

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 $(\alpha_{||}-\alpha_{\perp})/\alpha_V$ for $(\beta_{||}-\beta_{\perp})/\beta_V$ 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 $(\alpha_{||}-\alpha_{\perp})$ 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 $(\alpha_{||}-\alpha_{\perp})$ and the variations are quite large, thus creating large differences in the computed $\Delta(c/a)$ contributions to the shear moduli. The negative $(\alpha_{||}-\alpha_{\perp})$ 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 $(\alpha_{||}-\alpha_{\perp})$ 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 $(\alpha_{||}-\alpha_{\perp})$, 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 $(\alpha_{||}-\alpha_{\perp})/\alpha_V$ for $(\beta_{||}-\beta_{\perp})/\beta_V$.

| | $\bar{\gamma}_L^a$ | $\gamma_L(\alpha_V)$ | $\bar{\gamma}_H^a$ | $\bar{\gamma}_H(\alpha_V)$ |
|----|--------------------|----------------------|--------------------|----------------------------|
| 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 $(\alpha_{||}-\alpha_{\perp})$ 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)[1 $\bar{1}$ 0] 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.

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