Room-temperature compression and equation of state of body-centered cubic zirconium

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Abstract
Zirconium (Zr) has properties conducive to nuclear applications and exhibits complex behavior at high pressure with respect to the effects of impurities, deviatoric stress, kinetics, and grain growth which makes it scientifically interesting. Here, we present experimental results on the 300 K equation of state of ultra-high purity Zr obtained using the diamond-anvil cell coupled with synchrotron-based x-ray diffraction and electrical resistance measurements. Based on quasi-hydrostatic room-temperature compression in helium to pressure $P = 69.4(2)$ GPa, we constrain the bulk modulus and its pressure derivative of body-centered cubic (bcc) $\beta$-Zr to be $K = 224(2)$ GPa and $K' = 2.6(1)$ at $P = 37.0(1)$ GPa. A Monte Carlo approach was developed to accurately quantify the uncertainties in $K$ and $K'$. In the Monte Carlo simulations, both the unit-cell volume and pressure vary according to their experimental uncertainty. Our high-pressure studies do not indicate additional isostructural volume collapse in the bcc phase of Zr in the 56–58 GPa pressure range.

Keywords: zirconium, equation of state, diamond-anvil cell, synchrotron, x-ray diffraction, high pressure

(Some figures may appear in colour only in the online journal)
1. Introduction

The group IVB metals titanium, zirconium (Zr), and hafnium (Hf) crystallize in the hexagonal close-packed (hcp) α-phase at ambient pressure and temperature. At room temperature, α-phase Zr transitions to the more open-packed hexagonal ω-phase (space group: P6/mmm) at pressure \( P = -5-12 \text{ GPa} \) [1]. Under further compression (\( P = -30-35 \text{ GPa} \)) at room temperature, the body-centered cubic (bcc) β-phase becomes stable [2–4]. Due to its resistance to corrosion and low neutron cross-section, Zr is conducive to use as cladding in nuclear reactors and various other engineering applications. Additionally, zirconium alloys are used as gasket material in high-pressure neutron scattering experiments and Zr oxides are used in refractory applications. The three solid phases of Zr have very different properties such as stiffness and brittleness which can play a role in failure mechanisms. Therefore, the use of Zr and its compounds in chemical, nuclear, biomedical, and refractory applications necessitate the accurate characterization of relevant physical parameters of Zr such as the bulk modulus (\( K \)). The bcc-Zr equation of state (EoS) has been measured at \( T = 300 \text{K} \) using a diamond-anvil cell (DAC) [5, 6] but these studies show discrepancies. For example, Akahama et al [5] reported a pressure derivative of the bulk modulus \( K' < 1 \) which leads to a softening in the pressure-volume (\( V \)) curve because of saturation in the bulk modulus-volume relationship. Conversely, Stavrou et al [6] determined that \( K' = -5 \). A first-order isostructural phase transition has been proposed to occur at \( P = -56-58 \text{ GPa} \) with an associated \( \approx 1\% - 4\% \) volume collapse [5, 6] but has not been supported by some theoretical studies [2, 7]. In previous studies, the EoS of β-Zr at \( P > 30 \text{ GPa} \) was determined using commercial-grade Zr along with a gold (Au) pressure marker in the DAC without the use of a pressure-transmitting medium (PTM) [5, 6]. Commercial-purity Zr may contain 2 wt\%-3 wt\% Hf [8, 9] along with significant amounts of oxygen (O) which can affect physical properties and behavior such as phase transitions [1]. Without a PTM, a sample compressed in a DAC experiences deviatoric stress and pressure gradients affecting the accuracy of EoS measurements. In this study, we determined the \( 300 \text{K} \) EoS and stability of ultra-high purity bcc β-zirconium under quasi-hydrostatic (helium PTM) and non-hydrostatic (no PTM) conditions.

2. Methods

We performed quasi-hydrostatic and non-hydrostatic DAC experiments measuring \textit{in situ} x-ray diffraction (XRD) of ultra-high purity, polycrystalline Zr [10] up to \( P = 74 \text{ GPa} \). We also measured the electrical resistance of the same ultra-high purity Zr under rapid, non-hydrostatic compression to \( P = 85 \text{ GPa} \). The 4-probe electrical resistance measurements were performed with a DAC equipped with a specialized anvil with electrodes patterned on the surface [11]. Further details of the electrical-resistance measurements can be found elsewhere [12]. We carried out the \textit{in situ} XRD experiments at high pressure collaborative access team (HPCAT) beamline 16-BM-D of the advanced photon source (APS). The diamonds had 200 \( \mu \text{m} \) flat culet and the x-ray beam had a wavelength of \( \lambda = 0.4133 \text{ Å} \) and was focused to a \( 4-5 \times 4-5 \mu \text{m}^2 \) spot size. The sample chamber was formed by laser-drilling [13] a 75 \( \mu \text{m} \) diameter circular hole in a stainless steel or rhodium gasket pre-indented to a thickness of \( \approx 30 \mu \text{m} \). We used a remotely-controlled gas membrane [14] to reliably collect data in \( \approx 1-2 \text{GPa} \) steps and data collection times were typically 300 s. For quasi-hydrostatic compression, Zr was loaded with a platinum (Pt) pressure marker [15] (figure 1) in helium at Sector 13 of the APS [16]. To draw comparisons to previous studies, we also conducted a non-hydrostatic XRD experiment by compressing only Zr and Pt without any pressure-transmitting medium. This non-hydrostatic XRD experiment took place separately from the rapid, electrical resistance experiment discussed above. Two-dimensional diffraction patterns collected on a Mar345 image plate were integrated using the Dioptas software [17]. We obtained \( V \) by least-squares fitting of the d-spacings of the (1 1 1), (2 0 0), and (2 2 2) peaks for the Pt pressure marker [15] and (1 1 0), (2 0 0), and (3 1 0) for β-Zr. These peaks were chosen because they did not overlap with each other and they had sufficient signal-to-noise to be distinguishable over the entire pressure range of the experiments. The \( P-V \) data were fit to the 3rd-order Birch–Murnaghan (BM) equation of state [18],

\[
P - P_{\text{ref}} = \frac{3}{2} K_{\text{ref}} \left[ \left( \frac{V_{\text{ref}}}{V} \right)^{\frac{7}{3}} - \left( \frac{V_{\text{ref}}}{V} \right)^{\frac{5}{3}} \right]
\times \left[ 1 + \frac{3}{4} (K'_{\text{ref}} - 4) \left( \left( \frac{V_{\text{ref}}}{V} \right)^{\frac{2}{3}} - 1 \right) \right].
\]

(1)

Here, \( V_{\text{ref}} \) is the volume at \( P_{\text{ref}} \) which is the lowest pressure that the ω-phase is completely absent, \( K_{\text{ref}} \) is the bulk modulus and \( K'_{\text{ref}} \) is its pressure derivative at the reference pressure. We measured \( P, P_{\text{ref}}, V, V_{\text{ref}} \), and fit for \( K_{\text{ref}} \) and \( K'_{\text{ref}} \) in order to accurately account for and fully propagate the errors in \( P, P_{\text{ref}}, V, \) and \( V_{\text{ref}} \). We developed a Monte Carlo (MC) fitting approach where we generated \( 10^5 \) synthetic datasets. Each Monte Carlo dataset had \( 10^5 \) random values for pressure (\( P_{\text{MC}} \)) and normalized volume (\( V_{\text{ref}}/V_{\text{MC}} \)). The Monte Carlo values were chosen from a normal distribution centered on our experimental (expt) value and having a standard deviation equivalent to the experimental error (\( \delta \)) such that

\[
\frac{V_{\text{ref}}}{V}_{\text{MC}} = \left( \frac{V_{\text{ref}}}{V} \right)_{\text{expt}} + (X) \left( \frac{V_{\text{ref}}}{V} \right)_{\text{expt}}
\]

and

\[
P_{\text{MC}} = P_{\text{expt}} + (X) P_{\text{expt}}.
\]

(3)
$X$ is a random number with 68%, 95%, and 99.7% probabilities to fall between $-1$ and $1$, $-2$ and $2$, and $-3$ and $3$, respectively. Each $P$-$V$ dataset was fit to equation (1) by a non-linear least squares method and weighted according to the uncertainty in pressure resulting in $10^5 K$-$K'$ pairs.

### 3. Results and discussion

Figure 2 shows Zr electrical resistance as a function of time during rapid, non-hydrostatic DAC compression [12]. The electrodes are made of tungsten and encapsulated in diamond [11] therefore dimensional changes of the electrodes are not significant. In our dynamic-DAC (d-DAC) experiments [12], a buffer is filled with gas then rapidly released to the membrane that drives compression of the DAC by triggering a solenoid valve. The pressure before gas release was 0.9 GPa and stabilized at 85.2 GPa following the rapid compression. During the rise in pressure, time-resolved XRD was used to constrain three intermediate pressures. Between $P = 1.2$ GPa and $P = 71.9$ GPa there is a discontinuity in the derivative of electrical resistance versus time curve which we attribute to the transition to the $\beta$-phase at $P \approx 35$ GPa (figure 2 inset). This interpretation is supported by the corresponding XRD which shows the presence of hcp-Zr at $P = 0.9$ GPa and bcc-Zr at $P = 71.9$ GPa. We do not observe any kinks that would be indicative of a phase transition with associated volume collapse at $P \approx 60$ GPa. Upon pressure increase from 71.9 GPa to 85.2 GPa, the bcc-Zr resistance and volume decrease by $-23\%$ and $-5\%$, respectively. Here, the $\alpha \rightarrow \omega$ transition is ambiguous perhaps due to kinetics [10, 20] or grain growth [1].

We conducted two quasi-hydrostatic experiments collecting XRD as a function of pressure. In the first experiment, we compressed straight to $P = 39$ GPa then collected XRD up to $P = 69$ GPa. During the second experiment, we compressed Zr from $P = 9$ GPa to $P = 51$ GPa.

Under quasi-hydrostatic conditions, the $\omega$-phase was present at $P \approx 36$ GPa and disappeared by 37 GPa based on the disappearance of the (0001), (2 1 1 1), (0002), and (2 1 1 2) diffraction peaks at $\approx 2.9$ Å, 1.8 Å, 1.5 Å, and 1.2 Å, respectively.
respectively, and merging of the (1 0 1 1) and (2 1 1 0) doublet to the single (1 1 0) peak of the β-phase at ~2.1 Å (figure 3). Our observation of the ω → β transition is consistent with Xia et al [4] who reported a non-hydrostatic transition pressure of 35 ± 5 GPa but discrepant with Akahama et al [5] and Stavrou et al [6] who place the transition at 33 GPa and ~31 GPa, respectively. In a third experiment, we non-hydrostatically compressed Zr from $P = 7$ GPa to $P = 74$ GPa collecting XRD during compression and decompression. The volumes during non-hydrostatic and quasi-hydrostatic compression are identical at $P = 39$ GPa with $V = 34.78(3)$ Å$^3$ and $V = 34.73(2)$ Å$^3$, respectively, and differ by <1% at $P = 69$ GPa. Our P-V curves (figure 4) are fit to a single EoS (equation (1)) with parameters reported in table 1. The $K$ and $K'$ values with uncertainties are the mean and standard deviation of $10^5$ Monte Carlo simulations. The Zr bulk modulus is ~10% greater under quasi-hydrostatic conditions compared to non-hydrostatic compression. Our non-hydrostatic bulk modulus (~200 GPa) is comparable to Akahama et al [5] but we report a significantly larger $K' = 2.6(1)$ compared to the fairly low $K' = 0.81$. The quasi-hydrostatic EoS determined in this work predicts a bulk modulus that is ~60% greater compared to the non-hydrostatic EoS of Stavrou et al [6] and therefore a stiffer structure. From the Monte Carlo simulations, the trade-off between $K$ and $K'$ is quantified in the form of error ellipses (figure 5). At the 95% confidence level, the quasi-hydrostatic and non-hydrostatic equations of state are different. Furthermore, there is not overlap between our results and previous studies [5, 6]. The $K'$ reported here can be expected to be more tightly constrained than the lower value of Akahama et al [5] because the present dataset consists of 44 more points over a similar pressure range. Therefore, we do not predict softening and overturn in the compression curve at $P = ~60$ GPa that would result from $K' < 1$.

We do not see the volume collapse associated with a first-order phase transition observed in previous studies at $P = ~56$–58 GPa [5, 6]. Impurities have been shown to have a significant effect on the alpha to omega phase transition in zirconium [1]. In this study, we used Zr with 35 ppm Hf, <50 ppm iron, vanadium, and O, <20 ppm aluminum and nitrogen, and 22 ppm carbon [10]. Therefore, one possibility is that differences in composition between the Zr used here and commercial-grade Zr used in previous studies may also play a role in the higher-pressure phase transitions in Zr. Since we observed a slight difference (~0.5%–1% from $P = ~40$ GPa to $P = ~50$ GPa) in volumes measured in two separate, essentially identical (i.e. same starting material, pressure marker and pressure transmitting medium) quasi-hydrostatic experiments (figure 4), factors such as compression history, initial strain state, or subtle deviatoric stresses may also be important. Theoretically, a first-order phase transition has been attributed to anharmonicity and a change in lattice dynamics of bcc-Zr at high pressure [10, 21]. However, other electronic structure calculations do not show a volume collapse in the 50–60 GPa pressure range [2, 7]. Despite a decades-long effort in theoretical and experimental studies of zirconium, there is still clearly a need for further investigations. Systematic experimental and theoretical studies on the effect of impurities on the equation of state and phase transitions in bcc-Zr are needed.
4. Conclusion

In conclusion, we constrained the EoS of ultra-high purity bcc-Zr under quasi-hydrostatic and non-hydrostatic conditions. We developed a Monte Carlo EoS fitting routine which provides more accurate estimates of equation of state parameters due to a larger sampling of $P$-$V$ space than performing a least-squares fit to a single experimental dataset. Monte Carlo sampling allows for full propagation of uncertainties in dependent and independent variables which is an improvement over traditional fitting methods that may underestimate the true uncertainty. It also allows for easy visualization of the correlation between $K$ and $K'$ that is often neglected and can lead to an overestimate of the pressure uncertainty when extrapolating to the volumes relevant to shock phenomena. Our equation of state studies do not support an isostructural volume collapse in the bcc-phase of Zr. The bcc-Zr EoS presented here will allow for more accurate modeling of Zr under the extreme conditions of nuclear reactors as well as high-pressure and refractory applications.

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