

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]