Phase transition, elasticity, phonon spectra, and superconductive properties of equiatomic TiZr, TiHf, and ZrHf alloys at high pressure: Ab initio calculations

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\textbf{A B S T R A C T}

The pressure-induced behaviors of structural transformation, elasticity, phonon, and superconductivity of TiZr, TiHf, and ZrHf alloys are investigated by employing \textit{ab initio} method based on the density-functional theory. Our obtained equilibrium structural parameters and the pressure-included phase transition sequence ($\alpha \rightarrow \omega \rightarrow \beta$) accord well with available experimental and previous theoretical results. Based upon our calculated elastic constants, we have indicated that the $\alpha$ and $\omega$ phases at 0 K and 0 GPa are mechanically stable while the $\beta$ phase is unstable. The phonon and phonon density of states curves results for these three alloys show that the $\alpha$ and $\omega$ phases are dynamically stable at ambient conditions while the $\beta$ phases can be stabilized through compressing or heating, in accordance with what have been found in Zr and Hf elements. The superconducting transition temperatures and the related parameters of TiZr, TiHf, and ZrHf alloys are also calculated in wide range of pressure.

1. \textbf{Introduction}

Pressure increasing can reduce interatomic distances, modify electronic orbits, and change bonding patterns. Therefore, it becomes a versatile tool to research materials with unexpected physical and chemical properties [1–3]. For example, pressure can induce metal-to-insulator transitions, which have been predicted and experimentally observed in some systems [4–6], and also insulator-to-metal transitions [7,8]. It can compress isostuctural transitions for various solid materials [9–12]. Under pressure, many materials have been compressed to exhibit superconductivity, such as the hydrogen-rich compounds [2,3,13–15], the transition metal chalcogenides [16,17], the topological insulators or semimetals [18,19], and iron-based materials [20,21].

The materials, such as Ti, Zr, Hf, and their alloys, have a narrow $d$ band near the Fermi energy and such band is crucial for adjusting the electronic structure and superconductivity [22–28]. Furthermore, similar transformation sequences ($\alpha \rightarrow \omega \rightarrow \beta$) for Ti, Zr, and Hf have been confirmed by experiments and calculations [29–32,28]. At ambient conditions, they crystallize in the $\alpha$ phase (hexagonal close-packed structure). Upon heating, they translate to the $\beta$ phase (body-centered cubic structure). Upon compression, they first transform to the $\omega$ phase (space group No. 191, three atoms per unit cell) and then to the $\beta$ phase. For their equiatomic alloy systems, they also have the $\alpha \rightarrow \omega \rightarrow \beta$ and $\alpha \leftrightarrow \beta$ transformations by applying of pressure and/or temperature. Earlier experimental studies found the $\alpha \leftrightarrow \beta$ transformations at around 1023 K [33] for the TiZr alloy and $\sim$1200 K [34] for the TiHf alloy. Other experiments reported that the phase-transition of $\alpha \rightarrow \omega$ ($\omega \rightarrow \beta$) pressures are in the range of 5–11 (43) GPa for TiZr alloy [33,35,36]. Recently, theoretical results indicated that the $\alpha \rightarrow \omega$ ($\omega \rightarrow \beta$) structural transformation occurs at $\sim$13.8 (43) GPa for TiZr [23] and $\sim$11 (54.6) GPa for TiHf [24]. For ZrHf alloy, till now, the transformation sequence has not yet been reported.

Most of the transition-metal (TM) elements exhibit the superconducting properties [37]. For Ti, Zr, and Hf, their values of the superconducting critical temperatures are directly associated with their structural phase transitions induced by the pressure. At normal conditions, these three elements are low-temperature superconductors with the superconducting transition temperature ($T_c$) values in the range of 0.25–0.50 K for $\alpha$-Ti, 0.45–1.1 K for $\alpha$-Zr and 0.128 K for $\alpha$-Hf [38–40].
The pressure effects on the $T_c$ of Ti, Zr, and Hf were studied in several works [44,22,41,43,45,42]. The $T_c$ was found increasing until the $\omega-\gamma$ transition in Zr and Hf [42,41], and the $\omega-\gamma$ transition in Ti [43]. In addition, a similar $T_c(P)$ dependence was observed on Ti-Zr [35] and Zr-Hf [46] systems. At atmospheric pressure, the $T_c$ value of the TiZr alloy is very low (1.8 K) [35]. However, pressure can enhance it. At 47 GPa, after the $\omega-\beta$ transition, the $T_c$ is 15 K for $\beta$-TiZr [35]. Similarly, the pressure values of the $\omega-\beta$ transition, reported by Bashkin et al. [46], are 35 GPa ($T_c = \sim 11$ K) for the Zr$_6$Hf$_{10}$ alloy and 49 GPa ($T_c = \sim 10.4$ K) for the Zr$_5$Hf$_2$ alloy. For the Ti-Hf alloys, the pressure effect on their superconducting properties has not yet been investigated. It is well known that the solid-state phase transformation can be influenced by many factors, such as loading, plastic deformation, extra-high pressure, and so on. The influence of severe plastic deformation on changes in microstructure has been reported in many studies [47–49]. In addition, the complex load treatment also led to an expected refinement of the microstructure [47,50]. However, in order to make our work continuous, only the effects of ultra-high pressure on TiZr, TiHf, and ZrHf alloys will be discussed. The pressure-induced phase transitions for Zr, TiZr, and Hf have been investigated in our previous works [22,23,28], systematically. The pressure effects on their elastic constants, elastic moduli, phonon spectra, and superconducting properties have been carefully studied. In our present work, we want to extend our study to investigate the high pressure behaviors of TiZr, TiHf, and ZrHf alloys, including the phase transformations, elasticities, phonon vibrations, and superconductivity. In some cases, the temperature effects are also discussed.

2. Computational methods

2.1. Computational details

Our total-energy calculations are performed by utilizing \textit{ab initio} method based on the density functional theory (DFT) as implemented in the Vienna \textit{Ab Initio} Simulation Package (VASP) [51–53]. The Perdew-Burke-Ernzerhof (PBE) form of the projected augmented wave (PAW) [54] generalized gradient approximation (GGA) [55] is chosen to describe the exchange-correlation potential. The plane wave energy cutoff is set to 500 eV. Full geometry optimization at each volume is considered to be completed when the Hellmann-Feynman forces on the atoms are less than 0.02 eV/Å. The Γ-centered k-point meshes in the Brillouin zone (BZ) are sampled by $18 \times 18 \times 16$, $16 \times 16 \times 9$, and $18 \times 18 \times 18$ grids for $\omega$, $\beta$, and $\gamma$ phases, respectively. The Ti $3s^{2}3p^{6}3d^{4}4s^{1}$, Zr $4s^{2}4p^{6}4d^{4}5s^{1}$, and Hf $5s^{2}5p^{6}5d_{6}6s^{2}$ electrons are treated as valence electrons.

The electron-phonon coupling (EPC) calculations are performed using the pseudopotential plane-wave method within the PBE-GGA through the QUANTUM-ESPRESSO (QE) package [56]. A kinetic energy cutoff of 100 Ry with Gaussians width of 0.02 Ry is used for all three phases. $24 \times 24 \times 16$, $12 \times 12 \times 8$, and $32 \times 32 \times 32$ k-point meshes are employed for $\omega$, $\beta$, and $\gamma$ phases, respectively. The Ti spectra and phonon density of states (PhDOS) are computed using the density-functional perturbation theory [57] with $6 \times 6 \times 4$, $3 \times 3 \times 2$, and $8 \times 8 \times 8$ q-point meshes for $\omega$, $\beta$, and $\gamma$ phases, respectively.

2.2. Superconductivity

The Allen-Dynes modified McMillan equation [58,59] is used to evaluate the superconducting transition temperature $T_c$,

$$T_c = \frac{\omega_{\alpha \omega}}{1.2} \exp \left( -\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right)$$  \hspace{1cm} (1)

where

$$\omega_{\alpha \omega} = \exp \left[ \frac{2m}{\hbar \omega} \alpha^2 F(\omega) \ln\omega \right]$$  \hspace{1cm} (2)

is the logarithmic average frequency,

$$\lambda = \int_0^{\omega_{\alpha \omega}} \frac{\alpha^2 F(\omega)}{\omega} d\omega$$  \hspace{1cm} (3)

is the electron-phonon coupling constant, and $\mu^*$ is the Coulomb pseudopotential, $\alpha^2 F(\omega)$, written as

$$\alpha^2 F(\omega) = \frac{1}{2\pi N(E_F)} \sum_{q\nu} \frac{\gamma_{q\nu}}{\omega_{q\nu}} \delta(\omega - \omega_{q\nu})$$  \hspace{1cm} (4)

is the Eliashberg electron-phonon spectral function. $N(E_F)$ is the electronic density of state (DOS) at the Fermi level. Here, the $\lambda_{\alpha \omega}$ is calculated, according to the Migdal-Eliashberg theory [60], by

$$\lambda_{\alpha \omega} = \frac{\gamma_{q\nu}}{\rho_{\text{eff}}(E_F)\omega_{q\nu}}$$  \hspace{1cm} (5)

where $\lambda_{\alpha \omega}$ is the phonon linewidth, $\omega_{q\nu}$ is the phonon frequency. The $\gamma_{q\nu}$ can be calculated by

$$\gamma_{q\nu} = \frac{2m}{\hbar \omega_{q\nu}} \rho_{\text{eff}}^{\text{K},\text{k},\text{q},\omega^{1/2}} \delta(\omega_{q\nu} - \omega) \delta(\omega_{q\nu} - \omega_{q\nu})$$  \hspace{1cm} (6)

where $\omega_{q\nu}$ is the volume of BZ, $\omega_{q\nu}$ and $\omega_{q\nu}$ denote the Kohn-Sham energy, and $\rho_{\text{eff}}^{\text{K},\text{k},\text{q},\omega^{1/2}}$ represents the EPC matrix element. The $\rho_{\text{eff}}^{\text{K},\text{k},\text{q},\omega^{1/2}}$ which can be determined self-consistently by the linear response theory, describes the probability amplitude for the scattering of an electron with a transfer of crystal momentum $q$ [58].

3. Results and discussion

3.1. Ground state properties and phase transition

In our calculations, for a phase, a lamella structure, same with the conventional hcp unit cell, is used, where the A (Ti, Zr, and Hf) and B (Zr, Hf, and Ti) atoms are located on the layer along the $c$ axis alternately. For $\beta$ phase, the bcu unit cells are constructed with A atoms at corner and B atoms are located at center. For $\omega$ phase, $1 \times 1 \times 2$ supercells are used. The detailed explanation about the structures of the equatomic systems can be found in our previous literate [23]. We plot the total energy vs. volume curves for $\alpha$, $\omega$, and $\beta$ phases of TiZr, TiHf, and ZrHf alloys in Fig. 1. Obviously, the smallest total energies are obtained in the $\omega$ phase for TiZr and TiHf alloys, which is consistent with our previous calculations [23,24]. For the ZrHf alloy, the $\alpha$ phase is estimated to be the most stable structure, while the $\beta$ phase is unstable. Using the third-order Birch-Murnaghan equation of states (EOS) [61], we fit the energy-volume data and list the results of the theoretical equilibrium lattice parameter ($a$), bulk modulus ($B$), and pressure derivative of bulk modulus ($B'$) in Table 1. Compared with the experimental data [35] and other calculation results [23,24,62], our calculated results coincide well with them, except for the bulk modulus $B$ for $\alpha$ and $\omega$ TiZr alloys. But, our calculated bulk modulus $B$ of the $\alpha$-TiZr alloy is in between the experimental values of $\alpha$-Ti (102 GPa) [63] and $\alpha$-Zr (92 GPa) [64]. For TiHf alloy, our calculation results of those three phases are in agreement with results reported by Lu et al. [24]. For ZrHf alloy, the lattice parameter and bulk modulus results of $\alpha$ phase are consistent with results reported by Wei et al. [62]. Moreover, the calculated bulk modulus $B$ of 106.3 GPa lies within the range between our previous works of $\alpha$-Zr [97.4 GPa] [23] and $\alpha$-Hf (108.8 GPa) [28]. Furthermore, the predicted equilibrium lattice parameter results are $a = 5.017$ Å and $c/a = 0.622$ for $\omega$-ZrHf, as well as $a = 3.557$ Å for $\beta$-ZrHf, which lie within the corresponding values of Zr ($a_{\alpha-Zr} = 5.036$ Å, $c/a_{\alpha-Zr} = 0.626$ and $a_{\beta-Zr} = 3.574$) [23] and Hf ($a_{\alpha-Hf} = 4.989$ Å, $c/a_{\alpha-Hf} = 0.620$ and $a_{\beta-Hf} = 3.540$) [28].

The energy-volume curves (see Fig. 1) exhibit obvious intersections between $\alpha$ phase and other two phases, which indicate that there exist
phase transformations among them at specific pressures. Comparing their Gibbs free energy, we can obtain the transition pressures. At 0 K, the Gibbs free energy is equal to the enthalpy $H$, $H = E_{\text{total}} + PV$, where $P = \frac{\Delta H_{\text{total}}}{V}$. We present the enthalpy differences at different pressures for the $\alpha$ and $\omega$ phases with respect to the $\beta$ phase of TiZr, TiHf, and ZrHf alloys in Fig. 2. Clearly, for TiZr and TiHf alloys, there are no crossings between $\alpha$ and $\omega$ phases at $P = 0$ GPa, which means the $\omega$ phase is more stable than the $\alpha$ one. In addition, the enthalpy curves crossings between the $\omega$ and $\alpha$ phases lie at $P = -13.3$ GPa for TiZr and $P = -4.5$ GPa for TiHf alloys, which are consistent with our previous theoretical results [23,24]. Different with TiZr and TiHf alloys, the $\alpha$-ZrHf alloy is stable at ambient pressure. The intersection between the $\alpha$ and $\omega$ enthalpy curves lies at $P = 15.9$ GPa [see Fig. 2(c)], which is consistent with the transition sequence of Zr and Hf both experimentally and theoretically [70,31,67,74,28,81].

To further analyze the phase stability, we list the transition pressures for TiZr, TiHf, and ZrHf alloys as well as for pure Ti, Zr, and Hf metals from both experiments and calculations in Table 2. The crossing between the $\omega$ and $\beta$ enthalpy curves for TiZr and TiHf alloys give phase transition pressures of 35 and 68.3 GPa, respectively [see Fig. 2(a) and (b)], which accord well with those from Bashkin et al. [35] and Wang et al. [23] for TiZr alloy, except for $\sim 13.7$ GPa deviations from Lu et al. [24] for TiHf alloy. For ZrHf alloy, the phase transition of $\omega \rightarrow \beta$ occurs at 46.7 GPa. This value is larger than the experimental data of 30–35 GPa for Zr metal [63,29,31,67], and smaller than the experimental value of 71 GPa for Hf metal [74]. In general, our computational method and the corresponding results are sufficiently reasonable and reliable.

### 3.2. Elasticity

The elastic constants $C_{ij}$ can be obtained by means of linear fitting of the stress-strain curves obtained from first-principles calculations and provide important information to analyze the mechanical and dynamic properties of materials. The elastic constants of TiZr, TiHf, and ZrHf alloys for the $\alpha$, $\omega$, and $\beta$ phases at 0 GPa are listed in Table 1. Clearly, the results of the three alloy systems are well consistent with other theoretical investigations [23,24,62]. According to the mechanical stability criteria [75] of hexagonal crystal, $C_{44} > 0$, $C_{11} > |C_{12}|$, $(C_{11} + 2C_{12})C_{33} > 2C_{13}^2$, and cubic crystal, $C_{11} > 0$, $C_{44} > 0$, $C_{11} > |C_{12}|$, $(C_{11} + 2C_{12})C_{33} > 2C_{13}^2$, and cubic crystal, $C_{11} > 0$, $C_{44} > 0$.

### Table 1

<table>
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<th>$E$ (eV/atom)</th>
<th>$B$ (GPa)</th>
<th>$B'$ (GPa)</th>
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a Reference [23].
b Reference [35].
c Reference [24].
d Reference [62].
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Table 2  

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- a This work.  
- b Reference [23].  
- c Reference [33,35,36].  
- d Reference [24].  
- e Reference [65].  
- f Reference [66].  
- g Reference [63,31,29,67].  
- h Reference [22].  
- i Reference [68].  
- j Reference [69].  
- k Reference [70,31,64].  
- l Reference [31,71-73].  
- m Reference [28].  
- n Reference [32].  
- o Reference [74].  

Evidence for the existence of strong atomic bonding along the (001) directions for the α phase. For ω-ZrHf, similar pressure dependent behaviors also appear on the C44 and other Cij (see Fig. 3(b)). The increasing rates γ1 = 3.07 of the ω phase is larger than its R33 = 1.74, which means the C11 > C33 will occur at specific pressures. As indicated in Fig. 3(b), the crossing between the C11 and C33 curves is given at ~28 GPa. This value is slightly larger than our predicted α→ω transition pressure (15.9 GPa, listed in Table 2), but smaller than the ω→β transition pressure (46.7 GPa). One can be concluded that there also exist strong atomic bonding along the (0 0 0) directions for ω-ZrHf alloy. For β-ZrHf, similar to our previous works of β-TiZr and β-TiHf [23,24], it also can become mechanical stable through applying external pressure. As shown in Fig. 3(c), under pressure from 0 to 70 GPa, the differences between C11 and C33 almost increase linearly from ~37.7 to 50.2 GPa. Fig. 3(c) indicates that the inequation of C11 > C33 is always maintained at P = 32 GPa. Actually, the elastic constants at P = 32 GPa are C11 = 159.7 GPa, C12 = 157.7 GPa, and C44 = 55.6 GPa, respectively, which are fully satisfied with the mechanical stability criteria of a cubic crystal, and explicitly indicates that the β-ZrHf is elastic stable at this pressure.

Using our previous elastic constant data, the bulk modulus B and shear modulus G for the ZrHf alloy are also further evaluated by using the Voigt-Reuss-Hill (VRH) approximation [76-78] and presented in Fig. 4. At ambient conditions, the bulk moduli are 100.3, 101.0, and 101.1 GPa for α, ω, and β phases, respectively. These results are very close to our previous EOS fitting results (listed in Table 1), which means our calculations are consistent and reliable. Upon isotropic compressing, the bulk moduli increase monotonically for all the three phases, while the shear moduli first increase moderately and then decrease for α and ω phases. The resistance to fracture and plastic deformation are related to B and G. The ductility (brittleness) of polycrystalline materials is represented in a high (low) B/G value. If B/G > 1,75, the material is ductile, otherwise it is brittle [79]. As shown in Fig. 4, the difference between the bulk modulus B and shear modulus G becomes larger and larger at high pressure. The values of B/G increase from 2.25 to 4.06

- Reference [74].
under pressure from 0 to 30 GPa for \( \alpha \) phase and from 1.93 to 4.57 within 0–70 GPa for \( \omega \) phase, while they decrease from 28.07 to 5.34 upon compression from 40 to 70 GPa for \( \beta \) phase. Thus, we can be concluded that increasing of the pressure can enhance the ductility for \( \alpha \) and \( \omega \) phases while it could reduce the ductility for the \( \beta \) phase. The \( \alpha \) to \( \omega \) (or \( \beta \) to \( \alpha \)) phase transition will reduce (enhance) the ductility.

Essentially all known crystals are elastically anisotropic. For hexagonal crystals, the anisotropy factor \( A \) can be defined from the stiffness constants as [80]:

\[
A = \frac{4C_{14}}{C_{11} + C_{33} - 2C_{13}}.
\]  

We calculated the values of the anisotropy factors are 0.75 (0.61) for \( \alpha \)-ZrHf and 0.58 (0.48) for \( \omega \)-ZrHf at 0 (20) GPa. For an isotropic crystal, \( A = 1 \), while any value smaller or larger than 1 indicates anisotropy. The magnitude of the deviation from 1 is a measure of the degree of elastic anisotropy possessed by the crystal. According to this, the materials of \( \alpha \)-ZrHf and \( \omega \)-ZrHf are characterized by a profound anisotropy.

The three-dimensional (3D) Young's modulus surface can be defined by the equation [75]:

\[
\frac{1}{E} = S_{ij}(l_i^2 + l_j^2 + 2l_i^2l_j^2) + S_{44}(l_i^2 + l_j^2)(l_i^2 + l_j^2),
\]  

where \( S_{ij} \) is the elastic compliance constants and \( l_i \) is direction cosine. We plot the 3D Young’s modulus surface [81] of \( \alpha \)-ZrHf (or \( \omega \)-ZrHf) in Fig. 5(a) and (c) (Fig. 6(a) and (c)) under pressures of 0 and 20 GPa, respectively, as well as the corresponding shear modulus in (b) and (d). The magnitude of Young’s modulus and shear modulus can be reflected from the depth of the color. The deviation degree from the spherical shape reflects the degree of anisotropy. It can be seen from Figs. 5 and 6 that the \( \alpha \)-ZrHf and \( \omega \)-ZrHf alloys have elastic anisotropy. The 3D figures of Young’s modulus and shear modulus have the increasing deviation in shape from the sphere in pressure range from 0 to 20 GPa, which indicates that the ZrHf alloys show a increasing elastic anisotropy.

![Fig. 3. Calculated elastic constants \( C_{ij} \) at \( T = 0 \) K as a function of pressure for (a) \( \alpha \), (b) \( \omega \), and (c) \( \beta \) ZrHf alloy.](image)

![Fig. 4. Calculated bulk modulus \( B \) and shear modulus \( G \) for the \( \alpha \), (b) \( \omega \), and (c) \( \beta \) ZrHf alloys at different pressures.](image)

![Fig. 5. Directional dependences of Young’s Modulus for \( \alpha \)-ZrHf under (a) 0 and (c) 20 GPa with the corresponding shear modulus in (b) and (d), respectively.](image)
anisotropy. Meanwhile, the color begins to darken, which indicates that the Young-modulus and shear modulus increase with increasing the pressure. The Young’s modulus of α-ZrHf (ω-ZrHf) are 116.4 GPa (133.9 GPa) at 0 GPa and 122.6 GPa (161.0 GPa) at 20 GPa. The difference values of Young’s modulus between 0 GPa and 20 GPa are 6.2 GPa for α-ZrHf and 27.1 GPa for ω-ZrHf, respectively, which means the effect of pressure on the elastic anisotropy for ω-ZrHf is bigger than that for α-ZrHf. For the shear modulus, it increases moderately under pressure from 0 to 20 GPa, which agrees well with the previous calculations as illustrated in Fig. 4. Till now, the experimental results about the elastic constants, mechanical moduli, and elastic anisotropy for ZrHf alloys have not been reported. Further investigations are needed to verify our theoretical predictions.

3.3. Phonon dispersion

The phonon dispersion curves of α and ω phases along the Γ-K-M-Γ-A direction and β phase along the Γ-H-P-Γ-N direction as well as the corresponding PhDOS are calculated by employing the PHONOPY code [82]. For α, ω, and β phases, 3 × 3 × 3, 3 × 3 × 3, and 4 × 4 × 4 supercells are respectively constructed in the phonon calculations to ensure the convergence of the forces. We display the phonon dispersion curves and the corresponding PhDOS in Figs. 7–9. For TiZr and TiHf alloys, the phonon dispersion curves and the corresponding PhDOS at ambient pressure have been reported by Wang et al. [23] and Lu et al. [24]. Overall speaking, our results agree well with theirs. Here, we focus on the dynamical stability of the ZrHf alloy. Obviously, similar to TiZr and TiHf alloys, the α and ω phases of ZrHf alloys are dynamically stable at ambient conditions, while the β phase is unstable. The phonon vibrations of α-ZrHf are similar to those of metal Zr [22] and Hf [28]. The interactions do appear in α-TiZr and α-ZrHf alloys, as well as in metals Zr and Hf [22,28], while there are no obvious interactions between the acoustic and optical branches in α-TiHf [24]. For the ω-ZrHf, the phonons are stiffer along the c axis than in the basal plane due to the low c/a ratio. The same characteristics are found in ω-TiZr [23] and ω-TiHf [24] alloys. Same with Ti [83], Zr [22], and Hf [28], the β phase of these three alloys is dynamically unstable at low pressure and low temperature [Fig. 9]. However, our phonon spectra results show that the β phase can be tuned to become dynamically stable at high pressure. We display the phonon dispersion curves in Fig. 9 at 40, 70, and 55 GPa for β-TiZr, β-TiHf, and β-ZrHf, respectively. At given pressures, all the imaginary frequencies of these three alloys are raised to positive. This accord well with our previous study of β-Zr and Hf [22,28]. One can see that pressure will greatly enhance the phonon energies. The maximum values of the phonon frequencies are raised from 5.76, 5.88, and 4.45 to 8.12, 8.52 and 6.75 THz for β-TiZr, β-TiHf, and β-ZrHf. Earlier experiments have reported the β phase of TiZr at 1023 K and TiHf at 1203 K, while the β-ZrHf at high temperature has not been reported until now. Thus, we calculate the phonon dispersions at finite temperatures by the self-consistent ab initio lattice dynamics (SCAILD) method [84] and plot them in Fig. 9. The finite temperature calculations predict the stability of the β phase for TiZr, TiHf, and ZrHf alloys by promoting the frequencies of the phonons from imaginary to real. Results illustrate that the β phases are dynamically stable at 1023, 1203, and 1500 K for TiZr, TiHf, and ZrHf alloys, respectively. One can see that the temperature never raise the maximum phonon frequencies. But it do raise all the phonon branches to positive. As a result, the PhDOS is distributed in a narrow energy range at high temperature, which will enhance the vibration entropy [85].

3.4. Superconductive properties

For Ti, Zr, and Hf, their high pressure phases have evident predominance for high-temperature superconductivity [22,42,41,43,45,44], as well as TiZr and ZrHf alloys [35,46]. In the following, we will investigate vibration properties and the EPC of the experimentally observed TiZr alloys. Fig. 10 show the phonon dispersions, calculated within the QE package [56], along high-symmetry
paths for \(\alpha, \omega,\) and \(\beta\) phases, respectively. The absence of the imaginary modes clearly indicates that the TiZr alloys are dynamically stable for \(\alpha\text{-TiZr}\) at 0 GPa, \(\omega\text{-TiZr}\) at 0 GPa, and \(\beta\text{-TiZr}\) at 40 GPa, which turn out to be the same with our results obtained by employing the PHONOPY code [82] (see Figs. 7(a), 8(a), and 9(a)). For \(\alpha\text{-TiZr},\) the Zr vibrations dominate in the frequency below 140 cm\(^{-1}\) while the Ti vibrations dominate in the frequency region from 172 to 192 cm\(^{-1}\). The phonon modes of Ti\(_{\text{iv}}\) and Zr\(_{\text{iv}}\) vibrations spread over the full BZ. For \(\omega\text{-TiZr},\) the Zr vibrations mainly dominate in the frequency below 150 cm\(^{-1}\) while the Ti vibrations dominate in the frequency region from 200 to 225 cm\(^{-1}\). The phonon modes of Ti\(_{\text{iv}}\) and Zr\(_{\text{iv}}\) vibrations dominate in the intermediate-frequency region from 118 to 180 cm\(^{-1}\). For the \(\beta\text{-TiZr},\) the phonon modes of Ti and Zr vibrations spread over the full BZ.

The phonon dispersions weighted by the magnitude of the EPC \(\lambda_{\mu}\), the PhDOS, the Eliashberg electron–phonon spectral function \(\lambda^{\omega}(\omega)\), and the cumulative frequency-dependent of EPC \(\lambda(\omega)\) are displayed in Figs. 10(b)–(d), 10(f)–(h), and 10(j)–(l) for \(\alpha, \omega,\) and \(\beta\) phases, respectively. The \(\lambda_{\mu}, \lambda^{\omega}(\omega),\) and \(\lambda(\omega)\) can be determined from Eq. (3), Eq. (4), and Eq. (5), respectively. From our calculated cumulative frequency dependence of EPC \(\lambda_{\mu}\) for the \(\alpha\text{-TiZr}\) (see Fig. 10), we find that the low-frequency (below \(~60\) cm\(^{-1}\)) phonons, mainly associated with the Zr vibrations, account for 0.31 (35\%) of the total EPC (\(\lambda = 0.88\)).

The intermediate frequency phonons, in a range of 50–147 cm\(^{-1}\), contribute 53\%. As for the \(\beta\text{-TiZr},\) the phonons below \(~120\) cm\(^{-1}\) contribute \(~0.99\) (70\%) of the total EPC (\(\lambda = 1.42\)). The phonons in a frequency range of 102–271 cm\(^{-1}\) only contribute 30\%. Obviously, the large values of \(\lambda_{\mu}\) contribute the remaining 34\% of the total EPC in the intermediate-frequency region from 118 to 180 cm\(^{-1}\). For the \(\beta\text{-TiZr},\) the phonon modes of Ti and Zr vibrations spread over the full BZ.

The superconducting transition temperatures \(T_c\) are estimated from Eq. (1), and plotted in Fig. 11 as a function of pressure for TiZr, TiHf, and ZrHf alloys. The effective screened Coulomb repulsion constant \(\mu^*\) is set as 0.10. Clearly, our predicted \(T_c\) are in good agreement with experimental results [35,46], especially in the case of the TiZr system. Increasing pressure, the \(T_c\) of the \(\alpha, \omega,\) and \(\beta\) phases increase monotonically, while those of the \(\beta\) phase first increase and then decrease. The McMillan equation (Eq. (1)) indicates that the value of \(T_c\) is directly determined by \(\omega_{\text{ph}}\), \(\lambda\) and \(N(\epsilon_F)\). Our calculated \(\omega_{\text{ph}}\) and \(\lambda\) of TiZr, TiHf, and ZrHf alloys are plotted as a function of pressure in Fig. 12. For \(\alpha, \omega,\) and \(\beta\) phases, one can see that the \(\lambda\) increase with pressure, while the pressure dependent behaviors of \(\omega_{\text{ph}}\) are not linear. For \(\beta\) phase, the changing trends of \(\omega_{\text{ph}}\) and \(\lambda\) are opposite under pressure, and the changing rates are different. For \(\beta\text{-TiZr},\) the decreasing rate of \(\lambda\) is smaller than the increasing rate of \(\omega_{\text{ph}}\) under pressure from 40 to 50 GPa. Over 50 GPa, the increasing rate of \(\omega_{\text{ph}}\) becomes smaller than the decreasing rate of \(\lambda\). Different with the \(\beta\text{-TiZr},\) the decreasing rate of \(\lambda\) is always larger than the increasing rate of \(\omega_{\text{ph}}\) for \(\beta\text{-TiHf}\) in pressure range of 70 to 110 GPa and \(\beta\text{-ZrHf}\) in pressure range of 40 to 70 GPa.
Generally, one can conclude that the pressure dependent behaviors of $T_c$ for all three alloys are mainly due to the increase or decrease of $\lambda$ upon compression.

4. Conclusion

In summary, the structural, elastic, phonon, and superconducting properties of TiZr, TiHf, and ZrHf alloys are investigated by ab initio calculations. The calculated lattice parameters and the transition pressures of the $\alpha$, $\omega$, and $\beta$ phases are consistent with available experiments and other calculations. At $P = 0$ GPa, the elastic constants and the elastic moduli of the $\alpha$, $\omega$, and $\beta$ phases accord well with previous experiments and calculations. Mechanical stability of the $\alpha$, $\omega$, and $\beta$ phases is discussed in a series of pressures. We predicted that the $\beta$ phase for all three alloys is mechanically unstable at 0 GPa and can become mechanically stable upon compressing. The effects of pressure on these mechanical properties and the ductility were analyzed. Based upon our calculated phonon spectra, the $\alpha$ and $\omega$ phases are dynamically stable at ambient conditions, while the $\beta$ phase can be stabilized by increasing pressure or temperature. In addition, superconductivity has been obtained by electron-phonon coupling calculations and our calculated $T_c$ of TiZr alloy accords well with experiments. Under pressure, the increase or decrease of $T_c$ for all three alloys has tight relation with the corresponding behavior of the EPC constant $\lambda$. The large values of $T_c$ for the $\beta$ phase can be understood from its soft phonon modes at low frequencies. Finally, the material properties for $\alpha$, $\omega$, and $\beta$ phases of TiZr, TiHf, and ZrHf alloys are between their corresponding pure metals, as well as exist the similar high pressure behaviors with their corresponding single element systems. However, there also be some differences between the single element systems and the equatomic systems. For the $\beta$ phase, the soft modes along [1 1 1] and [1 1 0] directions have been shown for these single element systems, and along [1 1 1] and [0 0 1] directions for these equatomic systems. As a result, for these single element systems, the large $\lambda$ and $T_c$ for the $\beta$ phase are mainly due to the soft mode along [1 1 0] direction, while for these equatomic systems, they are due to the soft mode along [1 1 1] direction.

CRediT authorship contribution statement

Cheng-Bin Zhang: Conceptualization, Methodology, Data curation, Writing - original draft. Wei-Dong Li: Resources, Supervision. Ping

Fig. 10. Phonon dispersions, PhDOS, Eliashberg spectral function $\alpha^2F(\omega)$, and cumulative frequency-dependent of EPC $\lambda(\omega)$ for $\alpha$-TiZr, $\omega$-TiZr, and $\beta$-TiZr alloys. The phonon dispersions in (a)(e)(i) are weighted by the motion modes of Ti and Zr atoms while in (b)(f)(j) are weighted by the magnitude of the EPC $\lambda_{qv}$. $\lambda_{qv} = \frac{q_v}{\pi h N(E)}$. The green, blue, magenta, and orange hollow circles in (a)(e)(i) indicate Ti horizontal, Ti vertical, Zr horizontal, and Zr vertical modes, respectively. The magnitude of $\lambda_{qv}$ is displayed with identical scale except for the yellow circles in (j), which are displayed with 10% scale of the red.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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