $V$  and  $V_0$  are volumes at pressure  $P$  and at zero pressure, respectively. The value of  $(\partial K_T/\partial P)$ , obtained by using Overton's relationships [9], is calculated to be 4.35. Thus the compression equation becomes

$$V/V_0 = [1 + 0.0040923P]^{-0.22978}. \quad (6)$$

In Fig. 5, a comparison between the experimentally determined  $V/V_0$  values and the ultrasonic equation of state is shown. There is a fairly good agreement between the isothermal compressibility data of Bridgman[10] and the ultrasonic equation. There is a poor agreement between the latter and the shock-wave data[11], probably because of the phase change that has been reported for Ti near 90 Kbar[12].

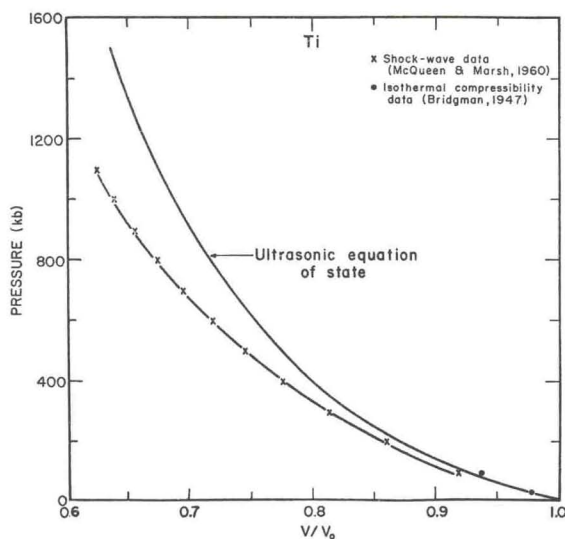


Fig. 5. Comparison of compression data for Ti as obtained from isothermal compressibility measurements of Bridgman[10], from ultrasonic equation of state derived from isothermal  $dK/dP$ , where  $K$  is the bulk modulus, and from shock wave data given in Ref. [11].

#### 4. DISCUSSION OF RESULTS

In Table 2 the pressure derivatives of the stiffness moduli for Ti are compared with those of other h.c.p. metals[13-15]. The purpose of this comparison is to show that there is a general decrease with the  $c/a$  ratio of the pressure derivatives of the  $C_{ij}$ , where  $i = j$ , and that the pressure derivatives of the  $C_{44}$  and  $C_{66}$  shear moduli are very significantly reduced at  $c/a < 1.62$ . The following discussion is based on the presumption that the



Table 2. Pressure derivatives at 25°C of the adiabatic stiffness moduli for Ti compared to those for Zr, Gd, Mg, and Cd

	Ti	Zr*	Gd†	Mg‡	Cd§
<i>c/a</i> ratio	1.587	1.593	1.590	1.62	1.88
$dC_{11}/dP$	5.01	3.93	3.12	6.11	9.29
$dC_{33}/dP$	4.88	5.49	6.02	7.22	7.26
$dC_{44}/dP$	0.52	-0.22	0.07	1.58	2.38
$dC_{66}/dP$	0.45	0.26	0.36	1.36	2.59
$dC_{12}/dP$	4.11	3.42	2.39	3.39	4.10
$dC_{13}/dP$	4.05	4.25	3.55	2.55	5.66
$dK_s/dP$	4.31	4.08	3.22	4.05	7.02

\*Ref. [1]

†Ref. [13]

‡Ref. [14]

§Ref. [15].

effect of changing the *c/a* ratio during application of hydrostatic pressure assumes a more significant role in changing the  $C_{ij}$  and the phonon frequencies when the initial *c/a* < 1.62. We first present a simple formal approach to show that the wide difference in  $dC_{44}/dP$  between Ti and Zr, and other differences between the elastic properties of the two metals, can be explained by the difference between the respective  $\beta_{\perp}$  values. We then show that the differences between the average mode Grüneisen  $\gamma^p(q)$ ,  $\bar{\gamma}_H$ , as calculated from the  $dC_{ij}/dP$  ( $i =$  or  $\neq j$ ) for Ti and Zr and as calculated from the volume thermal expansion can probably be explained by the differences in  $d(c/a)dV$  between the two experimental conditions.

(a) Separation of  $\Delta V$  and  $\Delta(c/a)$  effects on the  $C_{ij}$

The following equations are developed to show the parameters that relate the volume change and the *c/a* change, separately, to the total measured  $dC_{ij}/dP$ :

$$dC_{ij}/dP = (\partial C_{ij}/\partial P)_{c/a} + (\partial C_{ij}/\partial(c/a))_V \frac{d(c/a)}{dP} \quad (7)$$

$$= -\beta_V V (\partial C_{ij}/\partial V)_{c/a} - (\partial C_{ij}/\partial(c/a))_V \left( \frac{\partial(c/a)}{\partial V} \right)_T \frac{dV}{dP} \quad (8)$$

$$= -\beta_V C_{ij} (\partial \ln C_{ij}/\partial \ln V)_{c/a} + (c/a) (\beta_{\perp} - \beta_{\parallel}) (\partial C_{ij}/\partial(c/a))_V. \quad (9)$$

For cubic metal crystals[16] the measured  $dC_{ij}/dV$  values in all cases are negative ( $dC_{ij}/dP > 0$ ), as expected for normal solids with positive values of the Grüneisen  $\gamma$ , so we can reasonably expect  $(\partial C_{ij}/\partial V)_{c/a}$  to be negative. Thus the occurrence of a negative value for  $dC_{ij}/dP$  will depend on the difference  $(\beta_{\perp} - \beta_{\parallel})$  and the value of  $(\partial C_{ij}/\partial(c/a))_V$ . Since  $(\beta_{\perp} - \beta_{\parallel})$  is positive for Zr and negative for Ti, the wide difference in  $dC_{44}/dP$  for the two metals can be simply related to a relatively large and negative value for  $(\partial C_{44}/\partial(c/a))_V$ . If we go further and assume that the values for the two partial derivatives for each  $C_{ij}$  are the same for Ti as in Zr, an assumption which is perhaps reasonable in view of the many other similar properties, we arrive at the quantitative values given in Table 3. The first two columns list the values for the two unknowns that are obtained by simultaneously solving equation (9) with the known coefficients and measured  $dC_{ij}/dP$  for Ti and Zr. The components of  $dC_{ij}/dP$  due to  $\Delta V$  and to  $\Delta(c/a)$  for each metal are listed in columns 3 and 4, respectively. For Ti the change in modulus due to the *c/a* change is less than 4 per cent of the total pressure derivative for  $C_{11}$ ,  $C_{33}$ ,  $C_{12}$ , and  $C_{13}$ , whereas, the contributions to  $dC_{44}/dP$  and  $dC_{66}/dP$  are about 24 and 11 per cent, respectively. For Zr the  $\Delta(c/a)$  contributions are considerably larger, because of the relatively large anisotropy in  $\beta_{\perp}$  and  $\beta_{\parallel}$ , and the negative contribution to  $dC_{44}/dP$  overwhelms the positive effect of the volume decrease.

(b)  $\Delta V$  and  $\Delta(c/a)$  effects on the normal mode frequencies of lattice vibrations

In the quasi-harmonic approximation the



Table 3. Evaluation of the  $\Delta V$  and  $\Delta(c/a)$  contributions to the  $dC_{ij}/dP$ , from simultaneous solutions of equation (9)

	$-(\partial \ln C_{ij}/\partial \ln V)_{c/a}$	$(\partial C_{ij}/\partial c/a)_V$ 10 <sup>12</sup> dynes/cm <sup>2</sup>	$(\partial C_{ij}/\partial P)_{c/a}$		$(\partial C_{ij}/\partial P)_V$	
			Ti	Zr	Ti	Zr
$C_{11}$	3.18	-10.59	4.81	4.79	0.201	-0.86
$C_{33}$	2.81	5.034	4.98	5.08	-0.096	0.409
$C_{44}$	0.912	-6.506	0.397	0.306	0.124	-0.528
$C_{66}$	1.233	-2.432	0.404	0.457	0.046	-0.197
$C_{12}$	4.741	-2.486	4.07	3.60	0.047	-0.202
$C_{13}$	6.284	-0.753	4.04	4.31	0.014	-0.061

frequencies of the normal modes of crystal lattice vibrations are assumed to be dependent only on the volume of the crystal via the mode Grüneisen gamma,

$$\gamma^p(q) = -\frac{d \ln \omega_p(q)}{d \ln V} \quad (10)$$

where  $q$  is the direction in which the wave mode propagates in the crystal,  $p$  is the polarization direction and  $\omega_p(q)$  is the wave mode frequency. Since the  $\gamma^p(q)$  vary for different modes, the Grüneisen  $\gamma$  that is derived from the thermal expansion coefficient at a given temperature,

$$\gamma(\alpha_V) = \frac{\alpha_V V}{C_V \beta_V}, \quad (11)$$

(where  $C_V$  is the specific heat at constant volume) is an average of the individual mode  $\gamma^p(q)$  weighted according to its degree of excitation at the particular temperature. It has been shown[17, 2] that reasonably good agreement with equation (11) can be obtained by calculating  $\gamma^p(q)$  from the hydrostatic pressure derivatives of the stiffness moduli, which we shall denote in this discussion as  $C_p(q)$ . For hexagonal symmetry this approach gives[2]

$$\gamma^p(q) = \frac{\beta_{\perp}}{\beta_V} (1-n^2) + \frac{\beta_{\parallel}}{\beta_V} n^2 - \frac{1}{2} \times \left( 1 - \frac{1}{\beta_V} \left( \frac{\partial \ln C_p(q)}{\partial P} \right)_T \right) \quad (12)$$

where  $n$  is the cosine of the angle between the  $q$  direction and the  $c$  axis. Through the use of Gerlich's computer program[2] we have evaluated the  $\gamma^p(q)$  in Ti and Zr for each of the three normal modes at 300 different directions in the crystal and obtained weighted average  $\bar{\gamma}_L$  from the 4°K  $C_p(q)$  and 298°K values of  $dC_p(q)/dP$  and  $\bar{\gamma}_H$  from the simple average of the  $\gamma^p(q)$  over the 300 directions. Gerlich[2] has shown that for Mg and Cd the  $\bar{\gamma}_L$  and  $\bar{\gamma}_H$  values are in good agreement with the thermal expansion[18]  $\gamma_L(\alpha_V)$  and  $\gamma_H(\alpha_V)$ , as shown in Table 4. We have previously reported that this is not the case for Zr[1], where  $\bar{\gamma}_H$  is about  $\frac{3}{8}$  of  $\gamma_H(\alpha_V)$  (Table 4)[19, 20]. For Ti this deviation is not as severe as for Zr but it is still quite large, as shown in Table 4 where  $\bar{\gamma}_H$  is about 70 per cent of  $\gamma_H(\alpha_V)$  when the measured  $dC_p(q)/dP$  are used to evaluate the  $\gamma^p(q)$ . It should be noted here that the measured, adiabatic, stiffness moduli and pressure derivatives are converted to isothermal values before calculating  $\gamma^p(q)$ . At the present time the  $\gamma_L(\alpha_V)$  for Ti and Zr are

Table 4. Comparison of  $\bar{\gamma}$  calculated from measured  $dC_{ij}/dP$  with  $\gamma(\alpha_V)$  obtained from thermal expansion data

	$\bar{\gamma}_L$	$\gamma_L(\alpha_V)$	$\bar{\gamma}_H$	$\gamma_H(\alpha_V)$	Refs. to $\gamma(\alpha_V)$
Mg	1.45	1.40	1.52	1.50	18
Cd	2.16	2.3	2.06	2.3	18
Zr	0.018	0.2 ± 0.4	0.37	1.01	19, 20
Ti	0.50	1.0 ± 0.5	0.77	1.10	19, 5

are each known only from measurements [19] on two polycrystalline samples where the values differ considerably, as noted in the uncertainty given in Table 4. We are therefore in no position to even estimate the validity of the calculated  $\bar{\gamma}_L$  for these two metals.

To explain the large difference between  $\bar{\gamma}_H$  and  $\gamma_H(\alpha_V)$  for Zr it was proposed that the dependence of the frequencies,  $\omega_p(q)$ , on the change in  $c/a$  ratio must be separated from the effect of volume change so as to consider the differences in  $d(c/a)/dV$  under hydrostatic pressure and thermal expansion:

$$\gamma^p(q) = (\gamma^p(q))_{c/a} - \left( \frac{\partial \ln \omega_p(q)}{\partial \ln (c/a)} \right)_V \frac{d \ln (c/a)}{d \ln V}, \quad (13)$$

for thermal expansion

$$\frac{d \ln (c/a)}{d \ln V} = \left( \frac{\partial \ln (c/a)}{\partial \ln V} \right)_P = \frac{\alpha_{\parallel} - \alpha_{\perp}}{\alpha_V} \quad (14a)$$

whereas for hydrostatic pressure

$$\frac{d \ln (c/a)}{d \ln V} = \left( \frac{\partial \ln (c/a)}{\partial \ln V} \right)_T = \frac{\beta_{\parallel} - \beta_{\perp}}{\beta_V}. \quad (14b)$$

The measured values for equations (14a and 14b) for Mg, Cd, Zr, and Ti are listed in Table 5. The anisotropy in compressibility can be evaluated from the elastic moduli [21, 22, 3] within 2 or 3 per cent and are therefore quite reproducible. The  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  values are however very sensitive to small errors in the

temperature dependence of expansivity data and can therefore vary considerably with the methods of measurement and data treatment. Table 5 lists two different values for  $(\alpha_{\parallel} - \alpha_{\perp})$  in Zr and in Ti. The  $\alpha$  values taken from Refs. [20] and [5] are instantaneous temperature derivatives of the lattice constants at 300°K, whereas the other values [23, 24] correspond to the mean slope over wider ranges of temperature. For Mg we assume that the excellent agreement between  $\bar{\gamma}_H$  and  $\gamma_H(\alpha_V)$  can be ascribed to the very small difference between equations (14a and 14b) whereas for Cd we surmise that the  $(\partial \ln \omega_p(q) / \partial \ln (c/a))_V$  terms are very small.

To estimate the relative contributions of the volume and  $c/a$  changes to the  $\omega_p(q)$  of Ti and Zr we use the data of Table 3, obtained from simultaneous solutions of equation (9). The first term on the right of equation (13),  $(\gamma^p(q))_{c/a}$ , is related to  $(\partial \ln C_{ij} / \partial \ln V)_{c/a}$  as follows:

$$(\gamma^p(q))_{c/a} = - \left( \frac{\partial \ln \omega_p(q)}{\partial \ln V} \right)_{c/a} = - \frac{\beta_q}{2\beta_V} - \frac{1}{2} \left( \frac{\partial \ln C_{ij}}{\partial \ln V} \right)_{c/a} \quad (15)$$

where  $\beta_q$  is the linear compressibility in the  $q$  direction. The second term of equation (13) is derived from,

$$\left( \frac{\partial \ln \omega_p(q)}{\partial \ln (c/a)} \right)_V = \frac{c/a}{2C_{ij}} \left( \frac{\partial C_{ij}}{\partial (c/a)} \right)_V. \quad (16)$$

The calculated values for equation (13) are given in Table 6. For Ti the  $\Delta(c/a)$  contribution has a major effect only for the  $C_{44}$  mode, whereas for Zr the  $\Delta(c/a)$  effect is very large for the  $C_{44}$  mode and has a major role in reducing the  $\gamma^p(q)$  for the  $C_{11}$  and  $C_{66}$  modes.

Having arrived at a plausible explanation for the difference between  $\bar{\gamma}_H$  for Ti and Zr we can now test the proposal that the differences between  $\bar{\gamma}_H$  and  $\gamma_H(\alpha_V)$  are caused by the

Table 5. Differences between axial linear compressibilities and thermal expansion coefficients for Mg, Cd, Zr and Ti

	$\frac{1}{\beta_V} (\beta_{\parallel} - \beta_{\perp})$	$\frac{1}{\alpha_V} (\alpha_{\parallel} - \alpha_{\perp})$	Refs.
Mg	0.013	0.019	[21, 18]
Cd	0.660	0.361	[22, 18]
Zr	-0.049	0.136	[3, 20]
		0.045	[23]
Ti	0.013	-0.144	[3, 5]
		0.059	[24]



Table 6. Values of the  $\Delta V$  and  $\Delta(c/a)$  contributions to the  $\gamma^p(q)$  for the principal normal acoustic modes in Ti and Zr

$C_p(q)$	$(\gamma^p(q))_{c/a}$		$-(\partial \ln \omega_p(q)/\partial \ln (c/a))_V \frac{\beta_{\parallel} - \beta_{\perp}}{\beta_V}$		Total $\gamma^p(q)$	
	Ti	Zr	Ti	Zr	Ti	Zr
$C_{11}$	1.42	1.43	0.067	-0.288	1.49	1.14
$C_{33}$	1.23	1.20	-0.029	0.120	1.20	1.32
$C_{44}$	0.29	0.26	+0.14	-0.79	0.43	-0.53
$C_{66}$	0.45	0.44	+0.07	-0.27	0.52	0.17

$(\partial(c/a)/\partial V)_T$  and  $(\partial(c/a)/\partial V)_P$  terms of equations (14a and 14b). This can be done by replacing the second term on the right of equation (8) with the  $(\partial(c/a)/\partial V)_P$  term,

$$\left(\frac{\partial C_{ij}}{\partial(c/a)}\right)_V \left(\frac{\partial(c/a)}{\partial V}\right)_P \frac{dV}{dP} = \left(\frac{\partial C_{ij}}{\partial(c/a)}\right)_V \times \frac{\beta_V}{\alpha_V} \cdot \frac{c}{a} (\alpha_{\parallel} - \alpha_{\perp}) \quad (17)$$

This leads to the following version of equation (9):

$$dC_p(q)/dP = -\beta_V C_p(q) \left(\frac{\partial \ln C_p(q)}{\partial \ln V}\right)_{c/a} - \frac{c}{a} (\alpha_{\parallel} - \alpha_{\perp}) \frac{\beta_V}{\alpha_V} \left(\frac{\partial C_p(q)}{\partial(c/a)}\right)_V \quad (18)$$

The pressure derivatives calculated from equation (18) using two different values of  $(\alpha_{\parallel} - \alpha_{\perp})$  for each metal are listed in Table 7. For Ti,  $\alpha_{\perp} > \alpha_{\parallel}$  according to the data given in Ref. [5], hence, the calculated pressure derivatives for  $C_{11}$ ,  $C_{44}$ , and  $C_{66}$  are considerably smaller than the measured values. The  $\bar{\gamma}_L$  and  $\bar{\gamma}_H$  values computed from incorporating these  $dC(q)/dP$  in equation (10) would obviously be smaller values than given by the measured values of Table 2. The  $(\alpha_{\parallel} - \alpha_{\perp})$  obtained from the 300° to 700°K slope of the linear lattice constant vs. temperature plots [24] of Ti is, however, positive in sign and the calculated  $dC_p(q)/dP$  incorporated into equation (12) gives a  $\bar{\gamma}_H^{(b)}$  value of 1.06, which is in excellent agreement with the

Table 7. Pressure derivatives of elastic moduli of Zr and Ti calculated from equation (18), assuming  $\Delta(c/a)$  dictated by thermal expansion data from Table 5

	Ti		Zr	
	(a)	(b)	(a)	(b)
$(\alpha_{\parallel} - \alpha_{\perp})/\alpha_V$	-0.144	0.059	0.136	0.045
$dC_{11}/dP$	2.552	5.729	7.193	5.590
$dC_{33}/dP$	6.047	4.537	3.937	4.699
$dC_{44}/dP$	-0.989	0.963	1.783	0.798
$dC_{66}/dP$	-0.114	0.616	1.009	0.641
$dC_{12}/dP$	3.540	4.285	4.160	3.784
$dC_{13}/dP$	3.880	4.102	4.482	4.368

$\gamma_H(\alpha_V)$  obtained from equation (11) (see Table 8).

For Zr the instantaneous  $(\alpha_{\parallel} - \alpha_{\perp})$  value from dilatation measurements [20] produces relatively large calculated  $dC_p(q)/dP$  and  $\bar{\gamma}_H^{(a)}$  is about 80 per cent greater than  $\gamma_H(\alpha_V)$  (see Table 8). The smaller value of  $(\alpha_{\parallel} - \alpha_{\perp})$ , again obtained from nearly linear lattice constant vs. temperature curves [23], give  $dC_p(q)/dP$

Table 8. Comparison of  $\bar{\gamma}$  computed from the values of  $dC_p(q)/dP$  (or  $dC_{ij}/dP$ ) obtained from equation (18)

	$\bar{\gamma}_L$	$\gamma_L(\alpha_V)$	$\bar{\gamma}_H$	$\bar{\gamma}_H(\alpha_V)$
Zr	1.82 <sup>(a)</sup> 0.90 <sup>(b)</sup>	0.2 ± 0.4	1.83 <sup>(a)</sup> 1.09 <sup>(b)</sup>	1.01
Ti	0.50 <sup>(b)</sup>	1.0 ± 0.5	1.06 <sup>(b)</sup>	1.10

(a) and (b) refer to subheadings of Table 7.



values that result in  $\bar{\gamma}_H^{(b)}$  for Zr within 10 per cent of  $\gamma_H(\alpha_V)$  (Table 8). There is, then, reasonably valid quantitative evidence that the measured values of  $dC_{11}/dP$ ,  $dC_{44}/dP$ , and  $dC_{66}/dP$  in Ti and Zr contain an appreciable negative contribution from the change in  $c/a$  with hydrostatic volume change and that the disagreement between  $\bar{\gamma}_H$  and  $\gamma_H(\alpha_V)$  arises from the difference between  $d(c/a)/dV$  under thermal expansion and hydrostatic pressure conditions.

(c) *Relation of  $\Delta(c/a)$  effect to specific contributions to the shear moduli*

For a polyvalent metal it is assumed that there are three important contributions to the elastic shear strain energy of the crystal,  $W_E$ ,  $W_R$ , and  $W_F$  [25].  $W_E$  is the electrostatic or Coulomb term derived from the shear displacement of the positively charged ion-core in an electron sea.  $W_R$  is derived from the ion-ion repulsion energy and  $W_F$ , the Fermi energy term, consists of two parts; the full zone term, where the energy change arises from the movement of planes of the Brillouin zone, and the overlap-hole term, where the Fermi surface is displaced and a transfer of electrons occurs between zone overlap or hole states. The problem of prime interest here is to arrive at some conclusions as to which of the contributions to  $C_{44}$  of Ti and Zr create the relatively large value for  $(dC_{44}/d(c/a))_V$ , given in Table 3. The theoretical calculations [26, 27] that have been carried out for  $C_{44}$  in h.c.p. metals (Mg, Cd, and Zr) have not treated the  $W_F$  term because of the difficulty caused by the change in crystal symmetry that accompanies the  $C_{44}$  shear. Nevertheless, these calculations do indicate that the  $W_E$  term is relatively important to  $C_{44}$  and that it is reasonable to assume that the variation of this term with  $c/a$  could account for our results.

Cousins [29] has carried out calculations of the effect of changing  $c/a$  at constant volume on the  $W_E$  and  $W_R$  contributions to the three second order shear moduli for h.c.p.

structures. From Cousin's calculations of  $W_E$ , assuming a uniform electron density distribution, it is clear that  $C_{44}$  is the volume conserving shear that is most affected by  $\Delta(c/a)$ . If we neglect the change in the first order term that enters into the calculations, it is found that  $(C_{44})_E$  decreases at a constant rate while  $c/a$  increases from 1.56 to 1.633 with slope

$$(\partial(C_{44})_E/\partial(c/a))_V = -\frac{Z^2}{a_0^4} \left( 26.4 \times 10^{12} \frac{\text{dynes}}{\text{cm}^2} \right)$$

where  $Z$  is the effective valence and  $a_0$  is the interatomic distance in the basal plane as given in Å. Assuming  $Z = 4$  for Ti or Zr we obtain

$$(\partial(C_{44})_E/\partial(c/a))_V = -5.28 \times 10^{12} \frac{\text{dynes}}{\text{cm}^2}$$

which is surprisingly near the value of  $-6.506 \times 10^{12}$  dynes/cm<sup>2</sup> that is derived for  $(\partial C_{44}/\partial(c/a))_V$  from equation (9).

For  $(\partial(C_{66})_E/\partial(c/a))_V$ , Cousin's calculations, again neglecting the first order term and using  $Z = 4$ , predict a value of  $-0.6$ , or about  $\frac{1}{4}$  of that obtained from equation (9). This suggests that the Fermi energy contribution to  $C_{66}$ ,  $(C_{66})_F$ , is the important factor in  $(\partial C_{66}/\partial(c/a))_V$ . This conclusion is consistent with the observations in Ref. [30] that  $dC_{66}/dT$  in h.c.p. transition metals is closely related to  $d\chi/dT$ , where  $\chi$  is the magnetic susceptibility. The relation of  $C_{66}$  to  $\chi$  of Ti and Zr is presumed to arise from the mechanism of electron transfer between zone overlaps during distortion of the Fermi surface, whereas this mechanism is less important or absent during  $C_{44}$  shear.

## 5. CONCLUSIONS

(1) In crystals with lower than cubic symmetry the changes in axial ratios with hydrostatic pressure can produce important contributions to the pressure derivatives of the elastic moduli. For h.c.p. Ti and Zr, with



$c/a$  ratio  $< 1.60$ , the changes in the shear moduli,  $C_{44}$  and  $C_{66}$ , with pressure are strongly influenced by the change in  $c/a$  ratio.

(2) The Grüneisen  $\gamma$  computed from an averaging of the mode  $\gamma$ 's, as derived from the hydrostatic pressure derivatives of the elastic moduli, can be widely different than the  $\gamma$  computed from thermal expansion data when the  $dC_{ij}/dP$  contain significant contributions from the changes in axial ratio and when the volume dependence of the axial ratio, or ratios, during hydrostatic compression differs from that during thermal expansion. This indicates that the high frequency thermal vibrations are also sensitive to changes in axial ratio with thermal expansion.

(3) A correlation of the quantitative effect of  $(c/a)$  on  $C_{44}$  and  $C_{66}$  for Ti and Zr with theoretical calculations for the strain energy contributions to h.c.p. crystals [28] indicates that  $dC_{44}/d(c/a)$  is derived primarily from electrostatic forces whereas  $dC_{66}/d(c/a)$  probably arises for electron transfer during Fermi surface distortion.

(4) The equations of state at very high pressures, predicted from the pressure derivatives of the bulk moduli of Ti and Zr at lower pressure, do not agree with the equations of state derived from shock-wave experiments for these two metals.

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#### REFERENCES

1. FISHER E. S., MANGHNANI M. H. and SOKOLOWSKI T. J., *J. appl. Phys.* **41**, 2991 (1970).
2. GERLICH D., *J. Phys. Chem. Solids* **30**, 1638 (1969).
3. FISHER E. S. and RENKEN C. J., *Phys. Rev.* **135**, A482 (1964).
4. McSKIMIN H. J., *J. Acoust. Soc. Am.* **33**, 12 (1961).
5. GOLDAK J. and LLOYD L. T., unpublished measurements of thermal expansion in Ti single crystals, private communication from L. T. Lloyd, Argonne National Lab. (Argonne, Ill.)
6. HILL R., *Proc. Phys. Soc. Lond.* **A65**, 349 (1952).
7. ANDERSON O. L., *J. Phys. Chem. Solids* **27**, 547 (1966).
8. MURNAGHAN F. D., "Finite Deformation of an Elastic Solid," p. 68 John Wiley, New York (1951).
9. OVERTON W. C., Jr., *J. Chem. Phys.* **37**, 116 (1962).
10. BRIDGMAN P. W., *Proc. Am. Acad. Arts Sci.* **76**, 55 (1958).
11. WALSH J. M., RICE M. H., McQUEEN R. G. and YARGER F. L., *Phys. Rev.* **108**, 196 (1957).
12. JAMESON J. C. *Science* **140**, 72 (1963).
13. FISHER E. S., MANGHNANI M. H., BENZING W. M. and GOODMAN G., *Proc. Int. Colloquium on Phys. Properties of Solids at High Pressures*, Grenoble (Sept. 8, 1969), C.N.R.S., Paris, (1970).
14. SCHMUNK R. E. and SMITH C. S., *J. Phys. Chem. Solids* **9**, 100 (1959).
15. CORLL J. A., *ONR Tech. Rep.* # 6 (1962).
16. DANIELS W. B. and SMITH C. S., *Phys. Rev.* **111**, 713 (1958).
17. SCHUELE D. E. and SMITH C. S., *J. Phys. Chem. Solids* **25**, 80 (1964).
18. McCAMMON R. D. and WHITE G. K., *Phil. Mag.* **11**, 1125 (1965).
19. COWAN J. A., PAWLOWICZ A. T. and WHITE G. K., *Cryogenics* **8**, 155 (1968).
20. GOLDAK J., LLOYD L. T. and BARRETT C. S., *Phys. Rev.* **144**, 478 (1966).
21. SLUTSKY L. J. and GARLAND C. W., *Phys. Rev.* **107**, 972 (1957).
22. CHANG Y. A. and HIMMEL L., *J. appl. Phys.* **37**, 3787 (1966).
23. RUSSELL R. B., *Trans. AIME* **200**, 1045 (1954).
24. WILLENS R. H., *Rev. Scient Instrum.* **33**, 1069 (1962).
25. LEIGH R. S., *Phil. Mag.* [7] **42**, 139 (1951).
26. REITZ J. R. and SMITH C. S., *Phys. Rev.* **104**, 1253 (1956).
27. HUNTINGTON H. B., *Phys. Rev.* **57**, 60 (1940).
28. COUSINS C. S. G., *J. Phys. C. (Proc. Phys. Soc.)* **1**, 478 (1968).
29. FISCHER O., PETER M. and STEINEMANN S., *Helv. Phys. Acta* **42**, 459 (1969).