

Experimental constraints on the phase diagram of elemental zirconium

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Abstract

The phase diagram of zirconium metal has been studied using synchrotron X-ray diffraction and time-of-flight neutron scattering at temperatures and pressures up to 1273 K and 17 GPa. The equilibrium phase boundary of the α - ω transition has a dT/dP slope of 473 K/GPa, and the extrapolated transition pressure at ambient temperature is located at 3.4 GPa. For the ω - β transition, the phase boundary has a negative dT/dP slope of 15.5 K/GPa between 6.4 and 15.3 GPa, which is substantially smaller than a previously reported value of -39 ± 5 K/GPa in the pressure range of 32–35 GPa. This difference indicates a significant curvature of the phase boundary between 15.3 and 35 GPa. The α - ω - β triple point was estimated to be at 4.9 GPa and 953 K, which is comparable to previous results obtained from a differential thermal analysis. Except for the three known crystalline forms, the β phase of zirconium metal was found to possess an extraordinary glass forming ability at pressures between 6.4 and 8.6 GPa. This transformation leads to a limited stability field for the β phase in the pressure range of 6–16 GPa and to complications of high-temperature portion of phase diagram for zirconium metal.

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1. 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 [1,2]. In other words, crystal structures in these elemental metals tend to have certain sequences when viewed as functions of atomic number. All three-transition series, excluding the four magnetic 3d metals, for example, show the canonical hcp \rightarrow bcc \rightarrow hcp \rightarrow fcc sequence of structures as their atomic number increase [2]. 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 [2,3]. 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 α phase) structure. It transforms to a body-centered cubic structure, commonly referred as the β phase, at temperatures higher than 1136 K. With increasing pressure at room temperature, the α phase transforms into another hexagonal structure called the ω phase, which is not close-packed and has three atoms per unit cell. The transition from the α to the ω 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 [3–6]. At further high pressure, the ω phase of zirconium metal transforms to the β phase at 35 ± 3 GPa [7,8].

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The phase transitions in zirconium metal have been investigated in the pressure range of 0–6.5 GPa using a differential thermal analysis [9] at elevated temperatures. The α – β phase boundary obtained from this study has a dT/dP slope of 24 K/GPa and the α – β – ω triple point was estimated to be at 5.5 ± 0.5 GPa and 973 K. No previous studies, however, have been reported for the α – ω phase boundary at temperatures higher than 298 K. Similarly, very limited data are available for the ω – β transition at high temperatures, except for those measured at 32 GPa and temperatures up to 448 K [8] and inferred from the shock-wave data at 540 K and 26 GPa [8,10]. In this work, the phase diagram of zirconium has been studied using synchrotron X-ray diffraction and time-of-flight neutron scattering at pressures up to 17 GPa and temperatures to 1273 K, with focuses on the α – ω and ω – β transitions at high temperatures.

2. 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, Al, and less than 50 ppm of O, V, and Fe. X-ray diffraction experiments were conducted using a DIA-type cubic anvil apparatus [11] and a ‘T-Cup’ multianvil high-pressure system [12]. 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 of Brookhaven National Laboratory and from the bending magnet at beamline 13-BM-D of the Advanced Photon Source of Argonne National Laboratory. In each of the three experiments we performed, NaCl was used as an internal pressure standard and temperatures were measured by a W/Re25%–W/Re3% thermocouple. The temperature variations over the entire sample length at 1500 K were of the order of 20 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.

The high P – T neutron diffraction experiments were performed on the High-Pressure Preferred Orientation Neutron Diffractometer (HIPPO) at the Los Alamos Neutron Science Center (LANSCE). With the newly developed 500-ton, toroidal anvil press TAP-98, we are currently able to accommodate in situ neutron-diffraction experiments up to 10 GPa and 1800 K with an improved toroidal cell assembly [13,14]. The zirconium metal of 4 mm diameter and 3 mm length was placed in a NaCl capsule, which serves as electric insulator and pressure standard. The cross-section of incident neutron beam has a diameter of 5 mm, which is defined by cadmium and B_4C collimators. The time-of-flight neutron diffraction patterns

of the polycrystalline sample were collected by eight detectors that are available for TAP-98, at a fixed Bragg angle of $2\theta = 90^\circ$ for the high P – T neutron diffraction experiments. The sample temperature was monitored using a W/5%Re–W/26%Rh thermocouple and was stable to within 10 K over a period of several hours of acquisition time under the present experimental P – T conditions.

Pressures were calculated from Decker’s equation of state for NaCl [15] 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 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 was collected at temperatures above 573 K, under which the deviatoric stress is expected to be fully relaxed in NaCl [16].

3. Results and discussion

Four experiments have been performed at pressure and temperature conditions up to 17 GPa and 1273 K, and the experimental P – T paths are shown in Fig. 1. The transition between α and ω phases can readily be distinguished by the appearance and disappearance of their characteristic diffraction peaks (Fig. 2). Determination of the transition

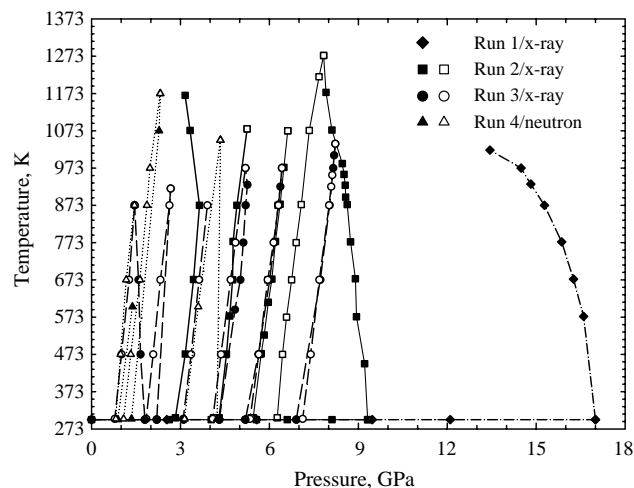


Fig. 1. Pressure–temperature paths for the four experiments conducted in this work. All symbols indicate the conditions at which X-ray and neutron diffraction data were collected, with solid ones corresponding to those collected on heating and open ones during cooling. In the experimental runs 1 and 2, zirconium metal was first compressed at room temperature to the maximum pressures, followed by heating to the target temperatures and subsequent cooling to room temperature. The same procedure was repeated several times at progressively lower pressures in Run 2. In Runs 3 and 4, the sample was first compressed at 298 K to 1.0–1.5 GPa and then followed by heating and cooling, with the same procedure repeated at higher pressures.

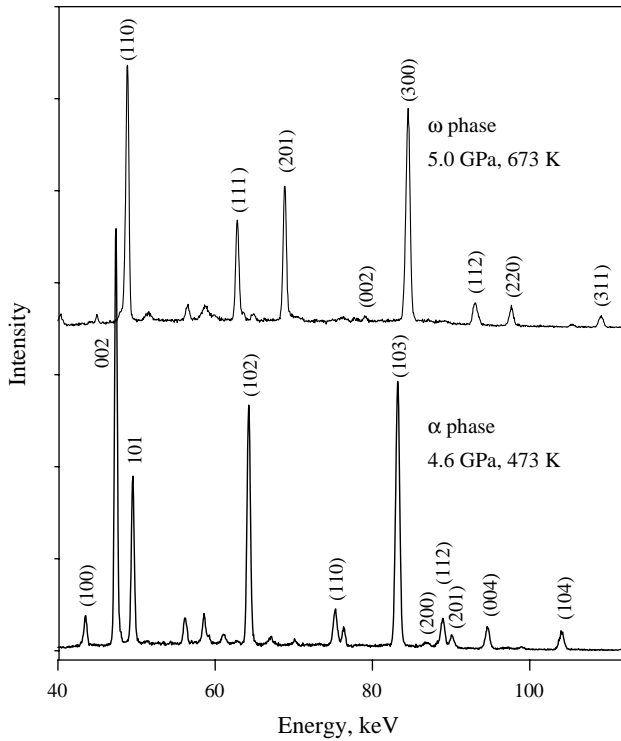


Fig. 2. Selected X-ray diffraction patterns showing phase identification between the α phase and the ω phase of zirconium metal. The X-ray diffraction patterns are chosen to present here and in Fig. 3a because the neutron diffraction patterns collected at the high P - T conditions show high signal-to-background ratios for both α and β phases and are therefore not as representative as the X-ray data for the present work.

temperatures for the ω - β phase transition, however, is not straightforward. It is known that the β phase is formed by the splitting of alternating (001) plane along the c axis of an ω structure into two (111) planes of the β phase. Therefore, diffraction pattern of the ω phase contains all the diffraction lines of the β phase and some characteristic lines associated its superlattice structure (Fig. 3a). In previous studies [7,8], the transition from the ω phase to the β phase at 32–35 GPa is identified by the disappearance of the superlattice diffraction lines, (111), (002), (112), and (031), of the ω phase, and the reversed transition from the β phase to the ω phase is characterized by the reappearance of these diffraction peaks. Under the pressure and temperature conditions of the present study, however, an irreversible transformation from the β phase to an amorphous phase has been observed [17], which makes it impossible to study the reversed transition from the β phase to the ω phase on cooling. As a result, the ω - β transition in this work are bracketed by the two temperatures between which the characteristic diffraction peaks of the ω phase show sudden decrease in their relative intensities (Fig. 3b). Our experimental results suggest that the temperatures for the ω - β transition would have been overestimated by 50–100 K if the transition had been defined by the disappearance of all characteristic peaks of the ω phase, a result that can obviously be attributed to the kinetics of the phase

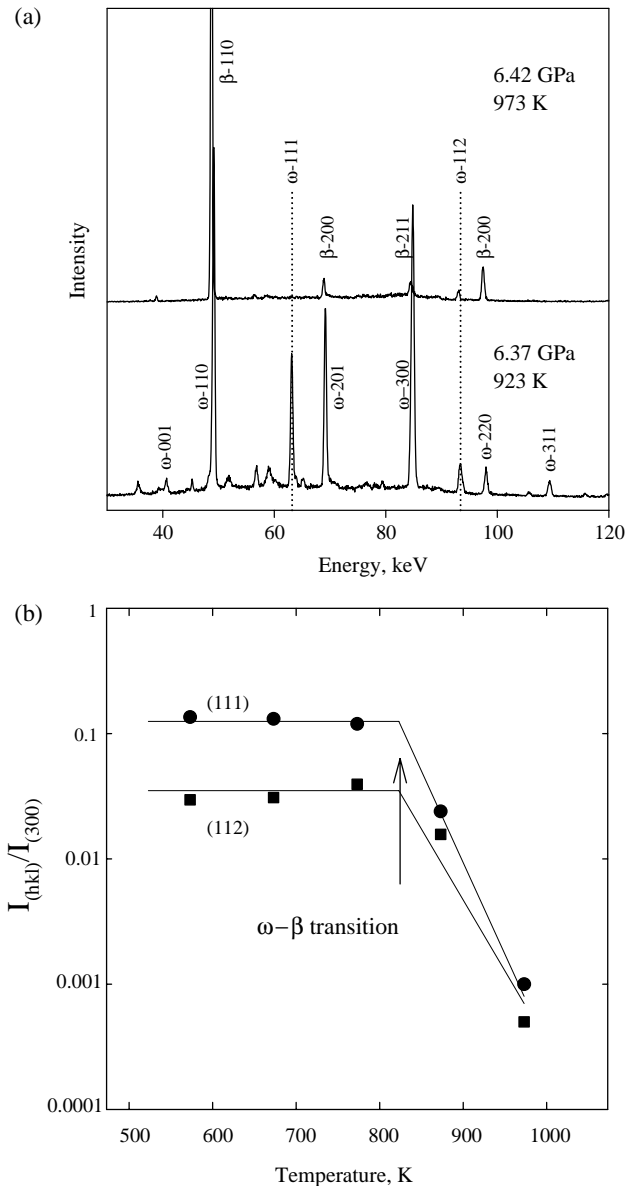


Fig. 3. (a) Selected X-ray diffraction patterns showing the transition from the ω phase to the β phase on heating. The ω -(111) and ω -(112) peaks are characteristic lines of the ω phase. (b) Variations of the normalized intensities with temperature at 15 GPa for the (111) and (112) diffraction lines of the ω phase. The temperature of the ω - β phase transition is bracketed by a sudden decrease in the normalized intensities between 773 and 873 K.

transformation. Therefore, our observations provide an upper bound in temperature for the ω - β phase transition.

At ambient conditions, the α phase of zirconium metal has a unit-cell volume of 46.3 \AA^3 and a c/a ratio of 1.592 [18], which is in agreement with chemical analysis that shows extremely low oxygen content and with previously established relationship between unit-cell parameters and oxygen content [19]. With increasing pressure at ambient temperature, the transition to the ω phase was observed between 5.5 and 6.5 GPa in two independent experiments (Fig. 4), and the calculated volume reduction at 6.0 GPa is

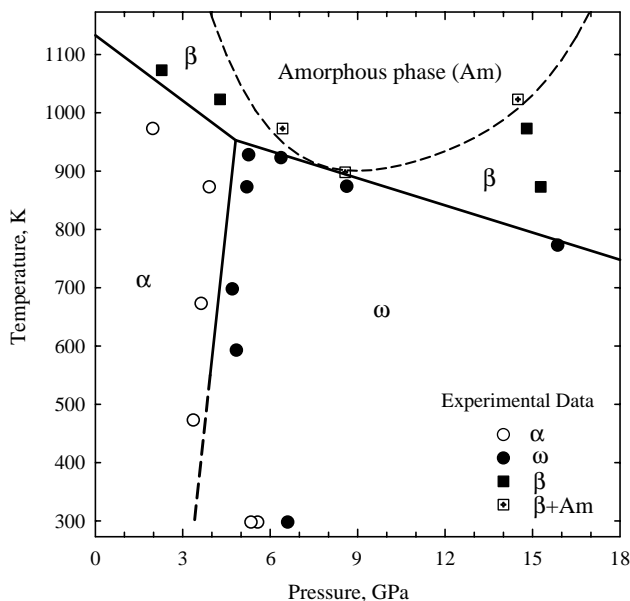


Fig. 4. Experimental constraints of the present study on the phase diagram of elemental zirconium. Consistent with previous experimental and theoretical studies, a negative dT/dP slope is indicated for the ω - β transition. The phase boundary of the α - β transition is taken from Jayaraman et al. [9], which is in general agreement with our observations from neutron diffraction. The α - ω - β triple point is determined by the interception of the α - ω and ω - β phase boundaries. The P - T field of amorphous zirconium, although highly speculative, is determined based on the observations from Ref. [17] and additional data presented in Figs. 5 and 6.

1.4%, which is comparable to a previous finding of 1.26% [5]. The experimental constraints on the α - ω transition at high temperatures are summarized in Fig. 4. The equilibrium phase boundary has a dT/dP slope of 473 K/GPa, and the extrapolated transition point at ambient temperature is located at 3.4 GPa, which is more than 1 GPa higher than had generally been believed [3–6]. In previous studies, however, significant deviatoric stress is expected to present on static compression at ambient temperature. The transition pressure determined in present study should be therefore viewed as a more accurate value as it is obtained from extrapolation of the high-temperature data. In all experiments we performed, both the recovered and starting samples do not show any Raman shifts except for the surface oxidation, indicating that zirconium metal remains in an elemental form under the present experimental conditions.

The difference between the observed and extrapolated pressures for the α - ω 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 ζ is the transformed volume fraction of a new phase, k the rate constant, and n a constant that characterizes the transition process [20]. 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 (ΔP), which provides a sufficiently large driving force (ΔG) to overcome activation energy needed for transformation to occur. The thermodynamic driving force is described by $\Delta G = \Delta V \Delta P$, where ΔV is the volume change upon transformation and ΔP 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 [21]. Our experimental results show that ΔP 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 α phase and the ω phase, which, as expected, decreases with increasing temperature (Fig. 4). For comparison, kinetic barriers of the phase transitions in other systems such as silicates can be substantially larger. Taking the coesite–stishovite phase transition in SiO_2 as an example [22], no transformation was observed at temperatures below 773 K when the pressures were well above the equilibrium transition points. This is primarily due to a substantially large volume difference between the two SiO_2 polymorphs ($\Delta V = 32\%$) and to a large activation energy needed to change the Si coordination from 4-fold in coesite to 6-fold in stishovite.

The experimental constraints on the ω - β transition between 6 and 16 GPa is also shown in Fig. 4, which indicates 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 ± 5 GPa [7,8]. This discrepancy can be reconciled if the ω - β phase boundary is strongly curved at pressures between 16 and 35 GPa, an explanation that needs further experimental efforts but 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 ω -to- β transition at room temperature [7,8]. Based on the Clausius–Clapeyron equation for the first-order phase transition, $dT/dP = \Delta V / \Delta S$, where ΔV and ΔS 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 ΔS is insensitive to the variations of temperature. Alternatively, one cannot exclude the possibility that previous studies may have underestimated the transition pressure. Under non-hydrostatic

conditions, the stress concentration in previous room-temperature experiments [7,8] would enhance the transition to occur at lower pressures than under hydrostatic conditions. This is a type of phenomenon that has often been observed in materials, such as FeO [23] and silicon [24].

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 [17]. The pressure and temperature conditions for the formation of amorphous zirconium metal are shown in Fig. 4. These observations demonstrate that a solid amorphous phase of zirconium metal can be formed at pressures above 6 GPa and at temperatures as low as 898 K, which is far below a melting temperature of 2128 K for zirconium metal at ambient pressure. The β phase appears to be particularly unstable relative to this amorphous phase, in the sense that the temperature interval between the first appearance of the β phase and the first appearance of an amorphous zirconium is extremely small, less than 25 K in the pressure range of 6.4–8.6 GPa (Fig. 5). In addition, no crystallization of the β or the ω phase from an amorphous zirconium was observed on slow cooling to ambient temperature and on subsequent heating to 1173 K at the pressures well below the glass forming conditions [17].

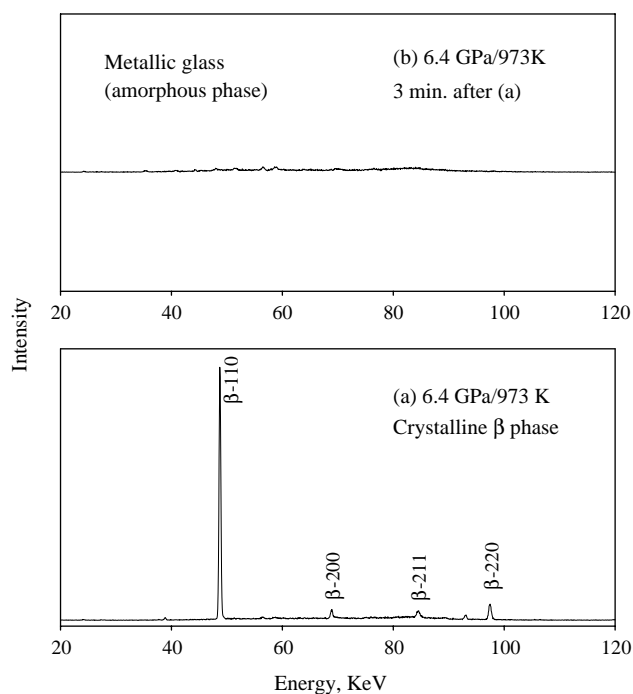


Fig. 5. Time-dependent X-ray diffraction patterns illustrating the instability of the β phase relative to amorphous zirconium at 6.4 GPa and 973 K. Intensities have been normalized to the data acquisition time, and the two panels are plotted within an identical intensity range. Formation of a glass is identified by the disappearance of all diffraction peaks of the β phase and by a significant reduction in the diffraction intensity. The weak diffraction peaks observed in the amorphous phase are also present in the patterns collected for crystalline zirconium phases, which can be indexed as materials surrounding the zirconium sample (i.e. NaCl, boron nitride and Al_2O_3).

In zirconium metal, formation of a glass occurs after the α phase transforms to its high-pressure and high-temperature phases. This characteristic differs 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 [25]. In this regard, it may be necessary to describe amorphous zirconium as an equilibrium high-pressure phase, which, however, cannot be attributed to the high-pressure melting of crystalline zirconium as discussed by Zhang and Zhao [17]. We therefore conclude that the observed crystalline-to-glass transition in this work represents a novel class of solid-state reaction at elevated temperature. This new phenomenon would eventually lead to the ‘melting’ of amorphous zirconium, which is in accord with a well-accepted expectation that an amorphous phase is thermodynamically continuous with a liquid.

The formation of an amorphous zirconium requires modifications of the high-temperature portion of the phase diagram for elemental zirconium. One of such revisions, as discussed in the preceding paragraph, is that the β phase only possesses a very limited stability field in the pressure range of 6–16 GPa (Fig. 4). Furthermore, there exists a confined region for amorphous zirconium to form at high temperatures, which has not been well constrained by the present study. This P - T space, however, can be speculated based on the following experimental observations [9,17]: (1) the α phase does not possess the glass forming ability and (2) zirconium metal can only be partially transformed to an amorphous phase at 1023 K and 14.5 GPa (Fig. 6) and therefore shows a somewhat diminishing GFA with increasing pressure between 9 and 15 GPa. Further experimental efforts are needed to map out the P - T space for the formation of zirconium metallic glass as well as to investigate its thermal stability at ambient 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 are shown in Fig. 7, which are in good agreement with the phase diagram determined in this study. The calculations based on first principles [26–28], such as local density approximation (LDA) and generalized gradient approximation (GGA), have predicted the pressures for the α - ω and ω - β transitions at ambient temperature that are comparable to the experimental observations. This success led to an overall confidence in these models, particularly in GGA, for calculating phase diagrams of zirconium metal and possibly more complicated systems [27]. However, as illustrated in Fig. 7, the predicted phase boundaries for the α - ω and ω - β transitions at high temperatures as well as the α - ω - β 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 Grüneisen constant, need to be further improved

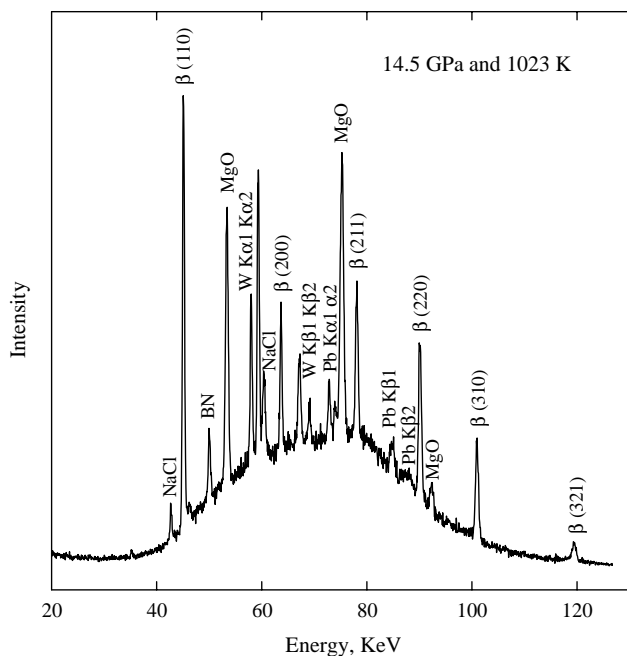


Fig. 6. X-ray diffraction pattern of zirconium metal at 14.5 GPa and 1023 K. Zirconium metal is observed to exhibit a somewhat diminishing glass forming ability when compared to the observations at lower pressures of 6.4 and 8.6 GPa [17] (see also Fig. 5). MgO diffraction lines are from the pressure medium used in the T-Cup experiment. The fluorescence peaks are from those of tungsten, which was used to define collimation of the multi-element detector, and those of lead, which was used as a shielding material to avoid air scattering.

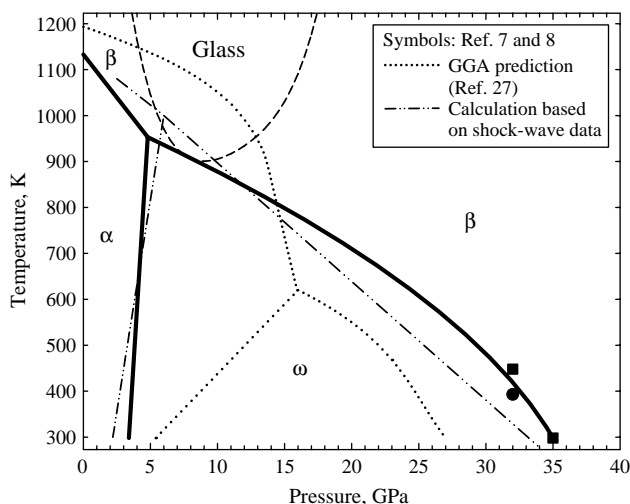


Fig. 7. Phase diagram of elemental zirconium constructed based on the available experimental data and theoretical calculations. The ω - β transition temperatures at 32–35 GPa (solid squares for the β phase and a solid circle for the ω phase) are from the work by Xia et al. [7,8]. These data, along with those plotted in Fig. 4, are used to determine the ω - β phase boundary. The α - β and α - ω phase boundaries as well as the glass field are from Fig. 4. The GGA predictions are taken from Ref. [27]. The dash-dot curves correspond to the recent unpublished work carried out at Los Alamos National Laboratory.

within the current framework of approximations. In addition, no calculations or experiments have yet provided any explanations regarding the driving mechanisms for the formation of amorphous zirconium at high P - T conditions. This remains to be an interesting question that warrants both theoretical and experimental efforts.

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