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Thermal equations of state of the α, β, and ω phases of zirconium

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We have conducted synchrotron x-ray diffraction studies on high purity zirconium metal at pressures (P) up to 17 GPa and temperatures (T) up to 973 K. Unit cell volumes (V) were derived from the refinements of x-ray diffraction data for the α, β, and ω phases of zirconium and fitted to a Birch-Murnaghan equation of state with the pressure derivative of the bulk modulus, $K_0{}'$, fixed at 4.0. The derived thermoelastic parameters for α zirconium are isothermal bulk modulus $K_0=92(3)$ GPa, temperature derivative of bulk modulus $(\partial K/\partial T)_P=-2.3(8)\times 10^{-2}$ GPa/K, volumetric thermal expansivity $\alpha_T=a+bT$ with $a=1.5(\pm 0.8)\times 10^{-5}\ \mathrm{K}^{-1}$ and $b=1.7(\pm 1.4)\times 10^{-8}\ \mathrm{K}^{-2}$, and the pressure derivative of thermal expansion $(\partial\alpha/\partial P)_T=-2.7(9)\times 10^{-6}\ \mathrm{GPa}^{-1}\ \mathrm{K}^{-1}$. For the β phase we obtained an isothermal bulk modulus of $K_T=66(3)$ GPa at 973 K and a unit-cell volume of $V(973\ \mathrm{K})=47.7(3)\ \mathrm{\AA}^3$ at ambient pressure. For the ω zirconium we obtained $K_0=90(5)$ GPa. Within the experimental errors, the K_0 values we determined for the α and ω phases and volumetric thermal expansion for the α phase are in agreement with previous experimental results, whereas all other thermoelastic parameters represent the first determinations for the three crystalline phases of zirconium metal.

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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. Zirconium occurs in more than 30 recognized mineral species and its chemical compounds, such as oxides and phosphates are often used in refractory applications for their resistance to thermal shock and their extremely low thermal conductivity. Generally speaking, zirconium-based alloys, such as Zr-Ti-Cu-Ni-(Al, Be, Nb), do not like to settle into a stable crystal structure and their atomic arrangements have tremendous tendency of being disordered. Such alloys have been demonstrated to exhibit extraordinary glass-forming ability and are currently the major species of bulk metallic glasses,[1] which exhibit intriguing thermomechanical and/or electronomagnetic properties. Most recently, the discovery of metallic glass formation in single-element zirconium and its wide stability field in P-T space[2] further demonstrates the unstable and noncrystalline nature of zirconium at the atomistic level. 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.[3–5]

Zirconium metal crystallizes into a hexagonal close-packed (hcp or α-phase) structure at ambient conditions. It transforms to a body-centered-cubic structure, commonly referred to β phase, at temperatures higher than 1136 K. With increasing pressure, the hcp phase transforms into another hexagonal structure called the ω phase,[6–9] which is not close-packed and has three atoms per unit cell, and the equilibrium phase boundary is described by $P(\mathrm{GPa})=2.8+2.2\times 10^{-3}T$ (K).[10]

The authors of Ref. 10 also determined the temperatures of the ω-β phase transition, and the phase boundary is given by $T=1028-15.5P$ (GPa) over a pressure range of 5–16 GPa. The β phase of zirconium, however, exhibits an extremely limited stability field due to the glass formation upon further heating. Previous EOS studies have been carried out on the α and ω phases of zirconium;[11,12] the pressure-volume measurements, however, were limited to ambient temperature. Thermal expansion data are only available for the α phase of zirconium and all the measurements were performed at atmospheric pressure.[13] 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[14] and inside planetary interiors.[15] However,

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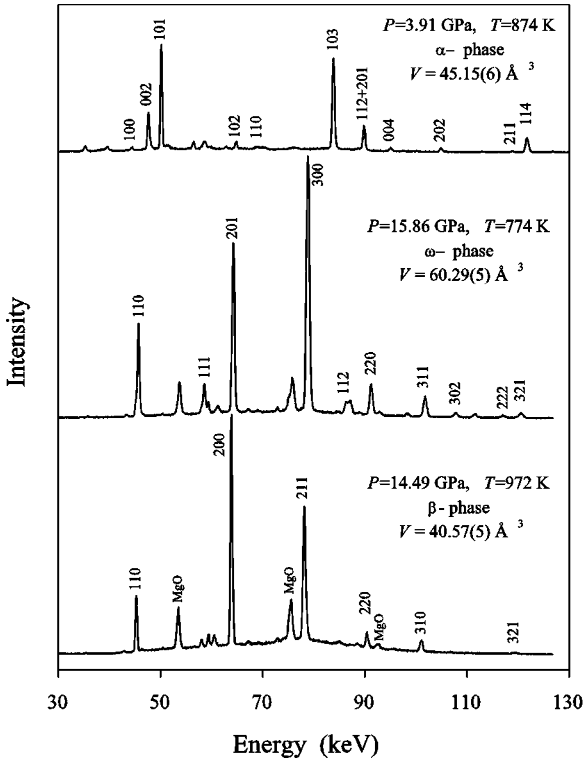

FIG. 1. Representative x-ray diffraction patterns used for the refinement of unit-cell parameters for the α, β, and ω phases of zirconium metal. The MgO diffraction lines were observed because the polycrystalline MgO octahedron was used as pressure transmitting medium in the "T-Cup" experiment. Other weak diffraction lines that are not indexed are from the materials surrounding the zirconium sample, such as NaCl (used as the pressure standard) and boron nitride (used as sample containers in the DIA experiments).

to date, the thermoelastic equations of state of most metals and ceramics have not been studied comprehensively.

EXPERIMENTAL METHODS

The starting zirconium metal has an hcp structure (α phase) and is of extremely high purity, with 35 ppm Hf, less than 25 ppm of C, N, Hf, Ti, and less than 50 ppm of O, V, and Fe. For comparison, most of the commercially available zirconium metal contains 2%–3% of hafnium and other impurities at much higher levels. High *P-T in-situ* x-ray diffraction experiments were conducted on polycrystalline zirconium metal using a DIA-type cubic anvil apparatus[16] and a "T-Cup" multianvil high-pressure system.[17] An energy-dispersive x-ray method was employed using white radiation from the superconducting wiggler magnet at beamline X17B2 of the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory and from the bending magnet at beamline 13-BM-D of the Advanced Photon Source (APS) of Argonne National Laboratory. Energy-dispersive patterns of the polycrystalline sample were collected with a Ge solid-state detector at APS and with a 13-element detector at NSLS, both at fixed Bragg angles (Fig. 1). The cell assemblies used in the experiments are similar to those previously described.[16,17] Briefly, in the DIA-type experiments, a mixture of amorphous boron and epoxy resin was used as pressure-transmitting medium, and amorphous carbon was used as furnace material. The zirconium samples were surrounded by NaCl and packed into a cylindrical container of boron nitride. In the "T-cup" experiments, the Co-doped MgO octahedron was used as pressure-transmitting medium with MgO as sample container, and rhenium foils were used as heating material. In each of five experiments we performed, NaCl was used as an internal pressure standard and temperatures were measured by a W/Re 25%–W/Re 3% thermocouple.

Temperature variations over the entire sample length at 1500 K were of the order of 20 K and 50 K, respectively, in the DIA and T-cup experiments, and the radial temperature gradients were less than 20 K at this condition. X-ray diffraction patterns were obtained for both samples and NaCl in close proximity to the thermocouple junction; errors in temperature measurements were thus estimated to be approximately 10 K. Pressures were calculated from Decker's equation of state for NaCl (Ref. 18) using lattice parameters determined from both x-ray and neutron diffraction profiles at each experimental condition. Five NaCl diffraction lines, 111, 200, 220, 222, and 420, were usually used for the determination of pressure. The uncertainty in pressure measurements is mainly attributed to statistical variation in the position of diffraction lines and is less than 0.2 GPa in the *P-T* range of this study. The effect of deviatoric stress on pressure determination or phase transition is minimal since a majority of the data reported here (except for those for ω phase at room temperature) were collected at temperatures above 573 K; under this condition deviatoric stress is expected to be fully relaxed in NaCl.[19]

RESULTS AND DISCUSSION

Five *in-situ* high *P-T* diffraction experiments have been performed at pressure and temperature conditions up to 17 GPa and 973 K. At ambient conditions, the starting α phase of zirconium metal has a unit-cell volume of 46.57 Å^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.[20] 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.

Examples of x-ray diffraction patterns for phase identification of α, β, and ω phases of zirconium are shown in Fig. 1. Unit cell parameters were refined for these phases and are listed as a function of pressure and temperature in Tables I–III. A modified high-temperature Birch-Murnaghan equation of state,[21–23] truncated at third order, was adopted to derive thermoelastic parameters based on the observed pressure-volume-temperature data for each crystalline phases of the zirconium. A general form of this equation of state is given by

$$P = 3K_T f(1+2f)^{5/2}\left[1 - \tfrac{3}{2}(4-K')f + \cdots\right], \qquad (1)$$

where

TABLE I. Unit-cell parameters of α (hcp) zirconium at high pressure and temperature conditions. In this table and Tables II and III the numbers in parentheses are standard deviations of unit-cell refinements and refer to the last digit.

P, GPa	T, K	a, Å	c, Å	V, Å^3
0.00	298	3.233(1)	5.146(1)	46.57(2)
0.79	298	3.217(2)	5.140(2)	46.08(4)
1.16	298	3.217(2)	5.126(3)	45.94(5)
1.85	298	3.218(3)	5.121(3)	45.72(7)
3.10	298	3.196(3)	5.104(2)	45.15(7)
3.14	298	3.195(2)	5.100(5)	45.09(7)
4.31	298	3.179(2)	5.086(1)	44.53(3)
4.93	298	3.176(1)	5.063(2)	44.22(2)
5.34	298	3.176(1)	5.061(3)	44.20(3)
1.01	473	3.221(2)	5.142(2)	46.19(4)
2.08	474	3.210(2)	5.123(2)	45.72(6)
3.36	474	3.195(2)	5.105(2)	45.13(6)
1.59	673	3.221(1)	5.135(1)	46.13(3)
1.27	674	3.222(2)	5.148(2)	46.27(4)
2.33	674	3.208(3)	5.130(2)	45.74(7)
3.63	674	3.192(3)	5.114(4)	45.12(8)
1.45	873	3.225(2)	5.154(1)	46.42(4)
2.63	873	3.206(2)	5.137(2)	45.74(5)
3.91	874	3.192(2)	5.118(3)	45.15(6)
2.67	918	3.211(3)	5.137(2)	45.87(7)

$$K_T = K_{T_0} + (\partial K/\partial T)(T - 300),$$

$$K' = \partial K/\partial P,$$

and

$$f = \tfrac{1}{2}[(V_T/V_{PT})^{2/3} - 1],$$

$$V_T = V_0 \exp\left(\int \alpha(0,T)dT\right).$$

In Eqs. (1), K_0 and K_T are isothermal bulk modulus at 300 K and at a higher temperature T, and $(\partial K/\partial T)$ and $(\partial K/\partial P)$ the temperature and pressure derivatives of the bulk modulus, respectively. V_0 is the unit-cell volume at ambient conditions, $V_T = V(0,T)$ at zero pressure and a given temperature, $V_{PT} = V(P,T)$ at simultaneous high P-T conditions, and α volumetric thermal expansion at the atmospheric pressure, given by $\alpha_T = a + bT - c/T^2$ (T in kelvin, see Ref. 24). Equation (1) modifies the isothermal Birch-Murnaghan equation of state by replacing K_0 with K_T and substituting V_0/V_P with V_T/V_{PT} so that the temperature effects are accounted for. Because of the limited pressure coverage that inhibits an accurate constraint on $K_0{}'$ for each of the three zirconium phases, we assume $K_0{}' = 4$ in Eq. (1) throughout the data reduction. Similarly, due to the limited thermal stability of three zirconium phases, we ignore the c/T^2 term in the thermal expansion and higher-order derivatives of the bulk modulus $\partial^2 K/\partial T^2$ and $\partial^2 K/\partial P \partial T$.

TABLE II. Unit-cell parameters of β zirconium at high pressure and temperature.

P, GPa	T, K	a, Å	V, Å^3
0.00	**973**	**3.627**	**47.73**[a]
6.38[c]	**973**	**3.526(1)**	**43.85(5)**
7.37	**972**	**3.518(5)**	**43.55(18)**
8.63[c]	898	3.494(1)	42.66(5)
8.63	**973**	**3.499**	**42.84**[b]
10.54	**974**	**3.478(5)**	**42.07(17)**
13.40	**975**	**2.449(7)**	**41.02(25)**
15.38[c]	873	3.420(2)	40.02(6)
14.82[c]	930	3.426(2)	40.21(7)
14.49[c]	**973**	**3.436(2)**	**40.57(5)**

[a] Obtained from the least-square fit to Birch-Murnaghan equation of state.

[b] Corrected from the data at 898 K and the estimated volume thermal expansion between 873 and 972 K at 14.49 and 15.38 GPa.

[c] Observed data from refinement of high P-T diffraction patterns; only the boldface type data for $T = 973$ K are used in the plot of Fig. 3.

For the α phase of zirconium all x-ray diffraction data were collected on cooling to minimize deviatoric stress built up during the room-temperature compression. As shown in Fig. 2, the collected volume data on α zirconium have a good P-T coverage within the stability field of this phase. From a least-squares fit to the P-V-T data using Eq. (1), we obtain $K_0 = 92(3)$ GPa, $(\partial K/\partial T)_P = -2.4(8) \times 10^{-2}$ GPa K^{-1}, and $\alpha = a + bT$, with $a = 1.5(\pm 0.8) \times 10^{-5}$ K^{-1} and $b = 1.7(\pm 1.4) \times 10^{-8}$ K^{-2}. Figure 2 shows that the thermoelastic param-

TABLE III. Unit-cell parameters of ω zirconium at various pressure and temperature conditions.

P, GPa	T, K	a, Å	c, Å	V, Å^3
0.00	298			68.94(2)[a]
0.00	298	5.039	3.316	68.96[b]
5.19	298	4.951(4)	3.078(3)	65.33(8)
5.57	298	4.936(2)	3.076(2)	64.89(5)
6.12	298	4.935(2)	3.067(2)	64.68(6)
7.76	298	4.904(3)	3.050(3)	63.51(8)
9.10	298	4.884(2)	3.040(2)	62.80(5)
9.31	298	4.890(3)	3.048(3)	63.14(8)
9.67	298	4.880(3)	3.041(3)	62.73(7)
10.48	298	4.864(3)	3.028(3)	62.04(7)
10.97	298	4.872(3)	3.031(3)	62.30(7)
12.09	298	4.849(3)	3.016(3)	61.41(7)
14.52	298	4.818(3)	3.006(4)	60.43(8)
16.99	298	4.791(3)	2.995(4)	59.54(7)

[a] Obtained from least-square fit to high-temperature Birch-Murnaghan equation of state.

[b] Reference 9.

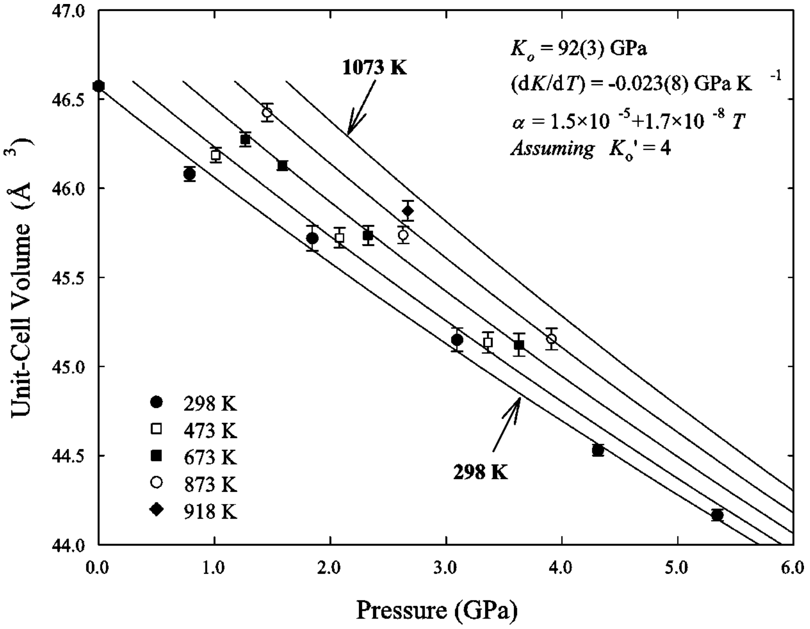

FIG. 2. Pressure-volume-temperature data (symbols) measured for the α phase of zirconium. The curves represent results of the least-squares fit using Eq. (1) at the indicated temperatures.

eters derived in the present study produce good fits to the experimental P-V-T data of the α-phase zirconium. Throughout this work, errors of thermoelastic parameters are those of the least squares fitting; uncertainties in the measurements of pressure, temperature, and unit-cell volumes were not included for error estimation. From the thermodynamic identity

$$(\partial\alpha/\partial P)_T = (\partial K/\partial T)_P K_{T0}^{-2} \tag{2}$$

the pressure derivative of the volume thermal expansivity, $(\partial\alpha/\partial P)_T$, is found to be $-2.7(9)\times 10^{-6}\ \mathrm{K}^{-1}\ \mathrm{GPa}^{-1}$. Within the experimental errors, the K_0 value and thermal expansion we obtained are in agreement with previous results (see Table IV), whereas the parameters $(\partial K/\partial T)_P$ and $(\partial\alpha/\partial P)_T$ are determined for the first time for the α phase of zirconium.

For the β-phase zirconium, the formation of the zirconium metallic glass at high P-T conditions leads to a very limited stability field in the pressure range of 6–16 GPa (Refs. 2 and 10), which prohibited us from collecting the volume data at temperatures above 973 K. As a result, only several data points (Table II) were obtained for the β phase in the five separate experiments we performed. Among them, the data point at $P=8.63$ GPa along the 973 K isotherm (Fig. 3) was obtained by the correction of the volume measurements at $T=898$ K and under other P-T conditions. The fit of these P-V data to Eq. (1) provides the first EOS data for the β-phase zirconium, with $K_{973\ \mathrm{K}}=66(3)$ GPa and $V_{973\ \mathrm{K}}=47.7(3)$ Å^3 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 β phase around 15 GPa (Ref. 10), 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 ω-phase zirconium upon room temperature compression and upon heating

TABLE IV. Summary of the equation of state parameters for three zirconium phases.

Phases	K_0 GPa	K_0'	$(\partial K/\partial T)_P$ GPa K^{-1}	α_T[a] K^{-1}, 10^{-5}	$(\partial\alpha/\partial P)_T$ GPa^{-1} K^{-1}, 10^{-6}	Study
α phase	92(3)	4.0	−0.023(8)	2.5(4)	−2.7(9)	*a*
	94(3)	3.10	−0.023(8)	2.4(4)	−2.6(9)	*a*
	102	3.10				*b*
				1.9		*c*
ω phase	90(5)	4.0				*a*
	109(6)	2.05				*a*
	104	2.05				*d*
β phase	$K_T(973\ \mathrm{K})=66(3)$ GPa					*a*

[a] Referring to average volumetric thermal expansion in the temperature range of 300–875 K. *a*, this study; *b*, Ref. 11; *c*, Ref. 13; *d*, Ref. 12. For direct comparison, the bulk moduli for the α and ω phases are also fitted with a K_0' value reported in previous studies. The numbers in parentheses are standard deviations (1σ) of least-squares fits using Eq. (1) and refer to the last digit.

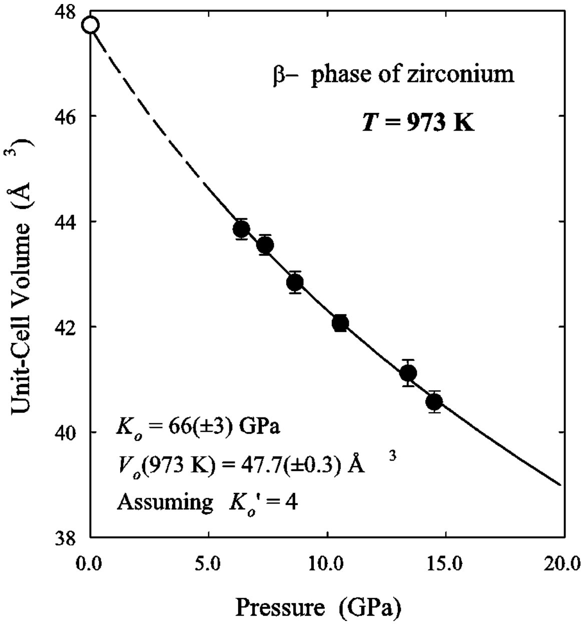

FIG. 3. The isothermal compression data (symbols) for the β phase of zirconium at 973 K. The solid curve represents results of the least-squares fit using Eq. (1). The dashed curve and an open circle indicate the extrapolated data from the solid curve.

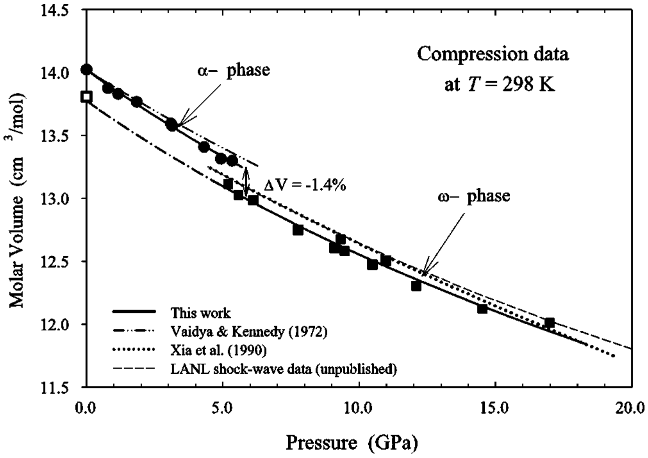

FIG. 4. The room-temperature compression data for the α (solid circles) and ω (solid squares) phases and comparison with results obtained in previous studies. The bold solid curves are the least-squares fittings to the present experimental data. The dashed-dotted curve and an open square symbol indicate the extrapolated data for the ω phase. Our results indicate a 1.4% volume reduction upon phase transition from the α phase to the ω 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.

to the ω-β phase transition in three experiments. The room-temperature data are plotted in Fig. 4 and compared with those of the α 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 ω phase, which show the identical slopes in the P-V plot. Our results reveal a 1.4% volume reduction as crystalline zirconium transforms from the α to the ω phase at a pressure near 5.5 GPa, which is comparable to a previous finding of 1.26% (Ref. 5). The fit of the P-V data of ω phase to Eq. (1) yielded $K_0 = 90(5)$ GPa, which, within the experimental uncertainties, is similar to the bulk modulus determined for the α phase (Table IV). This similarity is not surprised because both phases possess a hexagonal symmetry and similar atomic packing. Therefore, the structural distinctions are not significant between the two crystalline phases. This argument is further supported by the small molar volume changes (1.3%–1.4%) upon the phase transformation (Fig. 4) and by a relatively small hysterisis associated with transformation at 300 K ($\Delta P \approx 2-3$ GPa) (Refs. 5 and 10). The ambient unit-cell volume obtained from the fitting is $V_0 = 68.62(30)$ Å^3, which is in good agreement with a previously reported value of 68.96 Å^3 (Ref. 9).

At most pressure conditions of this work, the molar volumes for the ω phase are slightly lower than those of previous studies (Fig. 3). This most likely reflects the systematic errors that typically exist among measurements with different experimental techniques. Previous x-ray diffraction experiments,[13] for example, were carried out in diamond-anvil cells and therefore under strong nonhydrostatic conditions. The incident x-ray beam in these experiments was parallel to the maximum stress vector (σ_1) superimposed on the cell geometry, and, therefore, the diffraction signals sampled the lattice planes that corresponded to the minimum stress vector (σ_3). In our experiments the exact opposite relationship exists between the incident x rays and stress vectors.[25] This distinction can, at least partly, be responsible for the observed volume differences in Fig. 3. It is worthwhile mentioning that the procedures of data collection of this and previous studies[13] for the ω phase differ 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.[23] Again, this is due to the formation of zirconium glass and to the irreversible nature of the β phase-glass transition.[2,10] It is therefore likely that some errors in pressure and unit-cell volume measurements and hence in the bulk modulus determinations exist in both present and previous studies for the ω phase.

To minimize the effect of deviatoric stress on the P-V measurements and hence on the thermal equation of state determination for the ω phase, we have, in two of our experiments, collected the diffraction data at the temperatures up to 873 K but below the ω-β phase boundary (see Ref. 10). The volume data collected during cooling cycles, however, are found to be significantly different from those collected during heating cycles, and the results cannot be explained by the difference in the stress states under different temperature conditions. These observations seem to indicate some abnormal behaviors at elevated temperatures for the ω phase. Because these discrepancies require additional experimental confirmations and because the reasons behind these abnormal behaviors have currently not been understood, we will conduct further experiments and present the high-temperature data elsewhere for the ω phase of zirconium.

CONCLUDING REMARKS

In this work, we have measured unit-cell parameters of α-, β-, and ω-zirconium metal at pressures up to 17 GPa and temperatures up to 973 K. From these measurements, we have derived thermal and elastic properties for the three phases of zirconium. These results 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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