

TABLE IV. Intrinsic temperature dependence of elastic moduli for Zr at 298°K (units of 10<sup>-4</sup>/°K).

Modulus	$C_{ij}^{-1}(dC_{ij}/dT)$	$-(\alpha_V/\beta_V C_{ij})(\partial C_{ij}/\partial P)_T$	$(C_{ij})^{-1}(dC_{ij}/dT)_V$
$C_{44}$	-5.02	+0.114	-5.13
$C_{66}$	-10.00	-0.125	-9.88
$C_{11}$	-3.49	-0.45	-3.03
$C_{33}$	-1.94	-0.54	-1.40
$K_s = \beta_V^{-1}$	-0.76	-0.66	-0.10

creasing thermal-expansion coefficient and increasingly negative pressure coefficients for the shear moduli. This would require rather large effects of temperature on the pressure coefficients. It is also conceivable that it is not the volume change but the change in  $c/a$  ratio with thermal expansion that contributes most to the temperature derivatives of the shear moduli. This cannot be evaluated from hydrostatic pressure data alone but would require measurements of the dependence of  $C_{44}$  and  $C_{66}$  on uniaxial elastic stresses. The analysis of the Gruneisen parameters in the following discussion indicates that the change in  $c/a$  ratio is indeed an important factor.

#### Computation of the Gruneisen Mode $\gamma$ 's

The procedure for computing the volume dependence of the individual mode frequencies for hexagonal symmetry has been derived by Gerlich.<sup>8</sup> The basic definition of the mode gamma is

$$\gamma_{jk}^p(q) = -[\partial \ln \omega_p(q)] / \partial n_{jk}, \quad (4)$$

where  $q$  is the direction of wave mode propagation,  $p$  is the polarization index,  $n_{jk}$  denotes the Lagrangian strain component, and  $\omega_p(q)$  is the frequency of the lattice vibration corresponding to the mode  $p, q$ . For strains derived from hydrostatic pressure the strain indices are confined to  $j=k=1, 2$  or  $3$ , corresponding

TABLE V. Comparison of  $\bar{\gamma}$ , calculated from pressure dependence of elastic constant data, with  $\bar{\gamma}(\alpha_V)$ , obtained from thermal-expansion measurements.

	$\bar{\gamma}_L$	$\gamma_L(\alpha_V)$	$\bar{\gamma}_H$	$\gamma_H(\alpha_V)$
Mg	1.45 <sup>a</sup>	1.40 <sup>d</sup>	1.52 <sup>a</sup>	1.50 <sup>d</sup>
Cd	2.16 <sup>b</sup>	2.10 <sup>e</sup>	2.06 <sup>b</sup>	1.86 <sup>e</sup>
Gd	0.138 <sup>c</sup>	0.2 <sup>f</sup>	0.34 <sup>e</sup>	0.4 <sup>h</sup>
Zr	0.018	0.3 <sup>g</sup>	0.37	1.01 <sup>i</sup>

<sup>a</sup> Reference 16.

<sup>b</sup> Reference 17.

<sup>c</sup> Reference 18.

<sup>d</sup> Reference 19.

<sup>e</sup> Reference 20.

<sup>f</sup> K. Andres, Phys. Rev. Lett. 10, 223 (1963).

<sup>g</sup> Reference 22.

<sup>h</sup> Reference 21.

<sup>i</sup> Reference 4.

to compressions along the principal Cartesian axes of the hexagonal cell. We can compute only an average  $\gamma^p(q)$  that is a function of the individual  $\gamma_{p1}^p(q)$  and  $\gamma_{p3}^p(q)$ , where subscripts 1 and 3 correspond to the strains perpendicular and parallel to the  $c$  axis, respectively,

$$\begin{aligned} \beta_V^{-1} \cdot [\partial \ln \omega_p(q) / \partial P] \\ = \gamma^p(q) \\ = (2\beta_{\perp} / \beta_V) \gamma_{p1}^p(q) + (\beta_{\parallel} / \beta_V) \gamma_{p3}^p(q). \quad (5) \end{aligned}$$

To compute  $\partial \omega_p(q) / \partial P$  from the  $(\partial C_p(q) / \partial P)_T$ , where  $C_p(q)$  is the elastic modulus corresponding to the wave mode  $p, q$ , it is necessary to neglect dispersion and assume  $\omega_p(q)$  is directly related to the ultrasonic wave velocity corresponding to the  $p, q$  mode. We then obtain

$$\begin{aligned} \gamma^p(q) = (\beta_{\perp} / \beta_V) (1 - n^2) + (\beta_{\parallel} / \beta_V) n^2 \\ - \frac{1}{2} \{ 1 - \beta_V^{-1} [\partial \ln C_p(q) / \partial P] \}_T, \quad (6) \end{aligned}$$

where  $n$  is the cosine of the angle between the  $q$  direction and the  $c$  axis. The average  $\gamma^p(q) = \bar{\gamma}$ , which is to be compared with the Gruneisen  $\gamma$  derived from thermal expansion data, is, at high temperatures, obtained by computing  $\gamma^p(q)$  for  $N=300$  different  $q$  directions, with  $n$  varying from 0→1, and averaging to give

$$\bar{\gamma}_H = (3N)^{-1} \sum_1^{3N} \gamma^p(q). \quad (7)$$

For low temperatures

$$\bar{\gamma}_L = \sum_1^{3N} C_p(q)^{-3/2} \gamma^p(q) / \sum_1^{3N} C_p(q)^{-3/2}, \quad (8)$$

where the  $C_p(q)$  are the 4°K values of the elastic moduli for the  $p, q$  mode. This weighting process is necessary to take into account the differences in contributions to the heat capacity at low temperatures by the individual lattice modes.

The values of  $\bar{\gamma}_H$  and  $\bar{\gamma}_L$  for Zr as computed from Gerlich's computer program<sup>8</sup> are given in Table V. Included for comparison are the  $\bar{\gamma}_H$  and  $\bar{\gamma}_L$  for Mg, Cd, and Gd, as computed from the same program. In all cases the pressure coefficients<sup>16-18</sup> were measured at temperatures above 273°K, so the  $\bar{\gamma}_L$  values represent an assumption that the pressure coefficients at 4°K are

TABLE VI. Differences in linear compressibilities and linear expansion coefficients for Mg, Cd, and Zr.

	$\beta_V^{-1}(\beta_{  }-\beta_{\perp})$	$\alpha_V^{-1}(\alpha_{  }-\alpha_{\perp})$
Mg	0.013	0.019
Cd	0.660	0.361
Zr	-0.049	0.136

the same as measured. Also included in Table V are the Gruenisen coefficients computed from volume thermal-expansion measurements:

$$\gamma(\alpha_V) = (V/C_V)\alpha_V\beta_V, \quad (9)$$

where  $C_V$  is the lattice heat capacity at constant volume and  $C_V/V$  represents the thermal pressure causing the thermal expansion. For Mg, Cd, and Gd the agreement between the computations from the elasticity data and thermal-expansion data<sup>4,19,20,21</sup> are very good, with the Mg values giving excellent agreement. For Zr the  $\tilde{\gamma}_H$  value is far below, (1/3), the  $\gamma_H(\alpha_V)$  value. The apparent disagreement between  $\tilde{\gamma}_L$  and  $\gamma_L(\alpha_V)$  for Zr may be a result of the difficulties encountered in obtaining reproducible values from polycrystalline thermal-expansion data.<sup>22</sup> The near zero value for  $\tilde{\gamma}_L$  is consistent with the lack of significant change in lattice constants between 50° and 4°K in the x-ray diffraction data.<sup>4</sup>

The very low value for  $\tilde{\gamma}_H$  in Zr is evidently created by giving equal weight to the  $\gamma^p(q)$  values computed from the negative  $dC_{44}/dP$ . Nevertheless, in view of the good agreement in the cases of Mg and Cd, and in several cubic crystal cases,<sup>7</sup> it would appear that the  $\gamma_H(\alpha_V)$  should also reflect the presence of negative  $\gamma^p(q)$  and thereby give better agreement to  $\tilde{\gamma}_H$ . One possible explanation for this dilemma is that the effect of the change in the  $c/a$  ratio on the vibrational frequency spectrum is neglected in comparing the hydrostatic pressure effects to thermal expansion. If the  $c/a$  change is assumed to have an intrinsic effect the  $\gamma^p(q)$  should be composed of two parts:

$$\gamma^p(q) = [\gamma^p(q)]_{c/a} - \left( \frac{\partial \ln \omega_p(q)}{\partial \ln(c/a)} \right)_V \frac{d \ln(c/a)}{d \ln V}, \quad (10)$$

where  $[\gamma^p(q)]_{c/a}$  and  $\partial \ln \omega_p(q)/d \ln(c/a)$  are intrinsic properties, but the  $d(c/a)/dV$  term will depend on experimental conditions. For thermal expansion,

$$\frac{d \ln(c/a)}{d \ln V} = \frac{V}{c/a} \left[ \frac{d(c/a)}{dT} \cdot \frac{dT}{dV} \right] = \frac{\alpha_{||} - \alpha_{\perp}}{\alpha_V}, \quad (11)$$

whereas for hydrostatic pressure,

$$\frac{d \ln(c/a)}{d \ln V} = \frac{V}{c/a} \left[ \frac{d(c/a)}{dP} \cdot \frac{dP}{dV} \right] = \frac{\beta_{||} - \beta_{\perp}}{\beta_V}. \quad (12)$$

The  $\gamma^p(q)$  contributing to  $\gamma(\alpha_V)$  will be the same as those evaluated from Eq. (6) only when Eqs. (11) and

(12) are numerically equal or when  $[\partial \ln \omega_p(q)/\partial \ln c/a]_V$  vanishes. Table VI lists the differences between axial thermal-expansion and compressibility coefficients, respectively, for Mg, Cd, and Zr. It can be seen that Zr is somewhat unusual in that  $\alpha_{||} > \alpha_{\perp}$  but  $\beta_{||} < \beta_{\perp}$ . Assuming  $\partial \ln \omega_p(q)/d \ln c/a$  to be negative, the effect of the  $c/a$  change will enhance the total  $\gamma^p(q)$  during thermal expansion but have the reverse effect during hydrostatic compression. This would be consistent with the differences between the observed  $\tilde{\gamma}_H$  and  $\gamma(\alpha_V)$  for Zr. For Mg there would be no significant difference, as is observed. For Cd the  $c/a$  change under hydrostatic pressures would have about twice the effect on a given mode  $\omega_p(q)$  as the  $c/a$  change during thermal expansion. Assuming the average  $(\partial \ln \omega_p(q)/d \ln c/a)_V$  to be negative,  $\tilde{\gamma}_H$  should be greater than  $\gamma_H(\alpha_V)$ , as is observed.

The same kind of analysis for the  $C_{44}$  mode of Zr suggests that the negative  $dC_{44}/dP$  could be entirely due to the  $c/a$  change under hydrostatic pressure. Separating the volume change and  $c/a$  change effects we obtain

$$\frac{dC_{44}}{dP} = -\beta_V V \left( \frac{\partial C_{44}}{\partial V} \right)_{c/a} + \frac{c}{a} (\beta_{\perp} - \beta_{||}) \left( \frac{\partial C_{44}}{\partial(c/a)} \right)_V. \quad (13)$$

If we assume that  $(\partial C_{44}/\partial V)_V$  has a negative value as is normally found in cubic metals, the anomalous negative pressure derivative could arise entirely from a relatively large and negative  $(\partial C_{44}/\partial c/a)_V$ .

Assuming the above interpretation of the  $\tilde{\gamma}_H$  to  $\gamma_H(\alpha_V)$  difference is correct, the phenomenon should be of fundamental interest as a means for detecting wide departures from the quasiharmonic approximation, which assumes that the change in lattice frequencies are determined only by the volume change. If  $(\partial C_{44}/\partial a_0)_V$  is positive while  $(\partial C_{44}/\partial c_0)_V$  is negative or normal in sign, the implication is that there is a strong coupling in Zr between the  $C_{44}$  and  $C_{11}$  phonon modes.

Another possible cause of the  $\tilde{\gamma}_H$  to  $\gamma_H(\alpha_V)$  disagreement is that at high frequencies the  $C_{44}$  phonons frequencies have a normal pressure dependence and that the negative  $dC_{44}/dP$  is characteristic only of the ultrasonic frequency part of the spectrum. This would also imply a strong anharmonic coupling between the  $C_{44}$  and other modes, with the coupling strength being frequency dependent. There is some evidence<sup>23</sup> from neutron inelastic scattering studies of Zr that something like this mechanism is indeed occurring for  $C_{44}$ . This data shows frequencies at the long wavelength part of the spectrum that are considerably higher than expected from the ultrasonic  $C_{44}$ . Since these wavelengths are still shorter than in the ultrasonic range they could represent the uncoupled  $C_{44}$  phonons that in turn contribute to the thermal expansion. We know, however, that this is not true at 4°K since the Debye temperature,  $\theta_D$ , computed from the ultrasonic velocities at this temperature agrees extremely well with that determined from accurate low-temperature heat-capacity data.<sup>24</sup>