

TABLE II. Evaluation of ΔV and $\Delta(c/a)$ contributions to dC_{ij}/dP , from simultaneous solutions of Eq. (6).

	$-(\partial \ln C_{ij}/\partial \ln V)_{c/a}$	$[\partial C_{ij}/\partial(c/a)]_V$ 10 ¹² dyn/cm ²	$(\partial C_{ij}/\partial P)_{c/a}$		$(\partial C_{ij}/\partial P)_V$	
			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_6	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

and to indicate that large elastic anisotropy does not necessarily cause failure of the model. At present, no good basis exists for comparing the low temperature $\bar{\gamma}_L$ and $\bar{\gamma}_L(\alpha_V)$ of Zr and Ti, because the thermal-expansion data lack reproducibility.¹¹ There are, however, a relatively large number of measurements¹²⁻¹⁵ of α_V , between room temperature and the phase-transformation temperatures, that permit confidence in the values for $\gamma_H(\alpha_V)$ given in Table III. The $\bar{\gamma}_H$ values, computed without taking into account the $\Delta(c/a)$ effect in Zr and Ti, and the $\bar{\gamma}_H(\alpha_V)$ values are clearly different, with $\bar{\gamma}_H$ for Zr about 37% of the $\bar{\gamma}_H(\alpha_V)$. The immediate conclusions are (1) the average $\gamma^p(q)$ in Zr is heavily diminished by the negative value for $\gamma^p(q)$ derived from the negative dC_{44}/dP , and (2) the large difference between $\bar{\gamma}_H$ and $\bar{\gamma}_H(\alpha_V)$ is associated with the differences between the anisotropy in linear compressibilities and linear thermal expansion.

We can test the latter conclusion by assuming Eq. (1) is valid and by substituting $(\alpha_{11}-\alpha_{\perp})/\alpha_V$ for $(\beta_{11}-\beta_{\perp})/\beta_V$ in the $d \ln(c/a)/d \ln V$ term. From the relations

$$\begin{aligned} [\gamma^p(q)]_{c/a} &= - \left(\frac{\partial \ln \omega_p(q)}{\partial \ln V} \right)_{c/a} \\ &= - \frac{\beta_q}{2\beta_V} - \frac{1}{2} \left(\frac{\partial \ln C_{ij}}{\partial \ln V} \right)_{c/a}, \end{aligned} \quad (8)$$

where β_q is the linear compressibility in the (q) direction of the crystal, and

$$\left(\frac{\partial \ln \omega_p(q)}{\partial \ln(c/a)} \right)_V = \frac{c/a}{2C_{ij}} \left(\frac{\partial C_{ij}}{\partial(c/a)} \right)_V \quad (9)$$

we can compute new values for the individual $\gamma^p(q)$ and

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

	$\bar{\gamma}_L$	$\gamma_L(\alpha_V)$	$\bar{\gamma}_H$	$\gamma_H(\alpha_V)$
Mg	1.45	1.40	1.52	1.50
Cd	2.16	2.10	2.06	1.86
Zr	0.018	0.2±0.4	0.37	1.01
Ti	0.50	1.0±0.5	0.77	1.10

thus new values for $\bar{\gamma}_H$ that should agree with $\bar{\gamma}_H(\alpha_V)$, if our conclusions are correct.

A difficulty is encountered with the above procedure because of the variations in reported values of $(\alpha_{11}-\alpha_{\perp})$ for Zr and Ti (Table I). The variations in the values for Zr and Ti are primarily caused by the procedures for evaluating α_V from least-square treatment of lattice constant and dilatation measurements. Data noted as Zr(a) and Ti(a) were both obtained from third-order polynomials fitted to a combination of x-ray diffraction measurements at $T < 300^\circ\text{K}$ and interferometer dilatometer measurements at $T > 300^\circ\text{K}$.^{12,14} The other two sets of data, Zr(b) and Ti(b), were obtained from x-ray diffraction data fitted to second-order polynomials.^{13,15} The differences $(\alpha_{11}-\alpha_{\perp})$ and the variations are quite large, thus creating large differences in the computed $\Delta(c/a)$ contributions to the shear moduli. The negative $(\alpha_{11}-\alpha_{\perp})$ value for Ti, for example, causes the $\gamma^p(q)$ from both C_{44} and C_{66} shear modes to be negative and produces a considerably larger difference between $\bar{\gamma}_H$ and $\gamma_H(\alpha_V)$. The larger $(\alpha_{11}-\alpha_{\perp})$ for Zr, on the other hand, causes the computed $\gamma^p(q)$ to be too large, and $\bar{\gamma}_H$ is almost a factor of two greater than $\bar{\gamma}_H(\alpha_V)$. In contrast the smaller values for $(\alpha_{11}-\alpha_{\perp})$, produced by assuming smoother variations of lattice constants with temperature, give results that are in reasonably good agreement with the $\bar{\gamma}_H(\alpha_V)$ for both Ti and Zr, as listed in Table IV.

The wide differences between $\bar{\gamma}_H$ and $\gamma_H(\alpha_V)$ do not appear to be due to assumptions in the model for equating dC_{ij}/dP to the Gruneisen γ , but are in fact

TABLE IV. $\bar{\gamma}_L$ and $\bar{\gamma}_H$ computed from adjusted values of dC_{ij}/dP by using Eq. (6) and by substituting $(\alpha_{11}-\alpha_{\perp})/\alpha_V$ for $(\beta_{11}-\beta_{\perp})/\beta_V$.

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

^a $(\alpha_{11}-\alpha_{\perp})$ values obtained from Ref. 14 for Zr(a), Ref. 15 for Zr(b), and Ref. 13 for Ti(b).

TABLE V. Various parameters for rutile.^a

dC_{11}/dP	6.47		
dC_{33}/dP	8.34		
dC_{44}/dP	1.10		
dC_{66}/dP	6.43		
dC'/dP	-1.31,	$C' = (C_{11} - C_{12})/2$	
	$(\beta_{ } - \beta_{\perp})/\beta_V = -0.223,$	$(\alpha_{ } - \alpha_{\perp})/\alpha_V = 0.086$	
$\bar{\gamma}_L(\alpha_V) = 2.8$	$\bar{\gamma}_L = 0.47$		
$\bar{\gamma}_H(\alpha_V) = 1.43$	$\bar{\gamma}_H = 1.42$		

^a Elastic modulus data from Ref. 16. Thermal expansion data from Ref. 17.

caused by the differences in $d(c/a)/dV$ between hydrostatic-compression and thermal-expansion conditions.

CASES WHERE $\Delta(c/a)$ EFFECT IS NOT OBSERVED

Cd

The good agreement between $\bar{\gamma}_H$ and $\gamma_H(\alpha_V)$ for Cd cannot be explained on the basis of the relatively large $[\partial C_{44}/\partial(c/a)]_V$ term that is derived from the electrostatic contribution,⁹ assuming an effective valence, $Z=2$, and a uniform compensating electron sea. From the electrostatic term, the large difference between $(\beta_{||} - \beta_{\perp})/\beta_V$ and $(\alpha_{||} - \alpha_{\perp})/\alpha_V$ for Cd should produce a large difference in the C_{44} mode $\gamma^p(q)$ and, thus, in the $\bar{\gamma}_H$ values. We are forced to conclude that the $\Delta(c/a)$ effect on the lattice frequencies are, in fact, almost negligible in Cd, which reduces the significance of the $(\beta_{||} - \beta_{\perp})$ term.

Rutile (TiO₂)

Rutile has a squashed tetragonal unit cell with a distorted octahedral arrangement of the oxygen atoms about the Ti atoms. Considerable anisotropy in both compressibility¹⁶ and thermal expansion¹⁷ is found, with $(\beta_{||} - \beta_{\perp})/\beta_V = -0.223$ and $(\alpha_{||} - \alpha_{\perp})/\alpha_V = 0.086$. The room-temperature elastic moduli and their hydrostatic-pressure derivatives are given in Table V. The modulus of greatest interest is the (110)[110] shear $C' = 1/2(C_{11} - C_{12})$, which is more than a factor of two smaller than C_{44} and has a negative pressure derivative. As in the case of Zr where c/a also increases with hydrostatic pressure, one might expect that $dC'/dP < 0$ for rutile is derived from a negative $[\partial C'/\partial(c/a)]_V$, and that $\bar{\gamma}_H$ will not agree with $\gamma_H(\alpha_V)$ because $d(c/a)/dV$ is negative for hydrostatic pressure but is positive during thermal expansion. The results of the $\bar{\gamma}_L$ and $\bar{\gamma}_H$ calcula-

tions given in Table V are somewhat unexpected; $\bar{\gamma}_H$ is in almost perfect agreement with $\gamma_{\infty}(\alpha_V)$ derived from the thermal-expansion measurements of Kirby.¹⁷ This leads to two conclusions: (1) the changes in c/a ratio have no significant effect on the acoustic frequencies, and (2) the separation of $\gamma_{\infty}(\alpha_V)$ into acoustic- and optical-mode components, with heavy emphasis on the latter as proposed by Kirby,¹⁷ is incorrect. $\gamma_{\infty}(\alpha_V)$ of rutile appears to be primarily, if not all, due to the volume dependence of the acoustic modes.

The $\bar{\gamma}_L$ calculated from the dC_{ij}/dP at 25°C is in wide disagreement with $\gamma_0(\alpha_V)$ given by Kirby's measurements.¹⁷ The small value of $\bar{\gamma}_L$ is caused by the heavier weighting of the shear mode $\gamma^p(q)$ in the computer program and does not take into account the temperature dependence of dC_{ij}/dP . In addition, the actual values of the C_{ij} at 0°K were estimated from the dC_{ij}/dT at 25°C. In view of the anomalous dC'/dP at 25°C and the fact that dC'/dT is also anomalous,¹⁶ the $\bar{\gamma}_L$ may be subject to considerable change. Nevertheless, since the difference between $\bar{\gamma}_L$ and $\gamma_0(\alpha_V)$ is so large there appears to be a good reason for measurements that can define the contributions to the low-temperature thermal expansion in rutile.

ACKNOWLEDGMENTS

This work was carried out under the auspices of the U.S. Atomic Energy Commission, U.S. Air Force, and the University of Hawaii.

* Holder of National Research Council-National Academy of Sciences Senior Resident Research Associateship, supported by U.S. Air Force. On sabbatical leave from Hawaii Institute of Geophysics, University of Hawaii, Honolulu, Hawaii 96825.

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- 1 F. W. Sheard, *Phil. Mag.* **3**, 1381 (1958).
- 2 J. G. Collins, *Phil. Mag.* **8**, 323 (1963).
- 3 D. Gerlich, *J. Phys. Chem. Solids* **30**, 1638 (1969).
- 4 E. S. Fisher and M. H. Manghnani, *J. Phys. Chem. Solids* (to be published).
- 5 E. S. Fisher, M. H. Manghnani, and T. J. Sokolowski, *J. Appl. Phys.* **41**, 2991 (1970).
- 6 E. S. Fisher and C. J. Renken, *Phys. Rev.* **135**, A482 (1964).
- 7 R. E. Schmunk and C. S. Smith, *J. Phys. Chem. Solids* **9**, 100 (1959).
- 8 J. A. Corll, ONR Tech. Rep. No. 6 (1962).
- 9 C. S. G. Cousins, *J. Phys. C. (Proc. Phil. Soc.)* **1**, 478 (1968).
- 10 R. D. McCammon and G. K. White, *Phil. Mag.* **11**, 1125 (1965).
- 11 J. A. Cowan, A. T. Pawlowicz, and G. K. White, *Cryogenics* **8**, 155 (1968).
- 12 J. Goldak and L. T. Lloyd, unpublished measurements of thermal expansion in Ti single crystals (private communication).
- 13 R. H. Willens, *Rev. Sci. Instrum.* **33**, 1069 (1962).
- 14 J. Goldak, L. T. Lloyd, and C. S. Barrett, *Phys. Rev.* **144**, 478 (1966).
- 15 R. B. Russell, *Trans. AIME* **200**, 1045 (1954).
- 16 M. H. Manghnani, *J. Geophys. Res.* **74**, 4317 (1969).
- 17 R. K. Kirby, *J. Res. Nat. Bur. Std. (U.S.) A.* **71A**, 363 (1967).