

Hydrostatic Pressure Derivatives of the Single-Crystal Elastic Moduli of Zirconium

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The adiabatic elastic moduli of single-crystal Zr vary linearly with hydrostatic pressures up to 4.7 kbar. The pressure derivatives are $dC_{11}/dP=3.93$, $dC_{33}/dP=5.49$, $dC_{44}/dP=-0.22$, $dC_{66}/dP=0.26$, $dC_{12}/dP=3.42$, and $dC_{13}/dP=4.25$. The average high-temperature Gruneisen mode $\bar{\gamma}_H$ calculated from this data is in wide disagreement with that calculated from the volume thermal expansion coefficient. It is proposed that this disagreement arises because the negative dC_{44}/dP is caused by the change with pressure in the c/a ratio, rather than the volume change.

INTRODUCTION

The metallic crystals formed by the Group IVA elements of the periodic table Ti, Zr, and Hf are of great interest in the study of phase transformations in the solid state. At atmospheric pressures the low-temperature crystal structures, simple hcp with c/a ratio <1.6 , transform to the simple bcc (β) structures at temperatures T_c of 1135°, 1155°, and near 2000°K, respectively. This transformation occurs in several other metals at temperatures near the melting points. The hcp \rightarrow bcc ($\alpha\rightarrow\beta$) transformations in Ti and Zr are somewhat unique in that they occur at nearly one-half the respective melting temperature and involve a small but clear increase in density, i.e., $dT_c/dP < 0$.¹

The measurements of the temperature dependence of the shear moduli C_{44} and C_{66} in single crystals of Ti and Zr show some unusual features which suggest that the ($\alpha\rightarrow\beta$) transformation may be either closely associated with or the result of phonon interactions that occur during heating of the hcp crystals.² The C_{66} moduli have very large negative temperature coefficients, $d \ln C_{66}/dT$, and C_{66} becomes very small, but not zero, at the respective transformation temperatures. The C_{66} shear is precisely the kind of homogeneous shear that is required for the crystal structure change.³ The other important feature, related to the present work, is that d^2C_{66}/dT^2 in both metals and d^2C_{44}/dT^2 in Zr become positive at $T > 400^\circ\text{K}$. Expressing dC_{66}/dT as functions of temperature and thermal expansion,

$$dC_{66}/dT = (\partial C_{66}/\partial T)_V - (\alpha_V/\beta_V) (\partial C_{66}/\partial P)_T, \quad (1)$$

where α_V and β_V are volume thermal expansion coefficient and isothermal compressibility, respectively, and P is hydrostatic pressure, we note that a positive d^2C_{66}/dT^2 could arise from the volume expansion if $(\partial C_{66}/\partial T)_V$ remains a nearly constant negative term, while $(\partial C_{66}/\partial P)_T$ decreases with increasing temperature. Since α_V is known to increase to exceptionally large values during heating of Zr and Ti,^{4,5} the second term of Eq. (1) could indeed be a deciding factor if dC_{66}/dP is negative. In the present work the measure-

ments of the pressure derivatives of all five stiffness moduli for Zr at 298°K are reported.

The possible importance of the pressure derivatives of the stiffness moduli to the phase transformation comes about if it is assumed that the vibrational entropy difference of the atoms within the α and β phases supplies the driving force for the structural change.⁶ Equating the entropy to the vibrational amplitude and, thus, to the inverse of the vibrational frequency ω we conclude that the $\alpha\rightarrow\beta$ transformation must involve a decreasing average vibrational frequency. It is known, however, that the β phase has the smaller volume, so we are left with the implication that the Gruneisen coefficients ($\gamma_i = -d \ln \omega_i / d \ln V$) for some modes of vibration are negative in the α phase at the transformation temperature. The γ_i for the low-frequency modes can be closely approximated from hydrostatic pressure derivatives of the stiffness moduli,⁷ and Gerlich⁸ has shown that the average $\bar{\gamma}_i$ for all modes in several hcp crystals agree remarkably well with γ obtained from high-temperature thermal-expansion data. Thus, measurements of the pressure derivatives may be quite useful in understanding the temperature derivatives of the elastic moduli, as well as precursory phenomena leading to the first-order phase transformations in Zr and Ti.

In addition to the thermally induced structural change, it has also been found that hcp Ti and Zr will transform under pressures of 55–60 kbar to a structure that is similar to the omega phase found in certain Ti and Zr alloys.⁹ It may be possible to observe precursory phenomenon leading to this phase change from measurements of the elastic moduli in the 0–4 kbar pressure range.

SPECIMENS

Two α -Zr single crystals were prepared for velocity measurements in the specific crystallographic directions for determining the elastic moduli. Specimen No. 1 was used for wave propagation in directions parallel and perpendicular to the hexagonal (c) axis. Specimen No. 2 was used for wave propagation in a

TABLE I. Basic frequency data used to compute wave-propagation velocities and related elastic parameters of single-crystal zirconium at 1 bar and 25°C.

Crystal specimen	Length (cm)	Direction of propagation	Direction of vibration	Mode	Mode no.	Pulse repetition frequency (cycles/sec)	Velocity (km/sec)	Velocity notation	Elastic coefficient determined
1	0.48142	[100]	[100]	longit.	1	488 115	4.6998	v_1	$C_{11} = \rho v_1^2$
	0.48132	[001]	[001]	longit.	2	523 456	5.0390	v_2	$C_{33} = \rho v_2^2$
	0.48132	[001]	any	shear	3	230 893	2.2227	v_3	$C_{44} = \rho v_3^2$
	0.48142	[100]	[010]	shear	4	242 000	2.3301	v_4	$C_{66} = \frac{1}{2}(C_{11} - C_{12}) = \rho v_4^2$
2	0.30546	45° to [001] and [100]	~45° to [001] and [100]	longit.	5	766 387	4.6820	v_5	C_{RS}^a

$$^a C_{RS} = \rho v_5^2 = \frac{1}{4} [C_{11} + C_{33} + 2C_{44} + (C_{11} - C_{33})^2 + 4(C_{13} + C_{44})^2]^{1/2}.$$

direction 45° to the c axis. The modes of wave-propagation velocity measurements made on the two specimens at the ambient conditions and at high pressures are listed in Table I.

EXPERIMENTAL METHODS

The ultrasonic pulse superposition method¹⁰ was used to measure the wave-propagation velocities at pressures of 1 bar–4.7 kbar at 25°C. In this method an rf pulse is applied to a transducer, attached to one of the two parallel faces of the specimen, at a time interval t ($t = 1/f_r$) which is equal to the one round-trip delay time in the specimen. 30 MHz X -cut and Y -cut quartz transducers, 0.25 in. in diameter, were used to generate compressional and shear waves, respectively, in the specimen. Dow Corning resin 276-V9 was used for bonding the transducers to the specimen.

The pressure apparatus consisted of a pressure vessel, a two-stage compressing system, a manganin coil, a Carey-Foster pressure measuring bridge, and a Harwood dead-weight tester. The latter was used for calibrating the Carey-Foster bridge. The accuracy of pressure measurements is believed to be within $\pm 0.2\%$ of the values. A minimum time interval of 15 min was allowed between change of pressure and the measurement. The temperature of the test specimen in the pressure vessel was maintained at $25^\circ \pm 0.1^\circ\text{C}$ during all the measurements by circulating water in a constant temperature bath around the vessel.

DATA REDUCTION

The velocities were computed from the relationship, $v = 2lf_r$, where l is length of the specimen and f_r is the pulse repetition frequency (prf); the correction for phase angle in the bond was ignored. The basic measurements of prf and the calculated velocities and the elastic coefficients are listed in Table I. Table II shows a comparison of the values of the elastic constants deter-

mined in this study and those reported previously.¹¹ A good agreement (within $\pm 1\%$) is found.

The prf measurements were made at intervals of 0.276 kbar in increasing and decreasing pressure cycles. Figure 1 shows the plots of frequency ratio (f_r/f_{r0}) versus pressure for the modes of propagation explained in Table I; the zero subscript is for a 1 bar value. The least-squares fit equations for these plots are

$$\begin{aligned} v_1, & (f_1/f_{01}) = 1.0000 + 1.2088P, & r = 0.9995, \\ v_2, & (f_2/f_{02}) = 1.0000 + 1.4477P, & r = 0.9997, \\ v_3, & (f_3/f_{03}) = 1.0000 - 0.5542P, & r = 0.9989, \\ v_4, & (f_4/f_{04}) = 1.0000 + 0.2038P, & r = 0.9946, \\ v_5, & (f_5/f_{05}) = 1.0000 + 1.3200P, & r = 0.9998, \end{aligned}$$

where P is pressure in megabars and r is the coefficient of correlation.

The elastic constants at pressure were calculated after correcting for changes in length and density of the specimen under pressure by adopting an approximation to Cook's method.^{12,13} The general relationship is

$$(C_{ij}) = (C_{ij})_0 (f_r/f_{r0})^2 (l/l_0)^2 (\rho/\rho_0), \quad (2)$$

TABLE II. Comparison of the values of elastic constants obtained in this investigation and those previously determined. Values are given in kilobars.

Elastic constant	Value (this study)	Value (Fisher and Renken) ¹¹
C_{11}	1436.8	1434
C_{33}	1651.7	1648
C_{44}	321.4	320
C_{66}	353.2	353
C_{12}	730.4	728
C_{13}	658.8	653