Pressure-induced structural phase transitions of zirconium: an ab initio study based on statistical ensemble theory

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Abstract

Recently, we put forward a direct integral approach to solve the partition function with ultrahigh efficiency and precision, which enables the rigorous ensemble theory to investigate phase behaviors of realistic condensed matters and has been successfully applied to the phase transition of vanadium metal (Ning et al 2022 J. Phys.: Condens. Matter 34 425404). In this work, the approach is applied to the structural phase transitions of zirconium metal under compressions up to 160 GPa and ultrahigh calculation precision is achieved. For the obtained equation of state with pressure over 40 GPa, the deviations from latest experiments are within 0.7% and the computed transition pressure of $\alpha \rightarrow \omega$ is 6.93 GPa, which is about five times larger than previous theoretical predictions and in excellent agreement with the measured range of 5–15 GPa. Our results support the argument that there is no existence of the isostructural phase transition of Zr metal that was asserted by recent experimental observations.

Supplementary material for this article is available online

Keywords: structural phase transition, extreme-condition physics, free energy calculation

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

1. Introduction

Investigations on structural phase transitions of condensed matters under high pressure-temperature conditions are not only directly related to understanding the mechanism of how the planets work [1–3], but also significant for their potential applications as novel functional and structural materials [4–6]. As important fuel cladding materials widely used in industrial nuclear reactors [7], zirconium (Zr) and Zr-based alloys have been extensively studied for their high-temperature properties [8–10], and recently, the structural transformations of pure Zr metal under high pressures attracted broad interests and controversies. Among various structural phase transitions, the isostructural one may be the most unique because, in terms of the pure-element crystals, such a phenomenon so far has been solely confirmed in the cerium metal [11, 12] and the underlying mechanism remains unclear [13–17]. After the denials of osmium [18] and boron [19], Zr is regarded as the second pure-element candidate possibly possessing the feature of isostructural transformation.
Although an experimental consensus has been made on the structural stability of Zr metal in lower pressure zone that it is in a hexagonal-close-packed (HCP) structure (α-phase) at ambient conditions, and transforms into another HCP structure with space group P63/mmm (ω-phase) as the pressure is increased up to 5–15 GPa, and finally ends up into a bodycentered-cubic (BCC) structure (β'-phase) as the pressure reaches 30–37 GPa [20–28], the disputes start in the higher pressure zone that, when the pressure is larger than 56 GPa, Akahama et al [20] for the first time observed that the β-phase would undergo an isostructural transition to β'-phase associated with a discontinued 1.2% volume change. Despite of the following experiment [21] failing to find the phenomenon, the experiment by Stavrou et al [22] successfully reproduced the transition of β → β' at the transition pressure of 58 GPa accompanied with a prominent 4% volume collapse and attributed the driving force to the anharmonicity of lattice dynamics in β-phase [29], which was manifested by their quantum molecular dynamics (QMD) simulations of a quenching process from 1000 K to 300 K at a cooling rate of 100 K per picosecond. Gal [30] further indicated a second isostructural transition of β' → β'' above 110 GPa by more cautiously fitting the data from [22] to two commonly-used empirical Birch–Murnaghan [31] and Vinet [32] equations of states (EOSs). Nevertheless, latest hydrostatic and non-hydrostatic experiments up to 150 GPa separately conducted by Pigott et al [23], Anzellini et al [24] and O’Bannon et al [25] did not exhibit the phenomenon of the and the impacts from sample impurity, non-hydrostaticity or the inaccurately calibrated EOS of the pressure markers were respectively considered to be the cause accounting for the observed abnormal volume collapse in [20, 22].

Several theoretical works tried to understand the dependence of the structural stability on the pressures by the *ab initio* computations of mechanical stability and the criterion of enthalpy at 0 K [33–35]. The calculated elastic constants, $c_{11}$, $c_{12}$ and $c_{44}$, of the three structures were shown to increase monotonically with pressure and the shear modulus of β-structure was found to become positive at around 3~9 GPa [33, 34], implying its elastic stability under high-pressure zone. However, the determined transition pressure of α → ω, around 0 GPa, largely differs from the experimentally observed pressure range. The thermal contributions to the phase transitions from the lattice dynamics were also considered in other works by employing the phonon model with quasi-harmonic approximation (QHA) [36–40], and in the lower pressure zone, the calculated two transition pressures of the α → ω → β are getting closer to but still much lower than all the experimental observations, as also noticed by O’Bannon et al [25], especially the one for the α → ω transition where an about 5-times difference exits. In addition, it was mentioned in [40] that the calculated phonon dispersion of β-structure reflects dynamical instability with imaginary phonon frequency and largely deviates from the experimental measurement. As to the higher pressure zone, Trubitsin and Dolgusheva [36] considered the interactions between phonon modes of the β-phase by numerically solving a set of stochastic Langevin equations and supported the anharmonicity-driven isostructural transformation while, on the contrary, no more works based on phonon model predicted such a phenomenon. Actually, even if the asserted anharmonicity does affect the stability of β-phase, it has been in doubt of the QHA-based model being able to fully capture the anharmonic effects [40–42] and the accuracy for thermodynamic properties calculated by the QHA-based model from *ab initio* phonon density of state and empirical Debye approximation has been questioned in a recent research of pressure-induced solid–solid phase transitions of titanium metal [43].

From the perspective of thermodynamics, free energy (FE) is the very driving force that governs the phase stability [44], and the statistical ensemble theory has already paved a rigorous way to derive all the thermodynamic state functions as long as the partition function (PF) is solved [45–47]. Unfortunately, the complex high-dimension integral in the PF severely hinders the theory to be applied to realistic solid materials so that the capability of ensemble theory has been strongly questioned to tackle the first-order phase transitions of condensed matters [48, 49]. Despite of great progresses achieved for the solution of PF [50, 51], the computational efficiency is still the bottleneck [41, 52] that limits current algorithms to afford various *ab initio* electronic-structure computations [53–56] to characterize interatomic interactions for realistic condensed-matter materials but resort to model potentials, such as the embedded-atom-method potentials that may lead to about one-order deviations from experimentally determined phase boundary of aluminium metal [57].

We recently put forward a parameter-free direct integral approach (DIA) to the PF of condensed matters [58], the ultrahigh efficiency and precision of which were examined by previous comparisons with state-of-the-art sampling algorithm [59] and the QHA-based phonon model [60], and the method has been applied to study the EOS of copper [58], the optimum growth condition for 2D materials [61] and structural phase transitions of vanadium [62] and aluminum [63] with the density functional theory (DFT) computations incorporated for the interatomic interactions. In this work, we aim at applying DIA to compute the Gibbs FE and EOS of pure Zr metal in order to settle down the discrepancies from a different theoretical path. The paper is organized as follows: The theoretical model of DIA, the regarding implementations to the α, ω and β-Zr, and the detailed parameters of the DFT computations are presented in section 2. The obtained phase transitions and the EOSs by DIA are discussed and compared with both the results at 0 K and experiments in section 3. Finally, a conclusion is made in section 4.

### 2. Method

#### 2.1. Theoretical model: DIA

According to ensemble theory, the PF for a system consists of $N$ particles with their Cartesian coordinate...
potential energy, and

\[ U(q^N) = \int dq^N \exp[-\beta U(q^N)] \]

where \( h \) is the Planck constant, \( m \) the particle mass, \( \beta = 1/k_B T \) with \( k_B \) the Boltzmann constant, \( U(q^N) \) the total potential energy, and \( Q = \int dq^N \exp[-\beta U(q^N)] \) the so-called configurational integral (CI) that is related to the structures of the system at given conditions. If the CI is solved, then the pressure-volume (P–V) EOS and the Gibbs FE \( (\tilde{G}) \) can be computed as

\[ P = \frac{1}{\beta} \frac{\partial \ln Q}{\partial V}, \quad \tilde{G} = -\frac{1}{\beta} \ln \left( \frac{2 \pi m}{\beta h^2} \right)^{3N} - \frac{1}{\beta} \ln Q + PV. \]

For a crystalline system with atoms located on the lattice sites, \( \mathbf{Q}^N \), and with the total potential energy, \( U_0(\mathbf{Q}^N) \), the model of DIA \cite{58} firstly introduces transformations as

\[ q^N = Q^N - Q^0, \quad U'(q^N) = U(q^N) - U_0(\mathbf{Q}^N), \]

where \( q^N \) represents the displacements of atoms away from their lattice sites and \( U'(q^N) \) stands for the corresponding differences of total potential energy with respect to the \( U_0(\mathbf{Q}^N) \). Therefore, the CI can be expressed as

\[ Q = e^{-\beta U_0(\mathbf{Q}^0)} \int e^{-\beta U'(q^N)} dq^N. \]

Based on our reinterpretations of integrals, the 3N-fold integral in equation (5) is mapped to an effective 3 N-dimension volume, and may be further simplified as

\[ Q = e^{-\beta U_0(\mathbf{Q}^0)} \prod_{i=1}^N \left( \frac{2 \pi m}{\beta h^2} \right)^{3N} \int e^{-\beta U'(q^N)} dq^N \]

\[ = e^{-\beta U_0(\mathbf{Q}^0)} \prod_{i=1}^N \mathcal{L}_i \mathcal{L}_i \mathcal{L}_i, \]

where \( q_{m,0} \) denotes the distance of the \( i \)th atom moving along the \( x \) (or \( y \), \( z \)) axis relative to its lattice site while the other two degrees of freedom of the atom and all the other atoms are kept fixed, \( U'(q_{m,0}) \) represents the potential-energy curve (function) felt by the moved atom, and \( L_i = L_i \) is called the effective length of the atom along the \( x \) (or \( y \), \( z \)) axis. It should be emphasized here that equation (6) is the only approximation in the model of DIA and the original physics picture as well as detailed mathematical proof is referred to \cite{58}.

For pure-element crystals, such as a BCC structure, where all the atoms in the lattice are geometrically equivalent and the potential-energy curve \( U'_i \) felt by an arbitrary atom moving along \( x \) axis is the same as the one along \( y \) or \( z \) axis, the CI can thus be simplified as

\[ Q = e^{-\beta U_0(\mathbf{Q}^0)} \mathcal{L}^{3N}, \]

where \( \mathcal{L} \) represents the effective length of an arbitrary atom along either \( x \), \( y \) or \( z \) axis. For pure-element crystals, such as a HCP structure, where the atoms are geometrically equivalent but the three effective lengths \( \mathcal{L} \) of each atom are not equivalent to each other, the CI consequently turns into

\[ Q = e^{-\beta U_0(\mathbf{Q}^0)} \left( \mathcal{L}_x \mathcal{L}_y \mathcal{L}_z \right)^N. \]

For crystals with more complex structures or with multiple elements, the atoms may be divided into \( M \) groups with each containing a number of \( N_I \) equivalent atoms on the basis of the geometric symmetry of the lattice, and the CI would be

\[ Q = e^{-\beta U_0(\mathbf{Q}^0)} \prod_{i=1}^M \left( \mathcal{L}_i \mathcal{L}_i \mathcal{L}_i \right)^{N_I}, \]

the detailed applications of which can be found in our previous works of large molecules \cite{58} and 2D materials \cite{61}.

2.2. Implementation of DIA to Zr

As shown in figure 1(a), the \( \beta \)-phase is placed in a \( 3 \times 3 \times 3 \) cubic supercell with two atoms in the unit cell where the lattice vectors are set as \( a_1 = a_\beta(1,0,0) \), \( a_2 = a_\beta(0,1,0) \) and \( a_3 = a_\beta(0,0,1) \) with \( a_\beta \) being the lattice parameter, and the basis vectors are \( b_1 = (0,0,0) \) and \( b_2 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \). The DIA is applied by using equation (7) and an arbitrary atom is selected to move 0.5 Å from the lattice site at a step of 0.05 Å long its \( x \) axis to obtain the corresponding potential-energy curve.

For the \( \alpha \)-phase, as shown in figure 1(b), the atoms are placed in a \( 3 \times 3 \times 2 \) hexagonal supercell with two atoms in the unit cell where the lattice vectors are \( a_1 = a_\alpha(1,0,0) \), \( a_2 = a_\alpha(\frac{1}{2}, \frac{1}{2}, 0) \) and \( a_3 = a_\alpha(0,0,\frac{a_\alpha}{a_w}) \) with \( a_\alpha \) being the lattice parameter and \( \frac{a_\alpha}{a_w} \) the axial ratio, and the basis vectors are \( b_1 = (0,0,0) \) and \( b_2 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \). The DIA is applied by using equation (8) and an arbitrarily selected atom is moved from the lattice site along the \( x \), \( y \) and \( z \) axes separately by 0.5 Å at a step of 0.05 Å to obtain the three potential-energy curves.

The \( \omega \)-phase has the most complex structure among the three phases and a detailed elaboration of the structure can be found in supplementary materials. As shown in figure 1(c), the atoms are placed in a \( 3 \times 3 \times 2 \) hexagonal supercell with three atoms in the unit cell where the lattice vectors are set as \( a_1 = a_\omega(1,0,0) \), \( a_2 = a_\omega(-\frac{1}{2}, \frac{1}{2}, 0) \) and \( a_3 = a_\omega(0,0,\frac{a_\omega}{a_w}) \) with \( a_\omega \) being the lattice parameter and \( \frac{a_\omega}{a_w} \) the axial ratio, and the basis vectors are \( b_1 = (0,0,0) \), \( b_2 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \) and \( b_3 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \). Since neither the geometric symmetry of all the atoms nor the three potential-energy curves of each atom are equivalent, to apply DIA to the \( \omega \)-structure, equation (9) has to be used.
and the atoms are divided into two groups that the first one includes the atoms in the bottom layer (and equivalent repeated layers) and the second group includes the atoms in layers with \( z = \frac{1}{4}c_\omega \) (and equivalent repeated layers). In the first group, the actions on an arbitrarily selected atom are the same as those on the \( \alpha \)-structure, and in the second group, the arbitrarily selected atom is moved along its \( x \) and \( z \) axes separately by 0.5 Å for the potential-energy curves, while, for obtaining the curve along the \( y \) axis, the atom is moved by 0.5 Å in both positive and negative directions due to the asymmetric geometry of the \( \omega \)-structure (see details in supplementary materials). For all the three structures, the potential energies at each moving step are calculated by the DFT computations and afterwards smoothened by the spline interpolation algorithm [64, 65] (see potential-energy curves displayed in the supplementary materials).

2.3. Details of DFT computations

The DFT computations are all conducted in the Vienna Ab initio Simulation Package [66, 67] where the projector-augmented wave formalism [68, 69] is used for the pseudo-potential and the general gradient approximation of the Perdew–Burke–Ernzerhiff parameterizations [70] is adopted for the exchange-correlation functional with 12 valence electrons (4s2p2d5f0) considered. The Gaussian smearing method with a smearing energy of 0.026 eV is applied in order to smooth the transition of the electron number of orbital occupation [71], together with \( \Gamma \)-centered \( 7 \times 7 \times 7 \), \( 5 \times 5 \times 11 \) and \( 9 \times 9 \times 9 \) uniform \( k \)-mesh grids being set to sample the Brillouin zone of the \( \alpha \), \( \omega \) and \( \beta \)-structures by the Monkhorst–Pack scheme [72] respectively, 400 eV as the cut-off energy of the plane-wave basis, and \( 1 \times 10^{-6} \) eV as the stop condition for the electron self-consistent calculations of the total energy.

3. Results and discussions

3.1. Phase transition of \( \alpha \rightarrow \omega \) at 0 K and 300 K

We first consider the \( \alpha \rightarrow \omega \) phase transition at 0 K, where the Gibbs FE becomes equivalent to enthalpy as \( H = U_0 + P_0 V \) with \( U_0 \) the total potential energy and \( P_0 = -\partial U_0 / \partial V \) the cold pressure. Although the ideal axial ratios of \( \alpha \) and \( \omega \)-structures are \( c_\alpha / a_\alpha = \sqrt{8/3} \) and \( c_\omega / a_\omega = \sqrt{3/8} \) respectively, the realistic values of the most stable structures may vary from the ideal ones, and as a result, six \( \alpha \)-structures with axial ratio from 1.59 to 1.64 and three \( \omega \)-structures with axial ratio from 0.61 to 0.63 are considered, the calculated enthalpies of which with respect to the \( \alpha \)-structure with axial ratio of 1.59 are shown in figure 2(a). By the identifications of the one with minimum enthalpy, the axial ratio of the stable \( \alpha \)-structure remains to be 1.60 from 0 GPa up to \( \sim 5 \) GPa and then turns to be 1.61 afterwards. As to the \( \omega \)-phase, the entropy differences between the structure with axial ratio of 0.62 and that of 0.63 are quite negligible from 0 to 6 GPa, while the entropy of the one with 0.61 is over 3 meV/atom larger than the other two. The axial ratio of stable \( \omega \)-structure is determined to be 0.62 from 0 GPa to \( \sim 2.5 \) GPa and then to be 0.63 till 6 GPa.

With the determined stable \( \alpha \) and \( \omega \)-structures versus the changes of pressures, the phase transition of \( \alpha \rightarrow \omega \) in the cross point between the relative enthalpy curves belonged to the two stable structures as shown in figure 2(a) and the transition pressure locates at 0.51 GPa, which, as can be seen in table 1, agrees with the 0.14 GPa from [33] where the same frozen-core pseudopotential DFT method was used. In spite of the disagreement of the negative values from [33–35], it is notable that the calculated transition pressures at 0 K are all close to 0 GPa and quite different from the experimentally measured pressure range 5–15 GPa, which indicates the potential influences from the neglected thermal contributions on the phase transition.
The Gibbs FEs at 300 K calculated by DIA.

of the theoretical value coinciding with the experimental pressure range 6.5 GPa compared with the one at 0 K and is by far the only theoretical value relative to that

\( \omega \rightarrow \beta \rightarrow \beta' \) respectively, and the corresponding differences relative to the \( \omega \)-structure with axial ratio of 1.59 are shown in figure 2(b). Different from the case at 0 K, it is found that the axial ratio of stable \( \omega \)-structure at 300 K turns to be 1.61 from 0 to 8 GPa and becomes 1.62 till 10 GPa. As to the \( \omega \)-phase, the differences of the Gibbs FE are getting prominently larger to \( \sim 1 \) meV/atom between the structures with axial ratio of 0.62 and of 0.63, and unambiguously identify the former one to be the stable \( \omega \)-structure as the pressure is increased up to 10 GPa.

After the confirmations of the stable structures of the two phases, the transition pressure of \( \alpha \rightarrow \omega \) at 300 K is determined to be 6.93 GPa as the cross point highlighted in figure 2(b), which greatly lifts the pressure value by about 6.5 GPa compared with the one at 0 K and is by far the only theoretical value coinciding with the experimental pressure range of 5–15 GPa [20–22, 24, 25, 27, 28] (see table 1).

Table 1. Transition pressures (units in GPa) at room temperature of Zr metal predicted by theoretical computations and determined by experiments.

| Theoretical works | \( \alpha \rightarrow \omega \) | \( \omega \rightarrow \beta \) | \( \beta \rightarrow \beta' \) |
|-------------------|----------------|----------------|----------------|
| Present work (DIA) | 6.93 | 24.83 | Not found |
| Present work (0 K) | 0.51 | 27.86 | / |
| Trubitsin and Dolgusheva [36] | 3.99 | 22.65 | 46.08 |
| Zhang et al [33] | 0.14 | 27.01 | Not found |
| Wang et al [34] | -3.7 | 32.4 | / |
| Hao et al [35] | <0 | 26.8 | / |
| Schnell and Albers [37] | 2.61 | 26.28 | / |
| Greeff [38] | 2.2 | 32.6 | Not found |
| Hao et al [39] | 1.7 | / | / |
| Hu et al [40] | 2.1 | 28.4 | Not found |

Experimental works

| Akahama et al [20] | 6.7 | 33 | 56 |
| Zhao et al [21] | 5.5 | / | / |
| Stavrou et al [22] | 12.7 | 30 | 58 |
| Pigott et al [23] | / | 37 | Not found |
| Anzellini et al [24] | 14 | 35 | Not found |
| O’Bannon et al [25] | 10.7 | 34.9 | Not found |
| Liu et al [27, 28] | 6.8 | / | / |

\( ^{a} Ab\ initio \) phonon mode analysis.
\( ^{b} Ab\ initio \) 0 \( K \)-enthalpy.
\( ^{c} Ab\ initio \) QHA phonon computations.
\( ^{d} Static\ compression + x-ray diffraction. \)
\( ^{e} Static\ compression + Ultrasonic measurement. \)
\( ^{f} Values\ determined\ in\ two\ separate\ runs. \)
\( ^{g} Values\ determined\ in\ three\ separate\ runs. \)

As pointed by Velisavljevic et al [73] and O’Bannon et al [25], experimentally speaking, the transition pressure is closely related to the purity of Zr sample in a way that the value would be increased as the purity decreases, which may account for the deviations of our obtained pressure from the reported 12.7 GPa in [22] with 99.5% pure sample or 14–20 GPa in [24] with 98.8–99.2% pure samples. As a comparison, the observed values of the sample with 99.8% purity in [20] and with 99.9995% in [27, 28] are 6.7 and 6.8 GPa respectively, which are in excellent agreement with our result. The impurity effect on the structural transformations of Zr metal is worthy being carefully investigated in the future but beyond the scope of this work.

According to the determined transition pressure, the \( P-V \) EOSs of \( \alpha \) and \( \omega \)-phases in a pressure range of 0–25 GPa at 300 K by equation (2) are plotted in figure 3 (the higher end of the pressure range of the \( \omega \)-phase is discussed in the next subsection). The atomic volume at ambient conditions, \( V_0 \), by the EOS is determined to be 23.58 Å\(^3\)/atom, and the relative deviations, \( \left| V_0(DIA) - V_0(EXP) \right| / V_0(EXP) \), are about 1.11% compared with 23.32 Å\(^3\)/atom from R [27] using third-order Birch–Murnaghan EOS, 1.25% compared with 23.20 Å\(^3\)/atom from [24] using Rydberg–Vinet EOS [74] and 1.64% compared.

Figure 2. The \( \alpha \rightarrow \omega \) phase transition. (a) The enthalpies at 0 K of five \( \alpha \)-structures with axial ratio from 1.59 to 1.64 (denoted by blue, magenta, cyan, green and violet dashed-dotted lines respectively) and of three \( \omega \)-structures with axial ratio from 0.61 to 0.63 (denoted by black, skyblue and grey dashed lines respectively) relative to that of the \( \alpha \)-structure with axial ratio of 1.59 (red dashed-dotted line). (b) Similar to (a) except that the comparisons are on the basis of Gibbs FEs at 300 K calculated by DIA.
with 23.2 Å³/atom from [30] using Vinet EOS to fit the data measured in [22]. The relative deviations of $P$–$V$ EOS, $|P_{\text{DIA}} - P_{\text{EXP}}|/P_{\text{EXP}}$, of the $\alpha$-phase are 0.34%, 0.69% and 1.01% compared with the experimental data from [20, 22] and [24] respectively, and are 0.68%, 1.14% and 1.46% respectively in terms of the $\omega$-phase. At the transition point of $\alpha \rightarrow \omega$ where $V/V_0 = 0.93$, a discontinuity of the EOS accompanies with a $-1.05\%$ volume change, which is qualitatively consistent with the $-1.26\%$ reported in [21], $-1.36\%$ in [27] and $-1.5\%$ in [24]. The differences between the results at 300 K and 0 K clearly manifest the importance of thermal contributions to the phase stability of the $\alpha$ and $\omega$-phases, which was also observed in our previous work of aluminum metal in a much higher pressure range of 200–400 GPa [63], and the less than 1.5% difference between our calculated EOSs and those from experiments not only validate the accuracy of the PF calculated by DIA for the two phases, but may also ensure the accuracy of the following investigations on phase transitions related to $\omega$-phase in higher pressure zone.

3.2. Phase transition of $\omega \rightarrow \beta$ at 0 K and 300 K

For the phase stability in the pressure zone from 5 to 40 GPa, we do not take the $\alpha$-phase into account because of either the enthalpies or the Gibbs FEs of the $\alpha$-structures being apparently larger than that of the $\omega$-structure with the increased pressures according to the trends demonstrated in figures 2(a) and (b). We still consider the phase transitions at 0 K at first and the enthalpy differences of the three $\omega$-structures relative to that of $\beta$-structure are shown in the dotted lines in figure 4(a), where the $\omega$-structure with axial ratio of 0.63 possesses the minimum enthalpy up to $\sim 16$ GPa and then is replaced by the one of 0.62 till 35 GPa. The transition pressure identified by the cross point of enthalpy curves between the $\omega$ and $\beta$-structures locates at 27.86 GPa, which agrees with previous 0 K-based theoretical predictions about 27–28 GPa from [33, 35] but is lower than the 32.4 GPa from [34] that used same pseudopotential method and electronic exchange-correlation functional but considered less valence electrons ($4d^75s^1$) than this work. The Gibbs FEs at 0 K of the three $\omega$-structures with axial ratio of 0.61, 0.62 and 0.63 (denoted in black, skyblue and grey dashed lines respectively) relative to that of $\beta$-structure (denoted in yellow dotted line) is shown in figure 4(a). (a) $\omega \rightarrow \beta$, (b) $P$–$V$ EOSs of $\omega$-phase (skyblue dashed line) and $\beta$-phase (yellow dashed line) at 300 K by DIA along with those from experiments in a pressure range of 15–40 GPa. The region encircled by the yellow rectangle is inferred to a possible two-phase coexistence for experimental observations.

### Figure 3.

**P–V EOSs of the $\alpha$-phase (magenta dashed line) and the $\omega$-phase (skyblue dashed line) at 300 K by DIA along with those from experiments in a pressure range of 0–25 GPa. The region encircled by the skyblue rectangle is inferred to a possible two-phase coexistence for experimental observations.**

### Figure 4.

(a) The $\omega \rightarrow \beta$ phase transition. The Gibbs FEs at 300 K of three $\omega$-structures with axial ratio of 0.61, 0.62 and 0.63 (denoted in black, skyblue and grey dashed lines respectively) relative to that of $\beta$-structure (denoted in yellow dotted line) and the enthalpy at 0 K of the three structures (denoted in blue, green and cyan dashed lines) relative to that of $\beta$-structure (denoted in yellow dotted line). (b) $P$–$V$ EOSs of $\omega$-phase (skyblue dashed line) and $\beta$-phase (yellow dashed line) at 300 K by DIA along with those from experiments in a pressure range of 15–40 GPa. The region encircled by the yellow rectangle is inferred to a possible two-phase coexistence for experimental observations.
deviations from existing experimental values of 30–35 GPa (see table 1) when compared with the transition pressure at 0 K.

On the experimental side, one possible cause may be from the effects of sample impurity as discussed in section 3.1 and our obtained pressure is indeed closer to the 33 and 30 GPa measured in [20, 22] whose purity is higher than 99.95% while such effects cannot explain why the pressure at 0 K deviates less from experiments. On the theoretical side, since there is no adjustable parameters in the model of DIA, another possible cause may be resulted from the intrinsic precision limits of DFT computations of potential energies, which has been analyzed in our previous work of aluminum [63]. If there exists a ∼1 meV/atom error of potential-energy computations, we estimate a corresponding 4 meV/atom variation of Helmholtz FE (F), which can produce the pressure as \( P = -\frac{\partial F}{\partial V} \). According to our computations of F and the obtained EOSs as shown below, a 4 meV/atom variation would lead to a pressure variation of \( \Delta P \sim 0.1–0.2 \) GPa and the total variation of Gibbs FE, \( \Delta G = \Delta F + \Delta P \cdot V \), corresponds to ∼20 meV/atom at the transition region, which is much smaller than the total thermal contributions, \( G - H \), up to 180 meV/atom at the transition point (see figure 6 in section 3.3). As a result, the computational error may limitedly affect the obtained transition pressure but still cannot account for the 5–10 GPa deviations.

We further compare the P-V EOS in a pressure range of 15–40 GPa by DIA with recent experiments as shown in figure 4(b), and the agreement is excellent, where the relative differences of the ω-phase are 0.86%, 1.34% and 1.40% from those in [20, 22, 24], respectively, and of the β-phase are less than 0.78% compared with [20, 23–25]. At the transition point where \( V/V_0 = 0.82 \), the volume change is determined to be −2.9% and coincides with the measured −2.0% in [24]. In the pressure range of 25–32 GPa, it is noticeable that the calculated EOS of β-phase (encircled by a yellow rectangle in figure 4(b)) perfectly agrees with the observed data identified as ω-phase in [22] with a relative difference of 0.23%, as well as of 1.54% compared with the data in [24], and for the α → ω transition, such an coincidence also exists in the pressure range of 8–12 GPa where the calculated EOS of ω-phase (encircled by a skyblue rectangle in figure 3) coincides perfectly with the data of α-phase in [24]. Since there have been affirmative observations of α and ω-phase coexistence of Zr metal [28], and our former analysis excludes large influences from either purity effects or intrinsic computational variations, here we suggest that the onset of the ω → β transition is in advance than those reported in experiments, which may be more difficult to be experimentally discerned due to a two-phase coexistence and needs to be scrutinized in future experiments.

3.3. The stability of β-Phase at 300 K

By the computations of DIA, the β-structure becomes the dominant phase with the minimum Gibbs FE at 300 K as the pressure being larger than 24.83 GPa and the calculated P-V EOS of Zr up to 160 GPa by equation (2) is shown in figure 5. The EOS of the β-phase does not show any discontinuity and is in excellent agreement with the three latest experimental observations with the relative difference being 0.07% in terms of the second run of [23], 0.42% of [25] and 0.62% of [24], while deviates about 1.2% from the first run of [23]. Compared with the two experiments claiming the isostuctural transition, the relative differences are 0.96% in terms of [20], and 4.15% of [22], which is by far the largest deviation of P-V EOS between our computations and all the experiments.

By conducting the QMD simulations in [22], Stavrou et al attributed the observed anomaly to the anharmonicity of the β-phase, which was confirmed by previous theoretical works at high-temperature zone (over 1000 K) [75] and experimentally proved to be in close relationship to the strong glass forming ability of Zr with pressure over 6 GPa and temperature at 900 K [76], though not reported at room-temperature conditions in any literatures. As brought out by Anzellini et al [24], one questionable point towards the simulation lies in the usage of only one single k-point \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\) that may lead to less precision of \( ab\ initio \) interatomic interactions and result in artificial instability when compared with the outcomes from the reproduced QMD simulation in [24] employing a \( 2 \times 2 \times 2 \) k-mesh. Another point should be mentioned is the simulated cooling rate of \( 10^{14} \) K s\(^{-1} \) in [22], which is much faster than the critical cooling rate of \( 10^{10} \) K s\(^{-1} \) of Zr-based alloys [77, 78] or the estimated \( 10^{11–10^{12}} \) K s\(^{-1} \) of pure Zr metal [79, 80]. In the QMD simulation, the canonical system was relaxed at 1000 K and a pressure range of 40–70 GPa, where the disordered amorphous structure may be formed according to [76], and the cooled-down process with an ultrafast rate of \( 10^{14} \) K s\(^{-1} \) would make the final structure be more inclined to retain the metastable amorphous structure instead of a crystalline β-lattice.

In the model of DIA, the thermal contributions from both harmonic and anharmonic lattice motions are naturally included and entangled together [60], which are on the
we show that the thermal contributions are not negligible but are indeed important for the phase stability of Zr even at room temperature. By the method of DIA and a combination with more advanced \textit{ab initio} computations, the ensemble theory can be further applied to investigate the phase behaviors and thermodynamic properties of more complex materials under extreme conditions.

**Data availability statement**

All the data that support the findings of this work are included within the article and the supplementary material.

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**Figure 6.** The difference between Gibbs FE at 300 K by DIA and enthalpy at 0 K.
