

## High P-T phase transitions and P-V-T equation of state of hafnium

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## High $P$ - $T$ phase transitions and $P$ - $V$ - $T$ equation of state of hafnium

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We measured the volume of hafnium at several pressures up to 67 GPa and at temperatures between 300 to 780 K using a resistively heated diamond anvil cell with synchrotron x-ray diffraction at the Advanced Photon Source. The measured data allows us to determine the  $P$ - $V$ - $T$  equation of state of hafnium. The previously described [Xia *et al.*, Phys. Rev. B **42**, 6736–6738 (1990)] phase transition from *hcp* ( $\alpha$ ) to simple hexagonal ( $\omega$ ) phase at 38 GPa at room temperature was not observed even up to 51 GPa. The  $\omega$  phase was only observed at elevated temperatures. Our measurements have also improved the experimental constraint on the high  $P$ - $T$  phase boundary between the  $\omega$  phase and high pressure *bcc* ( $\beta$ ) phase of hafnium. Isothermal room temperature bulk modulus and its pressure derivative for the  $\alpha$ -phase of hafnium were measured to be  $B_0 = 112.9 \pm 0.5$  GPa and  $B_0' = 3.29 \pm 0.05$ , respectively.  $P$ - $V$ - $T$  data for the  $\alpha$ -phase of hafnium was used to obtain a fit to a thermodynamic  $P$ - $V$ - $T$  equation of state based on model by Brosh *et al.* [CALPHAD **31**, 173–185 (2007)]. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4726211>]

### I. INTRODUCTION

Hafnium has a hexagonal-close packed ( $\alpha$ -phase) structure typical of group IV transition metals (Ti, Zr). At ambient pressure ( $P$ ), hafnium transforms from a room-temperature  $\alpha$  to a body-centered cubic ( $\beta$ -phase) structure at temperatures ( $T$ ) above 2030 K. Upon increasing the pressure at room-temperature, hafnium is reported to undergo a sequence of  $\alpha \rightarrow \omega$  (simple hexagonal)  $\rightarrow \beta$  phase transitions, which is also typical of other group IV metals.<sup>1</sup> Although it is generally considered that hafnium would follow the general  $\alpha$ - $\omega$ - $\beta$  high  $P$ - $T$  phase diagram consistent with many other metals with *hcp* structure at ambient  $P$ - $T$  conditions.<sup>1,2</sup> Phase transitions for Hf have never been experimentally examined at simultaneous high pressures and high temperatures using static compression techniques. We undertook this study of hafnium at high pressure and temperature to produce data with which we could construct the phase diagram and the equation of state for the metal. Previous equation of state (EOS) measurements of hafnium has only been carried out at room temperature. In this study, we performed measurements of volume ( $V$ ) of hafnium at simultaneous high pressure and high temperature to obtain a  $P$ - $V$ - $T$  EOS for the  $\alpha$ -phase of hafnium. The thermophysical parameters obtained from the  $P$ - $V$ - $T$  EOS are fundamental properties of the material, which could be used to calculate the thermodynamic properties of  $\alpha$ -Hf at high pressure and high temperature.

### II. EXPERIMENT METHODS

Commercially obtained hafnium metal powder of 99.5% purity, 325 mesh (Sigma Aldrich) was ground with mortar and pestle to decrease the grain size to less than  $\sim 5$ – $10$   $\mu\text{m}$ . X-ray diffraction measurements of hafnium under pressures of up to 67 GPa and temperatures in the range between room

temperature and 780 K were conducted on the beamline IDB-16 ( $\lambda = 0.3981$  Å) of the advanced photon source (APS) at Argonne National Laboratory. Diffracted x-rays were collected between Bragg angles of  $2\Theta = 5^\circ$  and  $2\Theta = 25^\circ$  using a MAR3450 imaging detector. Measurements at high pressure were carried out using the diamond anvil cell (DAC) of symmetrical type with diamonds 300  $\mu\text{m}$  diameter culet. The gasket used in the DAC was made out of 302-type stainless steel and indented to thickness of  $\sim 40$   $\mu\text{m}$  and a hole for the sample was drilled with a diameter of 100  $\mu\text{m}$ . Platinum was used as an internal pressure standard and the DAC pressure was controlled remotely using a compressed gas membrane. Neon gas was used as a quasi-hydrostatic pressure transmitting medium. Neon loading into the DAC was done using the high pressure gas loading system in GSE-CARS. In one compression run, NaCl was alternatively used instead of neon because of technical difficulties associated with gas loading. The heating was done using a whole-cell external resistive heater provided by HPCAT and the temperature was measured using a thermocouple placed in contact with one of the diamonds. Due to the whole-cell heater design, the temperature variations within the volume containing the thermocouple and the sample are taken to be negligible; errors in absolute temperature measurement are estimated to be not more than  $\sim 5$  K. Sample to detector distance and other diffraction geometry parameters were calibrated using a CeO<sub>2</sub> standard. 2D angle-dispersive diffraction images were processed using the software FIT2D (Ref. 3) to generate the intensity versus two-theta diffraction patterns. Each diffraction peak was indexed and fitted with a pseudo-Voigt function to determine its  $d$ -spacing. To determine the  $a$  and  $c$  lattice parameters of  $\alpha$ -phase of hafnium,  $d$ -spacings of diffraction peaks (100), (002), (101), and (102) were fitted using least-squares to a hexagonal (space group:  $P6_3/mmc$ ) lattice. Pressures were calculated based on  $P$ - $V$ - $T$  equation of

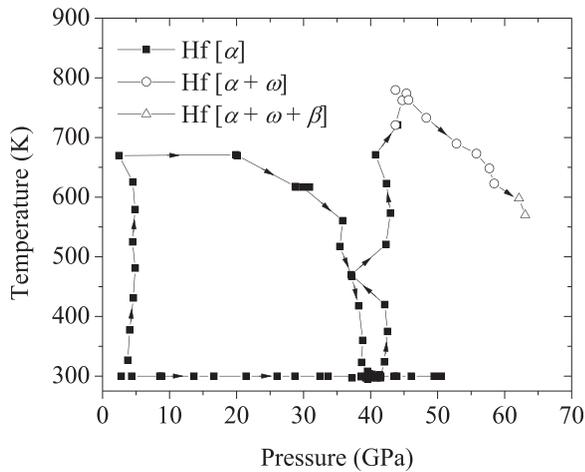
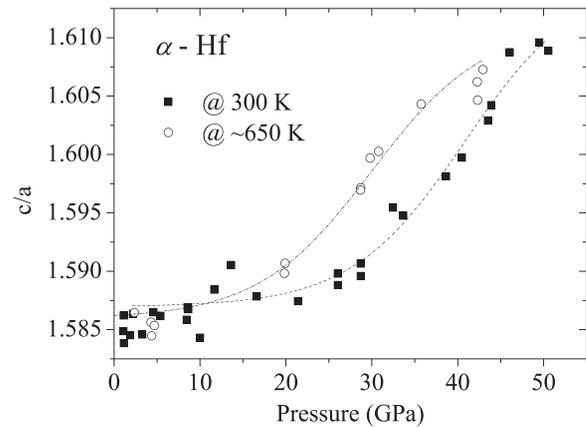


FIG. 1. P-T range surveyed in our experiment.

state of platinum by Jamieson *et al.*<sup>21</sup> Two platinum diffraction lines, (111) and (200) were used for determination of pressure.

### III. RESULTS AND DISCUSSION

Hafnium metal was first compressed to a nominal pressure which is required to seal the neon pressure medium between the diamonds and the gasket. The temperature was increased in steps to a given maximum, followed by a pressure increase in several steps. Subsequently, the temperature was decreased in steps back to room temperature and the pressure was increased again in several steps. Two heating  $\rightarrow$  compression  $\rightarrow$  cooling  $\rightarrow$  compression cycles were

FIG. 2. Variation of  $c/a$  ratio of  $\alpha$ -hafnium (*hcp*) unit cell with increasing pressure at two different temperatures.

completed. A plot with a spread of our experimental P-V-T data points is shown in Fig. 1.

#### A. High pressure phases of hafnium

Analysis of the obtained x-ray patterns shows that hafnium has two phase transitions in the studied  $P$ - $T$  range. Previously reported  $\alpha \rightarrow \omega$  phase transition<sup>1</sup> was not observed at room temperature in the pressure range studied (up to 51 GPa). According to Xia *et al.*, the  $\alpha \rightarrow \omega$  phase transition in hafnium occurs at 35 GPa under room temperature compression. Hafnium metal used in our experiment is of similar purity to that used by Xia *et al.* (Xia *et al.*: 99.6% purity, our experiment: 99.5% purity) therefore the discrepancy between  $\alpha \rightarrow \omega$  phase transition measurements of Xia *et al.* and our

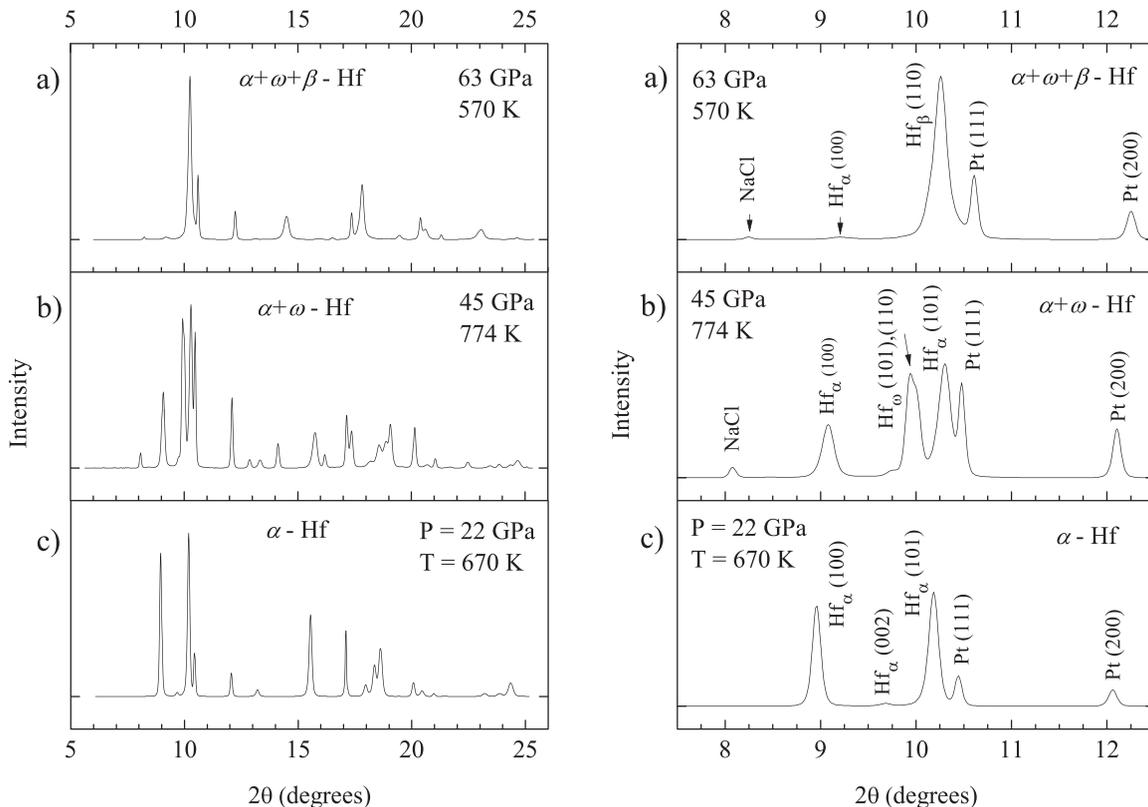


FIG. 3. Representative x-ray diffraction patterns of our sample in several P-T regimes.

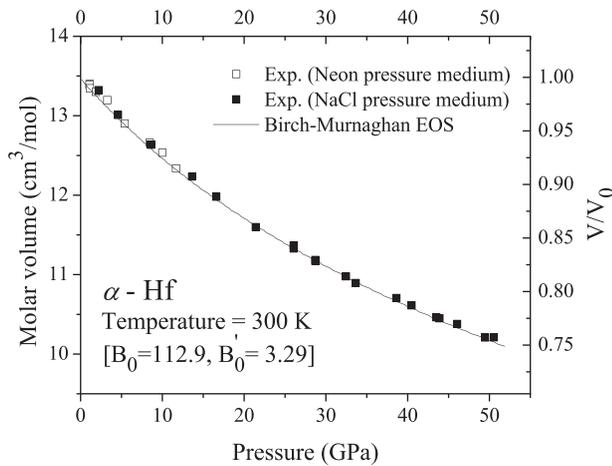


FIG. 4. Pressure-volume relation of  $\alpha$ -phase hafnium at room temperature.

experiment is not due to the differences in sample purity. Compression experiments by Xia *et al.* were done without any pressure transmitting media therefore their observation may be attributed to large non-hydrostaticity. The effects of non-hydrostaticity on the  $\alpha \rightarrow \omega$  phase transition pressure of other group-IV metals have been reported before.<sup>4,5</sup> It is generally accepted that in Ti, Zr, and many alloys,  $\alpha \rightarrow \omega$  phase transition is of a pressure activated martensitic type, not involving any long diffusion paths. The kinetics of  $\alpha \rightarrow \omega$  transition are slow due to a slow  $\omega$ -phase nucleation rate and non-hydrostatic stress is known as one possible driving force for speeding up such transitions.<sup>6</sup> The  $\alpha \rightarrow \omega$  phase transition was only observed in our x-ray diffraction patterns of compressed hafnium at elevated temperature. (Fig. 1) Moreover, the  $\omega$ -phase was always seen to be present together with the original  $\alpha$ -phase. The fact that the  $\alpha \rightarrow \omega$  transition was only observed in hafnium at high temperature could be due to several effects. One of the effects of temperature could be that raising the temperature increases the kinetics of  $\alpha \rightarrow \omega$  transition by speeding up the nucleation rate of the  $\omega$  crystallites, or alternatively by lowering the equilibrium size of stable  $\omega$  nuclei.<sup>6</sup> An alternate explanation could be that the  $\alpha \leftrightarrow \omega$  phase equilibrium pressure is actually lowered at higher temperatures. Several previous reports show an increase in the  $c/a$  lattice parameter ratio in  $\alpha$ -phase titanium with increasing pressure,<sup>4</sup> and others suggest that the effect of increasing of the  $c/a$  ratio is an artifact of non-hydrostatic compression in the DAC.<sup>7</sup> However, in some cases the change of the  $c/a$  ratio in an *hcp* lattice may actually be an indication of pressure induced change in electronic structure.<sup>8</sup> Effects of pressure on lattice parameters of transition metals have been investigated for a long time, including in titanium<sup>4</sup> which is usually a test case for studies of  $\alpha \rightarrow \omega$  transitions. In our observation at room temperature, the  $c/a$  ratio increases from an ambient pressure value of  $\sim 1.58$  to

$\sim 1.61$  at a higher pressure (Fig. 2). The  $c/a$  ratio increase in compressed hafnium is similar to those previously reported for titanium.<sup>4</sup>

As can be seen in Fig. 3, the increase of the  $c/a$  ratio is not linear but resembles a diffuse step from  $\sim 1.58$  to  $\sim 1.61$  at a certain crossover pressure. Unexpectedly, at a higher temperature the  $c/a$  ratio is seen to change over from its lower value to the higher value at a lower pressure. This observation suggests that the relative compressibility of  $a$  and  $c$  axes in  $\alpha$ -hafnium is temperature dependent which could explain the lowering of the observed  $\alpha \rightarrow \omega$  phase transition pressure at high temperatures.

At even higher pressures, the x-ray diffraction patterns show a predominant presence of a  $\beta$  phase of hafnium with very small amounts of residual  $\omega$  and  $\alpha$  phases. The  $\omega$  phase of hafnium remained stable in all region of the  $P$ - $T$  range studied. It was always present with other phases, either with  $\alpha$  phase or with both  $\alpha$  and  $\beta$  phases. In summary, x-ray diffraction patterns collected at  $P$ - $T$  range of our experiment show three distinct phase regions. Region I:  $\alpha$  phase only (Fig. 3(c)); region II:  $\alpha$  and  $\omega$  phases are observed (Fig. 3(b)); region III:  $\beta$ ,  $\omega$ , and  $\alpha$  phases are observed, with  $\beta$  as the most predominant (Fig. 3(a)).

## B. Isothermal equation of state of $\alpha$ -phase hafnium

The pressure ( $P$ )-volume ( $V$ ) relation for solids at room temperature can be accurately described by a two-parameter Birch-Murnaghan equation,

$$P = 3/2B_0[V/V_0]^{-7/3} - (V/V_0)^{-5/3} \times \left\{ 1 + 3/4(B_0' - 4)[(V/V_0)^{-2/3} - 1] \right\} \quad (1)$$

$B_0$  and  $B_0'$  are the zero pressure bulk modulus and the first pressure derivative of the bulk modulus at zero pressure, respectively.  $V$  and  $V_0$  are the volumes at a given high pressure and at zero pressure, respectively. The least squares fit of our experimental data for the  $\alpha$ -phase to Eq. (1) gives  $B_0 = 112.9 \pm 0.5$ ,  $B_0' = 3.29 \pm 0.05$  (Fig. 4).

## C. P-V-T equation of state of the $\alpha$ -phase hafnium

High pressure and high temperature EOS could be used to better understand the thermophysical behavior of  $\alpha$ -Hf in extreme conditions. Several studies<sup>9,10</sup> have shown that, the well-known Birch-Murnaghan EOS gives a wrong prediction of thermophysical properties at high pressure and high temperature, like negative heat capacity and thermal expansion. Thus, CALPHAD compatible EOS was used in this study. The EOS was first proposed by Brosh *et al.*<sup>11</sup> and has been used by Karbasi *et al.*<sup>12</sup> to obtain thermodynamically consistent PVT equations of state for several metals. In this formulation, volume should be written as the sum of the cold

TABLE I. Equation of state parameters for  $\alpha$ -phase of hafnium.

$Z$	$V_0$ (cm <sup>3</sup> /mol)	$B_0$ (GPa)	$B_0'$	$\theta_0$	$\gamma_0$	$\delta_0$	$b_0$	$\delta_1$	$b_1$
72	$13.432 \pm 0.015$	$112.9 \pm 0.5$	$3.29 \pm 0.05$	300	$0.231 \pm 0.015$	$0.76 \pm 0.07$	1	$9.50 \pm 0.58$	$0.65 \pm 0.09$

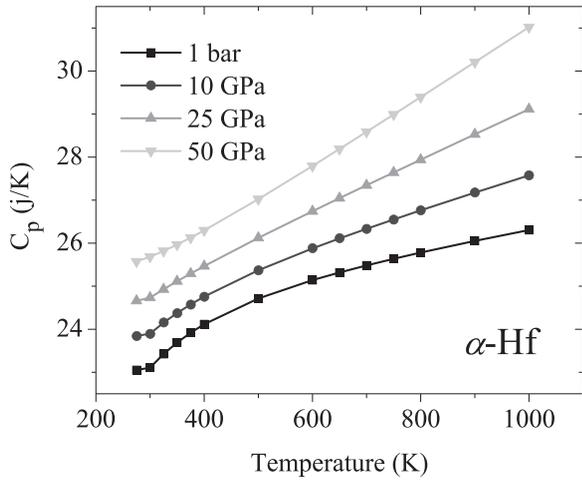


FIG. 5. Heat capacity of  $\alpha$ -phase hafnium as functions of temperature at several pressures calculated from  $P$ - $V$ - $T$  EOS.

compression volume and the thermal volume. In this way, the Gibbs free energy in the desired state of temperature and pressure can be written based on the addition of Gibbs free energy associated with integration of cold compression from the reference pressure to the extreme pressure, then the isobaric integration of the heat capacity up to the desired temperature and finally, by integrating backwards over pressure at the desired temperature, to attain the target thermodynamic state. The total Gibbs free energy can be written as<sup>12</sup>

$$G(T, P) = G_C(P) + G^{QH}(T, P) - [G^{QH}(T, P_0) - G(T, P_0)] \cdot I(P), \quad (2)$$

where the first term is the increase of Gibbs free energy due to cold compression from  $P_0$  to  $P$  and is determined by molar volume ( $V_0$ ), the bulk modulus ( $B_0$ ), and its first pressure derivative ( $B_0'$ ), taken at zero pressure and at the reference temperature of 300 K.  $G^{QH}$  is the increase of Gibbs free energy due to integration of the heat capacity at very high pressure and can be written as

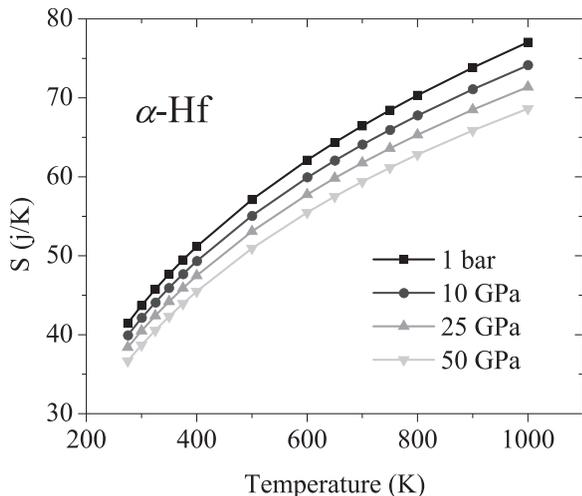


FIG. 6. Entropy of  $\alpha$ -phase hafnium as functions of temperature at several pressures calculated from  $P$ - $V$ - $T$  EOS.

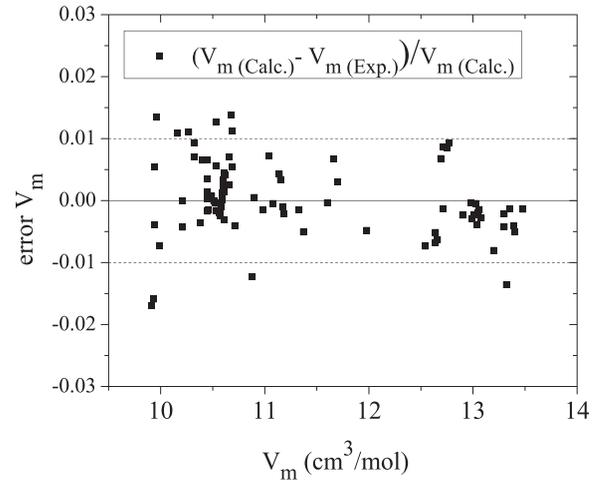


FIG. 7.  $P$ - $V$ - $T$  EOS molar volume calculation errors for the entire  $P$ - $T$  range of our experiment.

$$G^{QH}(T, P) = 3NRT \cdot \ln \left[ 1 - \exp \left( -\frac{\theta(P)}{T} \right) \right], \quad (3)$$

where  $N$  is the number of atoms per unit of molecular formula and  $\theta$  is the pressure dependent Einstein temperature and can be written as

$$\theta = \theta_0 \cdot \exp \left\{ \frac{\gamma_0}{1 + \delta_0} \left[ \Gamma_2(b_0, X_2^T) - \Gamma_2(b_0, 1) \right] \right\}, \quad (4)$$

while  $\Gamma_2(b_0, \frac{2T}{X}) - \Gamma_2(b_0, 1) = \frac{1 + \delta_0}{B_0} \int_0^P (X_2^T)^3 dP'$  and  $X_2^T = \left[ 1 - \frac{1}{3b_0 - 1} + \frac{1}{3b_0 - 1} \cdot \left( 1 + \frac{2}{3} \frac{3b_0 - 1}{1 + \delta_0} \frac{P}{B_0} \right)^{\frac{1}{2}} \right]^{-1}$ .

$\theta_0$ ,  $\gamma_0$ , and  $\delta_0$  model parameters are Einstein temperature, Grüneisen parameter, and Anderson-Grüneisen parameter respectively.  $b_0$  is the EOS adjustable parameter and usually is 1. The last term in Eq. (2) accounts for the backward integration.  $I(P)$  is a monotonically decreasing and

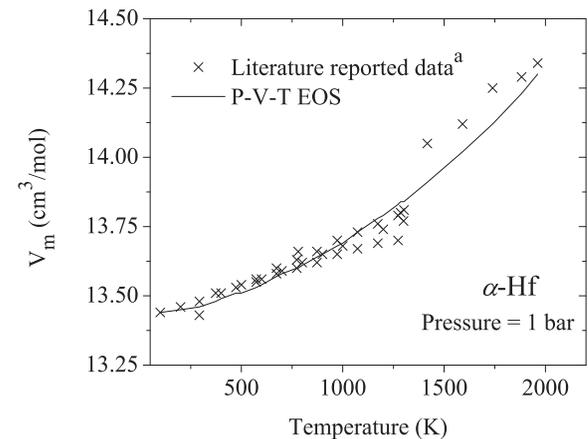


FIG. 8. Comparison of literature reported data on thermal expansion of hafnium and data calculated using our  $P$ - $V$ - $T$  EOS. Literature data on thermal expansion of hafnium was included in our  $P$ - $V$ - $T$  EOS determination. Superscript (a) in the figure denotes the data points compiled from several literature sources.<sup>14,15,17,18</sup>

TABLE II. Bulk modulus ( $B_0$ ), and derivative bulk modulus ( $B_0'$ ), Grüneisen ( $\gamma_0$ ) and Anderson-Grüneisen ( $\delta_0$ ) parameters of Group IVB transition metals (Figs. 9 and 10).

	$B_0$ (GPa)	$B_0'$	$\gamma_0$	$\delta_0$	References
Ti	114(3)	4.0 (fixed)	1.28, 1.18	2.21	7,19
Zr	93(2)	3.1–4.0	0.83, 0.71	1.56	19,20
Hf	$112.9 \pm 0.5$	$3.29 \pm 0.05$	$0.231 \pm 0.015$	$0.76 \pm 0.07$	<i>This work</i>

dimensionless interpolation function with the limiting values  $I(0) = 1$  and  $I(\infty) = 0$ , and expressed as,

$$I(P) = \frac{1}{1 + b_1} \cdot \left\{ b_1 + \left[ 1 + 2 \cdot b_1 \cdot (1 + \delta_1) \frac{P}{B_0} \right]^{\frac{1}{2}} \right\} \cdot \exp \left\{ \frac{1}{b_1} - \frac{1}{b_1} \left[ 1 + 2 \cdot b_1 \cdot (1 + \delta_1) \frac{P}{B_0} \right]^{\frac{1}{2}} \right\}, \quad (5)$$

where  $\delta_1$  and  $b_1$  are additional adjustable parameters of the EOS. The total value of thermal volume is the sum of  $V^{QH}$ , the change of volume due to isobaric expansion, and interpolation volume due to change of Gibbs free energy expressed in the square-bracketed term of Eq. (3).

We calculated bulk modulus and its derivative with the Birch–Murnaghan equation. The other parameters can be determined by the use of different experimental data to solve the multi parameter EOS. We used optimization module of the FactSage 6.2 thermodynamic software<sup>13</sup> as the tool for solving the multi parameter equation.  $P$ - $V$ - $T$  experimental data from the current study as well as ambient pressure thermal expansion data from the literature<sup>14,15</sup> were used as the sources of experimental data for calculating the EOS parameters. The software then optimized all the parameters to minimize the error between experimental value and calculated data. Calculated parameters are used as the input data for CHEMSAGE (Ref. 16) software to reproduce all thermodynamic properties. All the parameters needed to be assessed together with the optimized values and their calculated error for  $\alpha$ -phase hafnium are listed in Table I.

Fitting to the Brosh model, EOS involves thermodynamic variables such as entropy and heat capacity whose

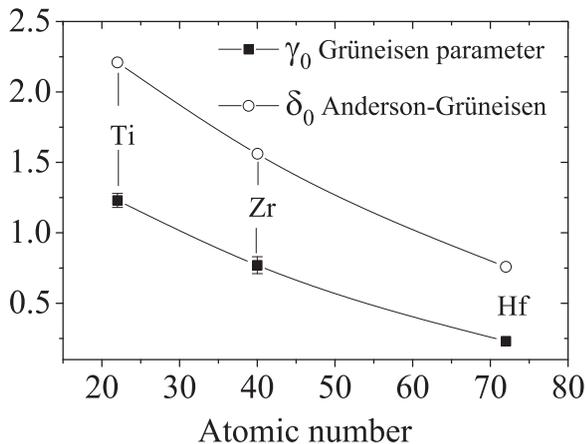


FIG. 9. For Group IVB transition metals,  $\gamma_0$  and  $\delta_0$  are seen to decrease with increasing atomic number of element.

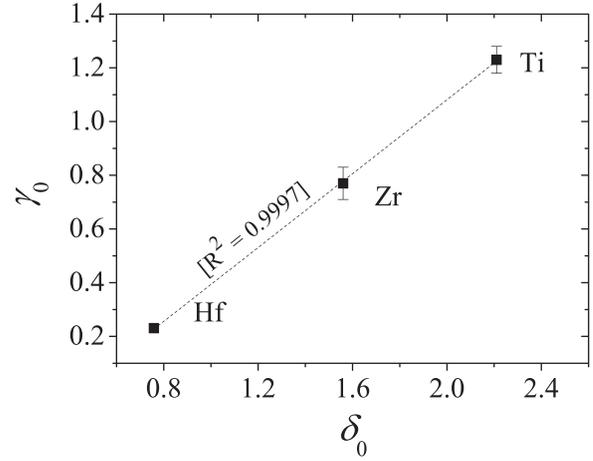


FIG. 10. The relationship between  $\gamma_0$  and  $\delta_0$  is nearly  $\delta_0 = 2 \gamma_0$ , which is consistent with previously reported trend.<sup>19</sup>

temperature dependence must vary in a physically consistent way under high pressure, i.e., the values for heat capacity must not anomalously become negative at very high pressures as is the case with other EOS models.<sup>11,12</sup> In order to check whether our EOS fit is physically consistent, pressure and temperature dependence entropy and heat capacity of  $\alpha$ -phase hafnium were calculated at several pressures using the fitted EOS. As can be seen in Figs. 5 and 6, respectively, heat capacity ( $C_p$ ) increases monotonically with pressure and entropy ( $S$ ) decreases. Clearly, the behavior of  $C_p$  and  $S$  that is predicted by the EOS model does not show any anomalous negative deviation at high temperatures.

The consistency of this calculated thermophysical data is encouraging because it could potentially be used to better understand the  $P$ - $T$  phase diagram of hafnium and mechanisms of its phase transitions in future studies. Our  $P$ - $V$ - $T$  EOS reproduces the experimental molar volumes of the  $\alpha$ -phase hafnium at all  $P$ - $T$  points with  $\sim 1\%$  error (Fig. 7), and fits well with the literature reported data on ambient pressure thermal expansion (Fig. 8).

The overall accuracy of the EOS prediction mostly depends on the accuracy of the input experimental data. With about 5% experimental error in original experimental data, the calculated thermophysical properties as compared to those from literature are well within the error margin.

Additionally, for a comparison with the common Mie-Grüneisen model, the calculated Grüneisen and Anderson-Grüneisen parameters (i.e.,  $\gamma_0$  and  $\delta_0$ ) for  $\alpha$ -Hf are consistent with the experimental data of other elements of Group IVB, as shown in Table II and Figs. 9 and 10. The values of the Grüneisen parameters are seen to decrease linearly with the atomic number. Similar behavior has been reported for metals in other transition metals.<sup>19</sup>

#### IV. CONCLUSION

In summary, we have explored the high pressure and temperature behavior of hafnium by *in situ* x-ray diffraction experiments at pressures up to 61 GPa and temperatures up to 780 K. We observed the  $\alpha \rightarrow \omega$  phase transition at high

temperature and pressure and the  $\omega \rightarrow \beta$  phase transition at still higher pressure. We observed unexpected temperature dependence of the  $c/a$  unit cell parameter ratio in  $\alpha$ -phase and discussed its relation to the  $\alpha \rightarrow \omega$  phase transition. From our volume measurements at high temperature and pressure, we have derived a  $P$ - $V$ - $T$  equation of state for the  $\alpha$ -phase which is in excellent agreement with our experimental data as well as with previous literature data on thermal expansion. The results from this study extend the understanding of the thermodynamics of hafnium at high pressures and temperatures. The new results would aid in theoretical modeling of transition metals and understanding of their phase transitions under extreme conditions.

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