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

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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 Gruneisen 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_{44} 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 TiO_2, rutile, where $\bar{\gamma}_H$ is in excellent agreement with the thermal expansion γ_∞.

INTRODUCTION

The model of Sheard[1,2] for calculating the Gruneisen γ from measured values of the hydrostatic-pressure derivatives of the elastic moduli of cubic crystals has been extended by Gerlich[3] 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's[3] 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	$(\beta_{\|\|}-\beta_{\perp})/\beta_V$	$(\alpha_{\|\|}-\alpha_{\perp})/\alpha_V$[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 $(\alpha_{||}-\alpha_{\perp})/\alpha_V$ differs from $(\beta_{||}-\beta_{\perp})/\beta_V$, 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 Ti [4] 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, $\beta_\perp$. As a consequence of the latter difference,

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

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

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

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

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 $\beta_\perp>\beta_{||}$, 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

$$\left(\frac{dC_{44}{}^E}{d(c/a)}\right)_V=-\frac{Z^2}{a_0^4}(26.4\times10^{12}\ \text{dyn/cm}^2), \qquad (7)$$

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 large[6] 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.

Gruneisen 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 Cd [10] serve to further verify the validity of the model