

# Thermal Equations of State of the $\alpha$ -, $\beta$ -, and $\omega$ - Phases of Zirconium

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## Introduction

Zirconium is a fascinating d-orbital transition metal. It has been widely used for nuclear and chemical applications owing to its low neutron absorption cross-section and its exceptional resistance to corrosion. The study of the fundamental thermodynamic properties of zirconium, such as equation of state (EOS) and phase stability, are very important for a better understanding of its crystal, chemical, and physical properties and to the development of theoretical modeling in computational physics [1,2].

Zirconium metal crystallizes into a hexagonal close-packed (hcp or  $\alpha$ -phase) structure at ambient conditions. It transforms to a body-centered cubic structure, commonly referred to  $\beta$ -phase, at temperatures higher than 1136 K. With increasing pressure, the hcp phase transforms into another hexagonal structure called the  $\omega$ -phase [3], which is not close-packed and has three atoms per unit cell. Previous EOS studies have been carried out on the  $\alpha$  and  $\omega$  phases of zirconium [4, 5]; the pressure-volume measurements, however, were limited to ambient temperature. Thermal expansion data are only available for the  $\alpha$  phase of zirconium and all the measurements were performed at atmospheric pressure [6]. In this study, we conducted x-ray diffraction at simultaneously high pressure and temperature to obtain the thermoelastic equation of state (EOS) for three different phases of zirconium. The term “thermoelastic” emphasizes that the ultimate results of the EOS determination are the thermoelastic properties of the matter, such as temperature derivative of bulk modulus and pressure derivative of thermal expansion. The thermoelasticity is a fundamental property of condensed matter and has been applied in the modeling of high P-T phenomena under dynamic shocks and inside planetary interiors. However, to date, the thermoelastic equations of state of most metals and ceramics have not been studied comprehensively.

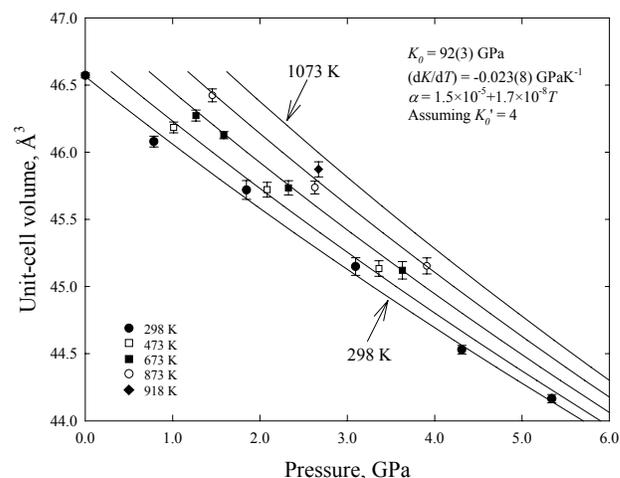
## Methods and Materials

The starting zirconium metal has an hcp structure ( $\alpha$ -phase) and is of extremely high purity, with 35 ppm Hf, less than 25 ppm of C, N, Al, and less than 50 ppm of O, V, and Fe. X-ray diffraction experiments were conducted using a DIA-type cubic anvil apparatus and a “T-Cup” multi-anvil high-pressure system. An energy-dispersive x-ray method was employed using white radiation from the bending magnet at beamline 13-BM-D of APS of ANL and from the superconducting wiggler magnet at beamline X17B2 of NSLS of BNL. In each of the five experiments we performed, NaCl was used as an internal pressure standard and temperatures were measured by a W/Re25%-W/Re3% thermocouple. The uncertainty in pressure measurements is less than 0.2 GPa in the P-T range of this study. Errors in temperature measurements were estimated to be approximately 10 K. The effects of deviatoric stress on P-V

measurements are expected to be minimal since a majority of the data reported here was collected at temperatures above 573 K, under which the deviatoric stress would be relaxed in NaCl and samples.

## Results

Four experiments have been performed at pressure (P) and temperature (T) conditions up to 17 GPa and 973 K. At ambient conditions, the  $\alpha$  phase of zirconium metal has a unit-cell volume (V) of  $46.57 \text{ \AA}^3$  and c/a ratio of 1.592, which are in agreement with chemical analysis that shows extremely low oxygen content and with a previously established relationship between unit-cell parameters and oxygen content. In all experiments we performed, both recovered and starting samples do not show any Raman shifts except for surface oxidation, indicating that zirconium metal remains in an elemental form under the present experimental conditions.

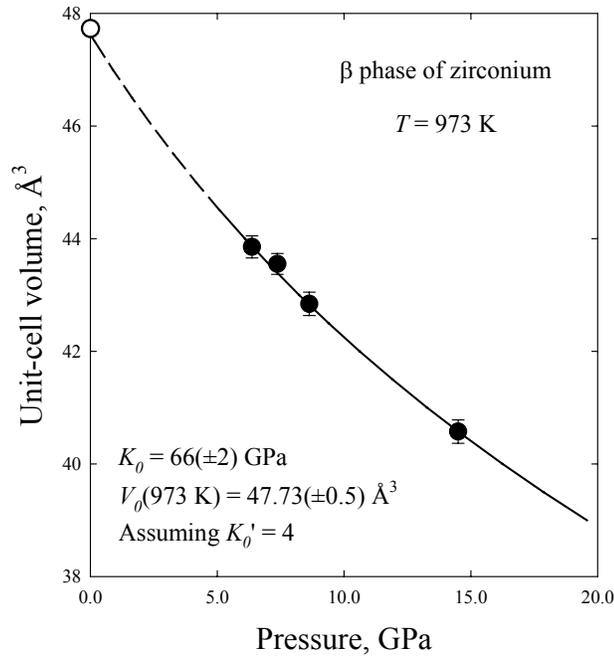


**Fig. 1** Pressure-volume-temperature data (symbols) measured for the  $\alpha$  phase of zirconium. The curves represent results of the least squares fit at the indicated temperatures.

Unit cell parameters were refined from the collected x-ray diffraction patterns for the three phases of zirconium and are shown in Figs. 1-4. A modified high-temperature Birch-Murnaghan equation of state [7], was adopted to derive thermoelastic parameters based on the measured P-V-T data. These fits allow us to obtain the following EOS parameters:  $K_0$  and  $K_T$  (isothermal bulk modulus at 300 K and at a higher temperature T),  $(\partial K/\partial T)$  and  $(\partial K/\partial P)$  (the temperature and pressure derivatives of the bulk modulus), and  $\alpha$  (volumetric thermal expansion at zero pressure, which is given in this work by  $\alpha_T = a + bT$ ). Because of the limited pressure range that inhibits an accurate constraint on  $K_0'$  (the pressure derivative of  $K_0$ ) for three zirconium phases, we assume  $K_0' = 4$  throughout

the data reduction. Similarly, due to their limited thermal stability, we ignore higher-order derivatives of the bulk modulus such as  $\partial^2 K / \partial T^2$  and  $\partial^2 K / \partial P \partial T$ .

For the  $\alpha$ -phase of zirconium all x-ray diffraction data were collected on cooling to minimize deviatoric stress built up during the room-temperature compression. From a least-squares fit to the P-V-T data we obtain  $K_0 = 92(3)$  GPa,  $(\partial K / \partial T)_P = -2.4(8) \times 10^2$  GPaK<sup>-1</sup>, and  $\alpha = a + bT$ , with  $a = 1.5(\pm 0.8) \times 10^5$  K<sup>-1</sup> and  $b = 1.7(\pm 1.4) \times 10^8$  K<sup>-2</sup>. Fig. 1 shows that the thermoelastic parameters derived in the present study produce good fits to the experimental P-V-T data of the  $\alpha$ - phase zirconium. From the thermodynamic identity,  $(\partial \alpha / \partial P)_T = (\partial K / \partial T)_P K_T^{-2}$ , the pressure derivative of the volume thermal expansivity,  $(\partial \alpha / \partial P)_T$ , is found to be  $-2.7(9) \times 10^{-6}$  K<sup>-1</sup>GPa<sup>-1</sup>. Within the experimental errors, the  $K_0$  value and thermal expansion we obtained are in agreement with previous results [4,6], whereas  $(\partial K / \partial T)_P$  and  $(\partial \alpha / \partial P)_T$  are determined for the first time for the  $\alpha$  phase of zirconium.

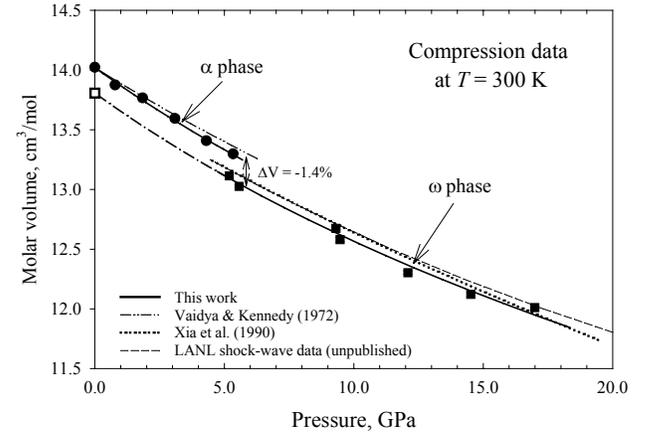


**Fig. 2** The isothermal compression data (symbols) for the  $\beta$  phase of zirconium at 973 K. The solid curve represents results of the least-squares fit. The dash curve and an open circle indicate the extrapolated data.

For the  $\beta$ - phase zirconium, the formation of the zirconium metallic glass at high P-T conditions leads to a limited stability field in the pressure range of 6-16 GPa [Refs. 8], which prohibited us from collecting the volume data at temperatures above 973 K. As a result, only four data points were obtained for the  $\beta$  phase in the four experiments we performed (Fig. 2). The least-squares fit of these P-V data provides the first EOS determination for the  $\beta$ - phase zirconium, with  $K_{973K} = 66(2)$  GPa and  $V_{973K} = 47.7(5)$  Å<sup>3</sup> at ambient pressure  $P = 0$ . Apparently, more P-V-T data are needed to constrain the EOS parameters better. Since our observations have demonstrated a somewhat diminishing glass-forming ability of the  $\beta$ -phase around 15 GPa

[Ref. 8], such data can be obtained at higher pressures from diffraction experiments using a laser-heated diamond anvil cell technique.

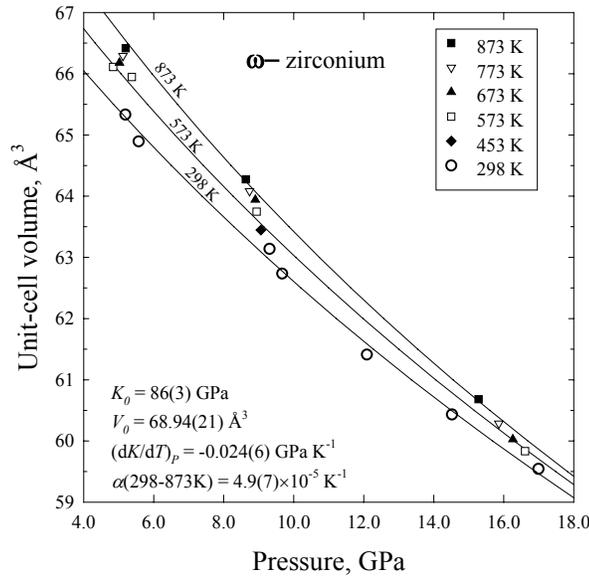
We have collected the P-V-T data for the  $\omega$ - phase zirconium upon room temperature compression and upon heating to the  $\omega$ - $\beta$  phase transition in three experiments. The room-temperature data are plotted in Fig. 3 and compared with those of the  $\alpha$  phase and with previous results for these two phases. It is seen that the P-V data from the different studies are generally in good agreement, particularly between this study and shock wave measurements for the  $\omega$  phase, which show the identical slopes in the P-V plot. Our results also reveal a 1.4% volume reduction as crystalline zirconium transforms from the  $\alpha$ - to the  $\omega$ - phase at a pressure near 5.5 GPa, which is comparable to a previous finding of 1.26% [Ref. 4]. The entire data set collected for the  $\omega$ -phase zirconium is shown in Fig. 4 and the derived EOS parameters are as follows:  $K_0 = 86(3)$  GPa,  $(\partial K / \partial T) = -2.4(7) \times 10^2$  GPa K<sup>-1</sup>,  $\alpha(300-875K) = 4.9(7) \times 10^5$  K<sup>-1</sup>, and  $(\partial \alpha / \partial P)_T = -3.2(9) \times 10^{-6}$  GPa<sup>-1</sup>K<sup>-1</sup>. The  $\alpha(300-875K)$  value represents an average thermal expansivity over the indicated temperature range. The ambient unit-cell volume obtained from the fitting is  $V_0 = 68.9(2)$  Å<sup>3</sup>, which is in excellent agreement with a previously reported value of 68.96 Å<sup>3</sup> (Ref. 9). Three isothermal compression curves, calculated from the fitted EOS parameters, are also illustrated in Fig.4 to compare with experimental data for the  $\omega$ -phase zirconium.



**Fig. 3** The room-temperature compression data for the  $\alpha$ - (solid circles) and  $\omega$ - (solid squares) phases and comparison with results obtained in previous studies. The bold solid curves are the least-squares fittings to the present experimental data. The dash-dot curve and an open square symbol indicate the extrapolated data for the  $\omega$  phase. Our results indicate a 1.4% volume reduction upon phase transition from the  $\alpha$  phase to the  $\omega$  phase. The LANL shock wave data refer to the recent unpublished work carried out at Los Alamos National Laboratory. The same zirconium specimens were used in the shock wave measurements and the present study.

It is worthwhile mentioning that the procedure for data collection for the  $\omega$  phase is different from a more conventional approach for high P-T diffraction experiments in which the data are collected on cooling to eliminate deviatoric stress built up during room-temperature compression [7]. Again, this is due to

the formation of zirconium glass and to the irreversible nature of the  $\beta$  phase-glass transition [8], which is also responsible for the limited data coverage in the experimental P-T space. It is therefore likely that there exist some errors in pressure and unit-cell volume measurements for the  $\omega$  phase, particularly for the data collected on cold compression. Since the incident x-ray beam in our diffraction experiments is perpendicular to the main stress vector superimposed on our cell geometry, we would expect a somewhat larger  $K_0$  value for the  $\omega$  phase if the volume measurements for both zirconium and NaCl were conducted under stress-free conditions. To achieve a better coverage of P-V-T data and to minimize the effect of deviatoric stress on the measurements, we recommend conducting future experiments at the temperatures below the  $\omega$ - $\beta$  phase boundary and collecting diffraction patterns under cooling conditions.



**Fig. 4** Pressure-volume-temperature data (symbols) measured for the  $\omega$  phase of zirconium metal. The curves represent results of the least-squares fit at indicated temperatures.

## Discussion

In this work, we have measured unit-cell parameters of  $\alpha$ ,  $\beta$ -, and  $\omega$ - zirconium metal at pressures up to 17 GPa and temperatures up to 973 K. From these measurements, we have derived, for the first time, thermoelastic properties for the three phases of zirconium. Our results indicate that the  $\alpha$  and  $\omega$  phases have similar ambient bulk modulus and its temperature derivative. Thermodynamics then implies that these two phases should also have similar pressure derivatives of volumetric thermal expansion, even though at ambient pressure the  $\omega$  phase appears to exhibit significantly larger thermal expansion than the  $\alpha$  phase (Table 4). These observations greatly extend our knowledge of the fundamental thermochemical properties on zirconium metal and are important to the understanding of the phase stability of different zirconium phases and to the theoretical modeling of these materials under dynamic conditions. Since elemental titanium and hafnium exhibit a sequence of structural changes similar to zirconium, future studies of the thermophysical properties on these two metals

may help us elucidate the role of d-electrons in the observed difference in the phase-transition pressure and temperature.

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