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

	$(\gamma^p(q))_{c/a}$		$-(\partial \ln \omega_p(q)/\partial \ln (c/a))_V \frac{\beta_\parallel - \beta_\perp}{\beta_V}$		Total $\gamma^p(q)$	
$Cp(q)$	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 $\gamma_H(\alpha_V)$ obtained from equation (11) (see Table 8).

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)
$(\alpha_\parallel - \alpha)/\alpha_V$	−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

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[a]	0·2 ± 0·4	1·83[a]	1·01
	0·90[b]		1·09[b]	
Ti	0·50[b]	1·0 ± 0·5	1·06[b]	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}/d_P 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

$$(\partial(C_{44})_E/\partial(c/a))_V = -\frac{Z^2}{a_0^4}\left(26{\cdot}4\times 10^{12}\,\frac{\text{dynes}}{\text{cm}^2}\right)$$

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

$$(\partial(C_{44})_E/\partial(c/a))_V = -5{\cdot}28\times 10^{12}\,\frac{\text{dynes}}{\text{cm}^2}$$

which is surprisingly near the value of $-6{\cdot}506\times 10^{12}$ dynes/cm^2 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 $-0{\cdot}6$, 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 χ is the magnetic susceptibility. The relation of C_{66} to χ 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