

ref. p. 661

EFFECTS OF CHANGES IN VOLUME AND c/a RATIO ON THE PRESSURE DERIVATIVES OF THE ELASTIC MODULI OF H.C.P. Ti AND Zr*

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Abstract—The hydrostatic pressure derivatives of the single crystal elastic moduli of Ti have been measured to 5.5 Kbar. The pressure derivatives are $dC_{11}/dP = 5.01$, $dC_{33}/dP = 4.88$, $dC_{44}/dP = 0.52$, $dC_{66}/dP = 0.45$, $dC_{12} = 4.11$, and $dC_{13}/dP = 4.05$. The positive value for dC_{44}/dP is in sharp contrast to $dC_{44}/dP < 0$ for Zr. This difference is assumed to arise from the difference between $d(c/a)/dP$ in the two h.c.p. crystals and quantitative values of dC_{ij}/dV and $dC_{ij}/d(c/a)$ are calculated. It is then shown that the large differences between the average Grüneisen mode γ_H calculated from dC_{ij}/dP and that obtained from thermal expansion data for both Ti and Zr can be explained by the differences between $d(c/a)/dV$ under hydrostatic pressure and during thermal expansion, respectively. The relatively large negative value for $dC_{44}/d(c/a)$ is quantitatively consistent with Cousins' calculations of the dependence of the electrostatic contribution to C_{44} on the c/a ratio in any h.c.p. metal lattice.

1. INTRODUCTION

IN A RECENT paper [1] we presented measurements of the hydrostatic pressure coefficients of the single crystal elastic moduli of h.c.p. Zr. It was then shown that the shear modulus C_{44} decreases with increasing hydrostatic pressure and that this negative pressure coefficient causes a severe difference between the high temperature Grüneisen γ , $\bar{\gamma}_H$, calculated from an averaging of the mode γ 's, and the Grüneisen γ calculated from the measurements of volume thermal expansion, $\gamma_H(\alpha_V)$. This wide difference was deemed significant in view of the fact that the same method of computing and averaging the mode γ 's from the hydrostatic pressure derivatives of the elastic moduli of Mg, Cd, and Gd produced exceptionally good agreement with the volume thermal expansion data [2]. It was

proposed that the failure to agree in the case of Zr is due to a significant dependence of the elastic moduli on the c/a ratio and the fact that $d(c/a)/dV$ derived from hydrostatic pressure at constant temperature differs in algebraic sign from $d(c/a)/dV$ during thermal expansion at constant pressure:

$$\left(\frac{\partial \ln(c/a)}{\partial \ln V}\right)_T \neq \left(\frac{\partial \ln(c/a)}{\partial \ln V}\right)_P \quad (1)$$

or

$$\frac{\beta_{||} - \beta}{\beta_V} \neq \frac{\alpha_{||} - \alpha_{\perp}}{\alpha_V} \quad (2)$$

where β and α are compressibility and thermal expansion coefficients, respectively, and the subscripts refer to the axial coefficients parallel ($\beta_{||}$, $\alpha_{||}$) and perpendicular (β_{\perp} , α_{\perp}) to the hexagonal axis and to the volume coefficients (β_V and α_V). The important conclusion from this work is that the transverse phonon frequencies and the elastic moduli are strongly dependent on the c/a ratio in h.c.p. Zr.

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The most direct method of verifying the proposed effect of the change in c/a ratio on the elastic moduli would be via uniaxial pressure effects. In the case of Zr, however, there appeared to be a unique opportunity to check the c/a effect by measuring the pressure derivatives of the elastic moduli of h.c.p. Ti. Zr and Ti are remarkably similar in electronic and thermal properties. Both are Group IV transition metals with 2 electrons in an unfilled d electron shell. The thermally induced h.c.p. \rightarrow b.c.c. structural transformations occur in both metals at nearly the same temperatures (i.e., 1135°K for Zr and 1156°K for Ti). The second order elastic properties contain some very marked similarities[3]: (1) the value of the C_{66} shear moduli and the β_{\parallel} values for Ti and Zr are the same to within 5 per cent at any given temperature and (2) the temperature derivatives of the C_{11} , C_{33} , and C_{66} stiffness moduli and the bulk moduli, K , are very nearly the same for Ti and Zr at all temperatures. The two important differences between the elastic properties are as follows: (1) the anisotropy in linear compressibilities as defined in equation (2) is negative for Zr, ($\beta_{\perp} > \beta_{\parallel}$), but positive for Ti, and (2) the C_{44} shear modulus for Ti is about 40 per cent greater than in Zr, in contrast to almost identical C_{66} values mentioned above and the ~ 10 per cent and ~ 15 per cent differences in C_{33} and C_{11} , respectively. If we ascribe the negative dC_{44}/dP in Zr to the increase in c/a ratio with increasing hydrostatic pressure, because of $\beta_{\perp} > \beta_{\parallel}$, then, on the basis of the otherwise strong similarities between the metals, we should find that dC_{44}/dP for Ti is positive. The measurement of dC_{44}/dP for Ti is then a qualitative test of the conclusions reached in the Zr work. By making certain reasonable assumptions regarding other similarities in the two metals we can arrive at a quantitative test of the conclusion that the average mode γ , $\bar{\gamma}_H$, computed from the pressure dependence of the elastic moduli in an anisotropic crystal will agree with the Grüneisen γ deduced from thermal expansion

if

$$(\partial \ln (c/a)/\partial V)_T = (\partial \ln (c/a)/\partial V)_P.$$

2. EXPERIMENTAL PROCEDURES

The Ti single crystals were obtained by zone melting a rod of crystal bar iodide Ti. The experimental procedure for measuring the changes in ultrasonic wave velocities in Ti as a function of pressure was the same as that for Zr[1]. Nitrogen gas was the pressure medium. The changes in the compressional moduli C_{11} and C_{33} with pressure at $25^\circ \pm 0.1^\circ\text{C}$ were determined from the changes in critical pulse repetition rate frequency[4], f_r , for longitudinal waves propagated perpendicular and parallel, respectively, to the c axis of a Ti single crystal. The change in the shear modulus $C_{66} = \frac{1}{2}(C_{11} - C_{12})$ was determined from the change in f_r of a transverse wave propagated and polarized perpendicular to c axis, whereas the change in the C_{44} shear modulus was determined from the transverse wave mode propagated parallel to the c axis. The change in C_{13} with pressure was derived from the change in f_r for the longitudinal wave propagated $45^\circ \pm \frac{1}{4}^\circ$ to the c axis. The basic data, f_r/f_{r_0} , where f_{r_0} corresponds to f_r at 1 bar, are plotted in Fig. 1. Mode numbers 1 through 5 correspond respectively to the C_{11} , C_{33} , C_{44} , C_{66} and the 45° quasi-longitudinal modes. Except for mode # 3, C_{44} , the f_r/f_{r_0} vs. pressure lines are straight, within experimental error, to 5.516 Kb. For the C_{44} mode the data suggests that a relatively abrupt change in slope occurs at approximately 2.5 Kb.

The changes with pressure of the thickness of the crystal parallel to the ultrasonic wave path and the volume change, that are necessary for computing the modulus change, were computed from the isothermal linear compressibilities calculated at 1 bar and at intervals of 0.0276 Kb from the stiffness moduli[1]. For the adiabatic to isothermal compressibility calculation the following volume thermal expansion coefficient, α_V , and the Grüneisen constant, $\gamma_H(\alpha_V)$, were used: $\alpha_V = 2.4 \times 10^{-5}/^\circ\text{K}$ and $\gamma_H(\alpha_V) = 1.10$ (Ref. [5]).