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Effect of Axial Ratio Changes on the Elastic Moduli and Grüneisen γ for Lower Symmetry Crystals

E. S. FISHER

Argonne National Laboratory, Argonne, Illinois 60439

AND

M. H. MANGHNANI*

University of Hawaii, Honolulu, Hawaii 96825†

Gerlich has shown that Sheard's model for calculating mode γ 's from hydrostatic pressure derivatives of the elastic moduli of hcp Mg and Cd yields Grüneisen γ 's at both high and low temperatures that are in good agreement with the γ 's derived from thermal-expansion measurements. For hcp Ti and Zr, however, large differences arise, primarily from very small values for dC_{44}/dP . It is proposed that these small values are caused by the changes in c/a ratio with hydrostatic pressure because of a large dependence of C_{41} on the c/a ratio. The disagreement with thermal-expansion data can be removed by taking into account the difference in $d(c/a)/dV$ between hydrostatic-pressure and thermal-expansion conditions. The effect of $\Delta(c/a)$ is not found in tetragonal TiO₂, rutile, where $\bar{\gamma}_H$ is in excellent agreement with the thermal expansion γ_∞ .

INTRODUCTION

The model of Sheard^{1,2} for calculating the Grüneisen γ from measured values of the hydrostatic-pressure derivatives of the elastic moduli of cubic crystals has been extended by Gerlich³ to hcp and tetragonal crystals. This extension does not consider the effects of the changes in c/a ratio with pressure on the mode frequencies. In this paper we present evidence that the effects of changing the axial ratios, expressed as $\Delta(c/a)$, are quite large in certain hcp metals and contribute to negative mode γ 's and large deviations between average gammas computed from thermal expansion and those derived from measured values of dC_{ij}/dP .

STATEMENT OF THE PROBLEM

The equations for analyzing the $\Delta(c/a)$ effect are stated as follows:

$$\gamma^p(q) = [\gamma^p(q)]_{c/a} - \left(\frac{\partial \ln \omega_p(q)}{\partial \ln(c/a)} \right)_V \frac{d \ln(c/a)}{d \ln V}, \quad (1)$$

where $\gamma^p(q)$ is the mode gamma for hydrostatic pressure as derived from the dC_{ij}/dP using Gerlich's³ Eq. (11). The first term on the right is the pure volume change contribution, and the second term is the $\Delta(c/a)$ contribution. A problem arises because $d \ln(c/a)/d \ln V$ differs under thermal-expansion and hydrostatic-pressure conditions, respectively, as follows:

$$\frac{d \ln(c/a)}{d \ln V} = \left(\frac{\partial \ln(c/a)}{\partial \ln V} \right)_P = \frac{\alpha_{||} - \alpha_{\perp}}{\alpha_V} \quad (2)$$

$$\frac{d \ln(c/a)}{d \ln V} = \left(\frac{\partial \ln(c/a)}{\partial \ln V} \right)_T = \frac{\beta_{||} - \beta_{\perp}}{\beta_V}, \quad (3)$$

where α and β are used for thermal-expansion coefficient and isothermal compressibility, respectively. The subscripts refer to the linear parameter values parallel and perpendicular, respectively, to the c axes of either hexagonal or tetragonal crystals, and α_V and β_V are the volume parameters. If

$$\left(\frac{\partial \ln \omega_p(q)}{\partial \ln(c/a)} \right)_V$$

TABLE I. Hydrostatic pressure derivatives of elastic moduli and the anisotropy parameters for Ti, Zr, Mg, and Cd at 300°K.

	dC_{11}/dP	dC_{33}/dP	dC_{44}/dP	dC_{66}/dP	$(\beta_{11}-\beta_{\perp})/\beta_V$	$(\alpha_{11}-\alpha_{\perp})/\alpha_V^a$
Ti	5.01	4.88	0.52	0.45	0.013	-0.144(a), 0.045(b)
Zr	3.93	5.49	-0.22	0.26	-0.049	0.136(a), 0.059(b)
Mg	6.11	7.22	1.58	1.36	0.013	0.019
Cd	9.29	7.26	2.38	2.59	0.660	0.361

^a Ti(a) Ref. 12, Ti(b) Ref. 13, Zr(a) Ref. 14, Zr(b) Ref. 15, Mg and Cd Ref. 10.

is a significant quantity and $(\alpha_{11}-\alpha_{\perp})/\alpha_V$ differs from $(\beta_{11}-\beta_{\perp})/\beta_V$, the average mode γ 's for low and high temperatures ($\bar{\gamma}_L$ and $\bar{\gamma}_H$), as defined by Gerlich, will necessarily differ from $\gamma_L(\alpha_V)$ and $\gamma_H(\alpha_V)$ computed from thermal-expansion data.

EVIDENCE FOR THE $\Delta(c/a)$ EFFECT

Experimental evidence that the $\Delta(c/a)$ effect must be considered arises when a comparison is made of the dC_{ij}/dP values for hcp Ti⁴ and Zr.⁵ These two metals are exceptionally similar in many physical and mechanical properties. In regard to elastic properties,⁶ they differ primarily in the values of the C_{44} shear modulus and in the linear compressibility perpendicular to the hexagonal axes, β_{\perp} . As a consequence of the latter difference,

$$d(c/a)/dP = (c/a)(\beta_{\perp}-\beta_{11}) \quad (4)$$

is negative for Ti and is positive for Zr.

The hydrostatic-pressure derivatives of the single-crystal elastic moduli of Ti, Zr, Mg, and Cd^{7,8} are listed in Table I. All the data are taken from ultrasonic velocity measurements at temperatures near 25°C and represent adiabatic pressure derivatives. From these data, the pressure derivatives of the shear stiffnesses dC_{44}/dP and dC_{66}/dP appear to decrease with the c/a ratio of the crystal at 1-bar pressure. The major difference between Ti and Zr appears in dC_{44}/dP , where we find a negative value for Zr.

To relate the measured dC_{ij}/dP to the volume and c/a changes, separately, we use the following equations

$$\frac{dC_{ij}}{dP} = \left(\frac{\partial C_{ij}}{\partial P}\right)_{c/a} - \left(\frac{\partial C_{ij}}{\partial(c/a)}\right)_V \left(\frac{d(c/a)}{dP}\right) \quad (5)$$

$$= -\beta_V C_{ij} \left(\frac{\partial \ln C_{ij}}{\partial \ln V}\right)_{c/a} + (c/a)(\beta_{\perp}-\beta_{11}) \left(\frac{\partial C_{ij}}{\partial(c/a)}\right)_V. \quad (6)$$

For cubic metals the measured values of dC_{ij}/dV are negative in all cases, ($dC_{ij}/dP > 0$), and we can reasonably presume that $(\partial C_{ij}/\partial V)_{c/a}$ for Ti and Zr are also negative. We then conclude that the negative value for dC_{44}/dP in Zr, where $\beta_{\perp} > \beta_{11}$, arises from a negative value for $[\partial C_{44}/\partial(c/a)]_V$. To estimate the relative values for volume and c/a contributions to dC_{ij}/dP , it appears

reasonable to compute $(\partial C_{ij}/\partial V)_{c/a}$ and $[\partial C_{ij}/\partial(c/a)]_V$ by assuming that these two unknown factors are the same in Zr and Ti. The computed values of the partial derivatives and the volume and c/a contributions to each dC_{ij}/dP are listed in Table II. The conclusions from this approach are that the change in c/a with pressure has a larger effect on the C_{44} of Zr than does the volume change, and also contributes significantly to dC_{44}/dP and dC_{66}/dP in both metals.

Two external factors indicate that the quantities derived from the above procedure are realistic. One is that the value for $dC_{44}/d(c/a)$ is very near the value derived by Cousins from calculations of the electrostatic contribution to C_{44} of hcp metals.⁹ These calculations give

$$\left(\frac{dC_{44}^E}{d(c/a)}\right)_V = -\frac{Z^2}{a_0^4} (26.4 \times 10^{12} \text{ dyn/cm}^2), \quad (7)$$

where Z is the effective valence, and a_0 is the ion separation in the basal plane in Å units. Assuming $Z=4$ for Zr and Ti, Eq. (7) gives $[\partial C_{44}^E/\partial(c/a)]_V = -3.88$ and -5.57×10^{12} dyn/cm² for Zr and Ti, respectively, whereas our common value is -6.5×10^{12} dyn/cm². This near agreement suggests that our assumptions in deriving $dC_{44}/d(c/a)$ are reasonably valid, and that the large effect of $\Delta(c/a)$ on C_{44} is caused primarily by the change in electrostatic energy contribution.

The other factor that lends confidence to the procedure is that the difference between the values of C_{44} in Ti and in Zr is quite large⁶ and can be reasonably accounted for from the $(\partial C_{44}/\partial V)_{c/a}$ and $[\partial C_{44}/\partial(c/a)]_V$ contributions. The total observed difference is 0.145×10^{12} dyn/cm². The volume difference can account for approximately 0.110×10^{12} , and the c/a difference accounts for 0.023×10^{12} dyn/cm², when the derived values are used for the partial derivatives.

Grüneisen γ Calculations in Ti and Zr

Some results of the $\bar{\gamma}_L$ and $\bar{\gamma}_H$ calculations, using Eq. (2), Gerlich's computer program,³ and measured dC_{ij}/dP , are listed in Table III. The results for Mg and Cd were obtained and reported by Gerlich.³ The excellent agreement between $\bar{\gamma}_L$ and $\bar{\gamma}_L(\alpha_V)$ and the good agreement between $\bar{\gamma}_H$ and $\bar{\gamma}_H(\alpha_V)$ for Mg and Cd¹⁰ serve to further verify the validity of the model

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

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

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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† Present address: Air Force Cambridge Research Laboratories, Bedford, Mass. 01730.

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