

# Experimental Constraints on the Phase Diagram of Elemental Zirconium

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## Introduction

Theoretical and experimental studies of phase stability trends in the periodic table have been one of the important goals in materials science and computational physics. It is now generally accepted that the valence d electrons per atom control structural phase stability in transition and rare-earth metals [1]. All three-transition series, excluding the four magnetic 3d metals, for example, show the canonical hcp→bcc→hcp→fcc sequence of structures as their atomic number increase. Since compression would lead to an increase in d-electron population by transfer of electrons from the s-orbital, similar structure sequences are expected to occur in individual transition metals with increasing pressure [1,2]. As one of the group IV transition metals and an important material used in nuclear and chemical applications, zirconium has been the subject of several experimental and theoretical studies at high pressure and temperature.

At ambient conditions, elemental zirconium crystallizes in a hexagonal close-packed (hcp or  $\alpha$  phase) structure. It transforms to a body-centered cubic structure, commonly referred as the  $\beta$  phase, at temperatures higher than 1136 K. With increasing pressure at room temperature, the  $\alpha$  phase transforms into another hexagonal structure called the  $\omega$  phase, which is not close-packed and has three atoms per unit cell. The transition from the  $\alpha$  to the  $\omega$  has been reported to occur at various pressures in the range of 2.0-6.0 GPa and the equilibrium transition at ambient temperature is generally believed to be at 2.2 GPa [2-5]. At further high pressure, the  $\omega$  phase of zirconium metal transforms to the  $\beta$  phase at  $35\pm 3$  GPa [Ref. 6]. At elevated temperatures, the  $\alpha$ - $\beta$  phase boundary has a  $dT/dP$  slope of 24 K/GPa and the  $\alpha$ - $\beta$ - $\omega$  triple point was estimated to be at  $5.5\pm 0.5$  GPa and 973 K. No previous studies, however, have been reported for the  $\alpha$ - $\omega$  phase boundary at temperatures higher than 298 K. Similarly, there only existed very limited data for the  $\omega$ - $\beta$  transition at high temperatures [7]. In this work, the phase diagram of zirconium has been studied at pressures up to 17 GPa and temperatures to 1273 K, with focuses on the  $\alpha$ - $\omega$  and  $\omega$ - $\beta$  transitions at high temperatures.

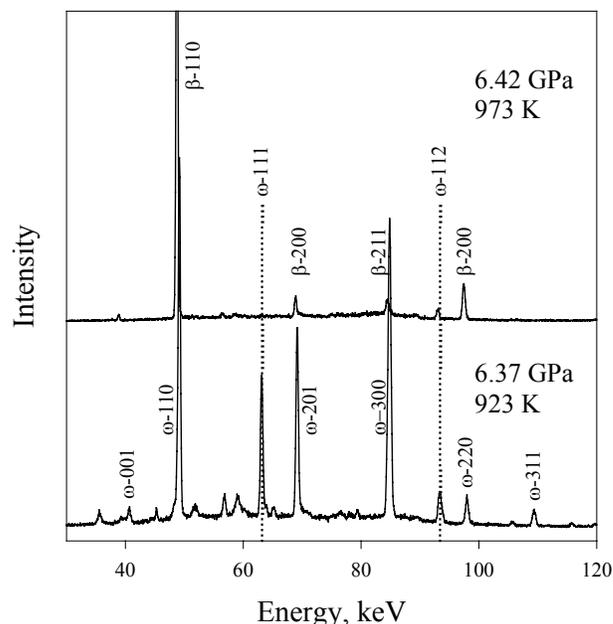
## Methods and Materials

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" multianvil 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 uncertainties are estimated to be less than 0.2 GPa in pressure and approximately 10 K in temperature. The effect of deviatoric stress on pressure determination or phase transition is minimal since a majority of the data reported here was collected at temperatures above 573 K, under which the deviatoric stress is expected to be fully relaxed in NaCl.

## Results

Five experiments have been performed at pressure and temperature conditions up to 17 GPa and 1273 K. The transition between  $\alpha$  and  $\omega$  phases can readily be distinguished by the appearance and disappearance of their characteristic diffraction peaks. For the  $\omega$ - $\beta$  transition, the transition from the  $\omega$  phase to the  $\beta$  phase is either identified by the disappearance of the superlattice diffraction lines, (111) and (112), of the  $\omega$  phase (Fig. 1), or bracketed by the two temperatures between which the characteristic diffraction peaks of the  $\omega$  phase show sudden decrease in their relative intensities (Fig. 2). The reversed transition from the  $\beta$  phase to the  $\omega$  phase is characterized by the first appearance of these diffraction peaks on cooling.



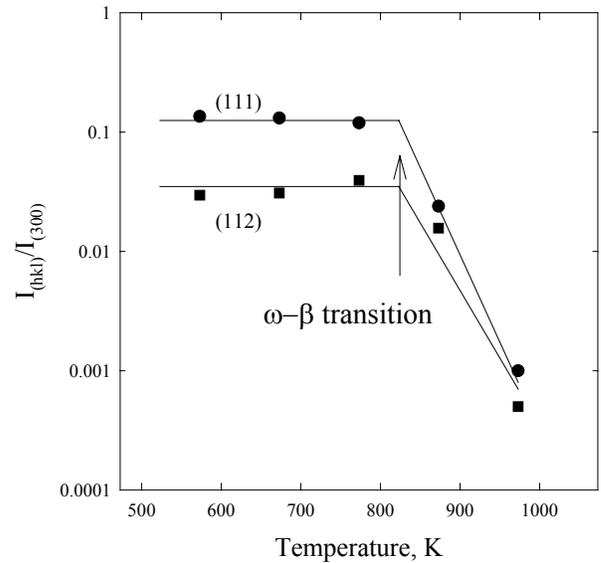
**Fig. 1** Selected x-ray diffraction patterns showing the transition from the  $\omega$  phase to the  $\beta$  phase on heating. The  $\omega$ - (111) and  $\omega$ - (112) peaks are characteristic lines of the  $\omega$  phase. Similarly, the reversed transformation from the  $\beta$  phase to the  $\omega$  phase was identified by the first appearance of the  $\omega$ - (111) and  $\omega$ - (112) peaks during cooling.

The experimental results are summarized in Fig. 3. With increasing pressure at 300 K, the transition to the  $\omega$  phase was observed between 5.5 and 6.5 GPa, and the calculated volume reduction at 6.0 GPa is 1.4%, which is comparable to a previous finding of 1.26% [Ref. 4]. The equilibrium phase boundary for the  $\alpha$ - $\omega$  transformation has a  $dT/dP$  slope of 473 K/GPa, and the extrapolated transition point at ambient temperature is located at 3.4 GPa.

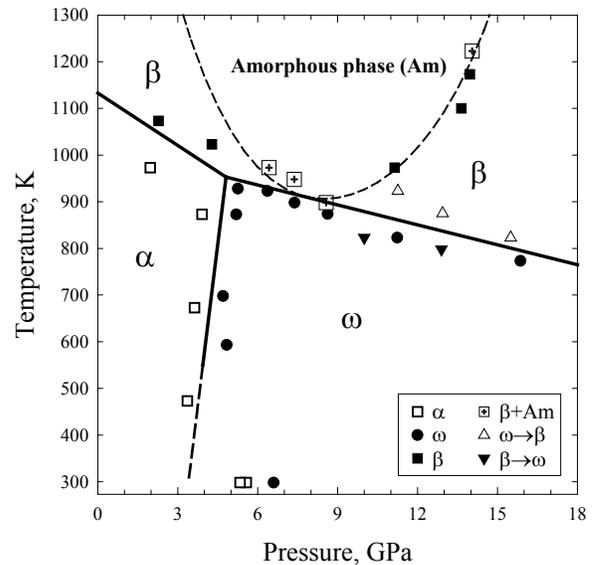
The difference between the observed and extrapolated pressures for the  $\alpha$ - $\omega$  transition at ambient temperature (Fig. 4) is a kinetically controlled phenomenon. For nucleation and growth process, kinetics of a solid-state transformation typically follows the well-known Avrami-Johnson-Mehl rate equation:  $\zeta = 1 - \exp(-kt^n)$ , where  $\zeta$  is the transformed volume fraction of a new phase,  $k$  the rate constant, and  $n$  a constant that characterizes the transition process. Nucleation is accompanied by the creation of the interface between new and original phases, which require energy. For transformation occurred at high pressures, the new phase usually has a larger density. This misfit creates elastic stress around nuclei and also consumes additional energy. As a result, the phase transformation cannot start immediately at the equilibrium phase boundary but only after some metastable overshoot in pressure ( $\Delta P$ ), which provides a sufficiently large driving force ( $\Delta G$ ) to overcome activation energy needed for transformation to occur. The thermodynamic driving force is described by  $\Delta G = \Delta V \Delta P$ , where  $\Delta V$  is the volume change upon transformation and  $\Delta P$  the difference between the observed pressure of the phase transformation and the pressure at equilibrium for a given temperature, also referred as kinetic barrier of the transformation. Our experimental results show that  $\Delta P$  is relatively small, less than 3.0 GPa at ambient temperature. This can be attributed to a relatively small volume difference ( $\Delta V = 1.4\%$ ) between the  $\alpha$  phase and the  $\omega$  phase, which, as expected, decreases with increasing temperature (Fig. 3). For comparison, kinetic barriers of the phase transitions in other systems such as silicates can be substantially larger.

The experimental constraints on the  $\omega$ - $\beta$  transition between 6 and 16 GPa indicate a negative dependence on pressure of the transition temperature, a trend that is in general agreement with previously suggested. Within our experimental conditions, the equilibrium phase boundary can be described by the equation  $T = 1028 - 15.5P$ , where  $P$  is in GPa and  $T$  in Kelvin. A linear extrapolation would result in a transition pressure of 47.0 GPa at ambient temperature, which is substantially higher than a previously determined pressure of  $35 \pm 5$  GPa [Refs. 6 and 7]. This discrepancy can be reconciled if the  $\omega$ - $\beta$  phase boundary is strongly curved at pressures between 16 and 35 GPa, an explanation that is supported by the molar volume changes observed at several P-T conditions of the phase transition,  $-0.80 \pm 0.1\%$  at 8.6 GPa/898 K and  $1.0 \pm 0.1\%$  at 15.3 GPa/873 K. In comparison, a volume decrease of 1.6% has been reported for the  $\omega$ -to- $\beta$  transition at 300 K [Refs. 6 and 7]. Based on the Clausius-Clapeyron equation for the first-order phase transition,  $dT/dP = \Delta V/\Delta S$ , where  $\Delta V$  and  $\Delta S$  are, respectively, molar volume and entropy changes of the transition, we would expect somewhat larger  $dT/dP$  values at higher pressures (or at lower temperatures), assuming that the  $\Delta S$  is insensitive to the variations of temperature. Alternatively, one cannot exclude the possibility that previous studies may have underestimated the

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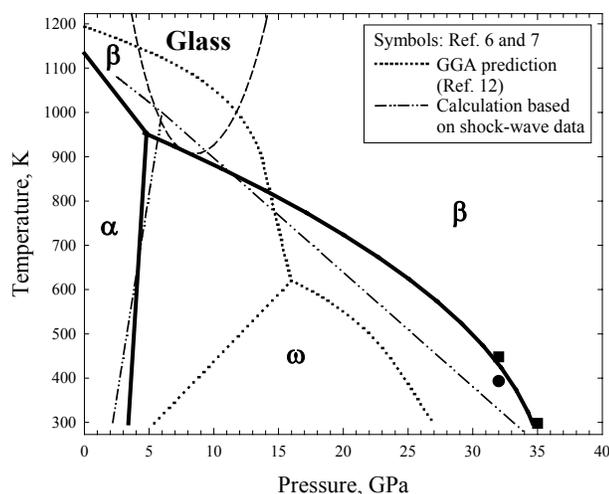
**Fig. 2** Variations of the normalized intensities with temperature at 15 GPa for the (111) and (112) diffraction lines of the  $\omega$  phase. The temperature of the  $\omega$ - $\beta$  phase transition is bracketed by a sudden decrease in the normalized intensities between 773 and 873 K.



**Fig. 3** Experimental constraints of the present study on the phase diagram of elemental zirconium. The phase boundary of the  $\alpha$ - $\beta$  transition is taken from Jayaraman et al. [Ref. 8], which is in general agreement with our observations. The  $\alpha$ - $\omega$ - $\beta$  triple point is determined by the interception of the  $\alpha$ - $\omega$  and  $\omega$ - $\beta$  phase boundaries.

Except for the three known crystalline forms, zirconium metal has been found to possess an extraordinary glass forming ability

(GFA) under high P-T conditions [9]. The pressure and temperature conditions for the formation of amorphous zirconium metal are shown in Fig. 3. In zirconium metal, formation of a glass occurs after the  $\alpha$  phase transforms to its high-pressure and high-temperature phases. These characteristics differ from the commonly observed pressure-induced amorphization, in which an amorphous phase is viewed as a kinetically preferred state of matter when transformation from a low-pressure phase to its high-pressure phase is hindered at ambient or low temperature [10].



**Fig. 4** Phase diagram of elemental zirconium constructed based on the available experimental data and theoretical calculations. The  $\omega$ - $\beta$  transition temperatures at 32-35 GPa (solid squares for the  $\beta$  phase and a solid circle for the  $\omega$  phase) are from the ref. 6 and 7. The  $\alpha$ - $\beta$  and  $\alpha$ - $\omega$  phase boundaries as well as the glass field are from Fig. 3. The GGA predictions are taken from the ref. [12]. The dash-dot curves correspond to the recent unpublished work carried out at Los Alamos National Laboratory.

## Discussion

The formation of an amorphous zirconium requires modifications of the high-temperature portion of the phase diagram for elemental zirconium. One of such revisions is that the  $\beta$  phase only possesses a limited stability field in the pressure range of 6-16 GPa (Figs. 3 and 4). Furthermore, there exists a confined region for amorphous zirconium to form at high temperature, which has not been well determined and are only constrained by the limited observations. However, our results suggest a general trend that at pressures above  $\sim 8$  GPa the GFA for zirconium diminishes with increasing pressure.

Phase stability and transition in zirconium metal has also been a subject of several theoretical studies. The phase boundaries calculated based on the recent shock wave measurements (Fig. 4) are in good agreement with the phase diagram determined in this study. The calculations based on first principles [11, 12], such as local density approximation (LDA) and generalized gradient approximation (GGA), have predicted the pressures for the  $\alpha$ - $\omega$  and  $\omega$ - $\beta$  transitions at 300 K that are comparable to the experimental observations. However, as illustrated in Fig. 4, the predicted phase boundaries for the  $\alpha$ - $\omega$  and  $\omega$ - $\beta$  transitions at

high temperatures as well as the  $\alpha$ - $\omega$ - $\beta$  triple point are substantially different from the present observations. This discrepancy indicates that anharmonic effects on the temperature-dependent properties, such as free energy, specific volume, Debye temperature, and Gruneisen constant, need to be further improved within the current framework of approximations. In addition, no calculations have yet predicted the formation of amorphous zirconium at high P-T conditions. This remains to be an interesting question that warrants theoretical investigations.

## Acknowledgments

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## References

- [1] R.S. Hixson, D.A. Boness, J.W. Shaner, J.A. Moriarty, Phys. Rev. Lett. **62**, 637 (1989).
- [2] Y.K. Vohra, J. Nucl. Matter. **75**, 288 (1978).
- [3] J.C. Jamieson, Science **140**, 72 (1963).
- [4] B. Olinger, J.C. Jamieson, High-Temp.-High Pressure **5**, 123 (1973).
- [5] S.K. Sikka, Y.K. Vohra, R. Chidambaram, Prog. Matter. Sci. **27**, 245 (1982).
- [6] H. Xia, S.J. Duclos, A.L. Ruoff, Y.K. Vohra, Phys. Rev. Lett. **64**, 204 (1990).
- [7] H. Xia, A.L. Ruoff, Y.K. Vohra, Phys. Rev. **B 44**, 10374 (1991).
- [8] A. Jayaraman, W. Klement, G.C. Kennedy, Phys. Rev. **131**, 644 (1963).
- [9] J. Zhang and Y. Zhao, Nature **430**, 332 (2004).
- [10] S.M. Sharma, S.K. Sikka, Progress Mater. Sci. **40**, 1 (1996).
- [11] F. Jona, P.M. Marcus, J. Phys.-Condens. Mat. **15**, 5009 (2003).
- [12] S.A. Ostanin, V.Y. Trubitsin, Phys. Rev. **B 57**, 13485 (1998).