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Some aspects of pressure-induced $\omega \rightarrow \beta$ transformation in group IVB elements

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Abstract

The ω (hexagonal) to β (bcc) transformation in Zr and Hf occurs at 30 and 71 GPa under static pressures. This transition has not been found in Ti up to 87 GPa. On the basis of full-potential linearized augmented plane wave calculations aided with thermal and entropy correction we predict an $\omega \rightarrow \beta$ transition in Ti at around 102 GPa along the 300 K isotherm. In addition to this, we calculate the $\omega \rightarrow \beta$ transitions in Zr and Hf at around 27 and 65 GPa respectively, which are in excellent agreement with the experimental values. The $\omega \rightarrow \beta$ transition pressures, 102, 27 and 65 GPa for Ti, Zr and Hf respectively, do not follow the trend implied by the principle of corresponding states. We have analysed the causes for this anomalous trend. We observe that the $\omega \rightarrow \beta$ transition depends on how the increased d-population due to s–d transfer under pressure is distributed in the different d-substates. For example, at ambient conditions, the bcc phase is unstable and the difference between the average charges in the bcc stabilizing d- t_{2g} state and the destabilizing d- e_g state are 0.008, 0.082 and 0.013 for Ti, Zr and Hf respectively. Compression increases this difference and stabilizes the bcc structure when it becomes about 0.1. The charge transfer needed for stabilizing the β structure is highest for Ti followed by Hf and then Zr, in line with the trend in transition pressures.

1. Introduction

The last decade has seen considerable activity on both the theoretical and experimental front on the pressure-induced phase transition in group IVB elements, Ti, Zr and Hf [1–3]. These elements are known to undergo α (hcp) to ω (three-atom simple hexagonal) phase transition at a few GPa pressure [1]. Using the linear muffin tin orbital (LMTO) method, Gyanchandani *et al* [2] predicted new ω to β (bcc) structural transitions in Zr and Hf under pressure. This was confirmed experimentally, using a diamond anvil cell [3]. The transition pressures reported were 30 ± 2 and 71 ± 1 GPa for Zr and Hf respectively. The transition pressure values calculated

theoretically using LMTO-ASA (Atomic Sphere Approximation), however, did not match well with the experimental ones. In titanium, Ahuja *et al* [4] based on their full potential linear muffin tin orbital (FP-LMTO) calculations predicted the $\omega \rightarrow \beta$ transition around 58 GPa, however, the experimental study by Xia *et al* [3] up to 87 GPa on this metal reported only an $\alpha \rightarrow \omega$ transition.

For a better understanding of the $\omega \rightarrow \beta$ phase transition in these elements in the present work, we have performed more accurate calculations employing the full-potential linearized augmented plane wave (FP-LAPW) method in conjunction with the generalized gradient density approximation (GGA) for exchange–correlation. In addition to obtaining excellent agreement between our theoretical and experimental pressures for the $\omega \rightarrow \beta$ transition in Zr and Hf, we predict an $\omega \rightarrow \beta$ transition in Ti at around 108 GPa (102 GPa at 300 K) [5], which recently has been observed to occur at 140 GPa experimentally by Akahama *et al* [6]. However, in a recent experimental study on Ti, based on energy dispersive x-ray diffraction measurement, Vohra and Spencer [7] report the occurrence of an orthorhombic (γ -phase) phase, i.e. an $\omega \rightarrow \gamma$ transition, at around 116 ± 4 GPa. This is unexpected as the group IVB elements are expected to undergo s to d electron transfer under pressure and, thus, mimic the transformation sequence $\alpha \rightarrow \omega \rightarrow \beta$ shown by these elements with increasing number of d electrons on alloying with d-electron-rich neighbours. On the basis of our theoretical calculations, in the present paper we point out that the γ phase is not the lower free-energy structure for the range of volume compression in the experiment of Vohra and Spencer. Moreover, we present our in-depth analysis that relates the stability of ω and β phases in terms of the pressure-induced change in the population of d substates.

2. Method of calculation

Total energy calculations have been performed for ω and β phases of all the three elements as a function of volume using the FP-LAPW method (WIEN97 package) [8] in conjunction with the GGA for the exchange–correlation effects. 150 k -points were used for sampling of the Brillouin zone. The ω -phase, which is an $A1B_2$ -type structure, is treated as having inequivalent sites with one atom at site (0, 0, 0) ('A' site) and one atom each at site (2/3, 1/3, 1/2) and (1/3, 2/3, 1/2) ('B' site). For the γ phase (space group $Cmcm$), the experimental values of the four atomic positions and the ratios of the cell constants ($b/a = 1.878$, $c/a = 1.639$) are used [7]. The value of the y parameter has been varied from 0.08 to 0.12 (experimental value of ' y ' is 0.1 [7]). A calculation has also been performed at a lower b/a value of 1.784 (y at 0.1).

3. Results and discussion

The calculated total energies of the ω , β and γ phases are plotted as a function of volume of the primitive unit cell. One such plot for Ti is shown in figure 1. In Ti, the plot shows that the β phase becomes more stable than the ω phase at a primitive cell volume of 10.98 \AA^3 , which corresponds to a pressure of 108 GPa. The energy of the γ phase at the ω – β crossover is 0.28 mRyd/atom more than that of the β phase. The energy of the γ phase does fall below that of the ω phase at higher compressions (the cell volume is 10.90 \AA^3), but it remains higher than that of the β phase. This implies that the γ phase is not a lower-energy structure with respect to the β phase at higher compression.

To understand the effect of temperature on the free energy we have used the method followed by Godwal and Jeanloz [9]. The entropy contribution to the free energy of the ω phase with respect to the β phase at 300 K has been evaluated to be ~ 1.2 mRyd/atom using

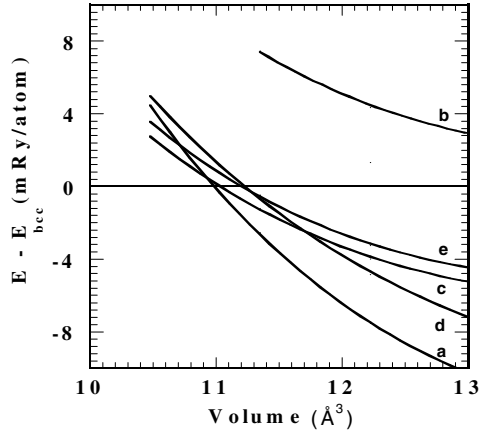


Figure 1. Calculated total energies for Ti in the ω , β and γ phases as a function of volume of the primitive unit cell. Total energies are plotted with reference to the energy of the β phase. The curve 'a' corresponds to the ω phase; b, c and d to the γ phase with γ as 0.08, 0.10 and 0.12 respectively, and e to the γ phase with $b/a = 1.784$ and $\gamma = 0.10$.

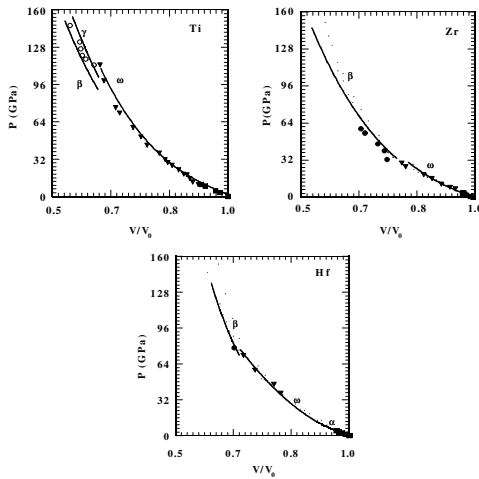


Figure 2. EOS (Equation of State) plots: the full curves show the theoretical 300 K isotherm. \blacksquare , \blacktriangledown , \bullet and \circ show the experimental static compression data for the α , ω , β and γ phases respectively [3, 7].

the $\delta S_{\beta-\omega}$ (the entropy difference between the β and the ω phase) value of $0.62k_B$ compiled by Kutsar [10]. The thermal contribution together with the entropy contribution shifts the ω - β crossover towards the higher volume of 11.26 \AA^3 . The corresponding $\omega \rightarrow \beta$ transition pressure is 102 GPa.

To examine the relative stability of the γ phase, the free-energy differences between the γ and β phases are evaluated at compression corresponding to the ω - β crossover. To estimate the entropy contribution to the free-energy difference we have assumed the entropy of the γ phase to be close to that of hcp as this structure can be treated as the distortion of hcp towards the bcc phase. The $\delta S_{\beta-\alpha}$ values of $0.415k_B$ determined by Sanati *et al* [11] and $0.43 k_B$ compiled by Kutsar [10] were used to evaluate the $T\delta S$ term. Including the thermal contribution and the entropy contribution at 300 K the free-energy difference between the γ and β phases turns out to be $\sim 0.6 \text{ mRyd/atom}$ at the ω - β crossover, suggesting that the bcc structure is energetically more favourable than the γ phase even at room temperature. In Zr and Hf our calculations show that the β phase becomes more stable than the ω phase at a primitive cell volume of 19 and 16 \AA^3 , corresponding to $\omega \rightarrow \beta$ transition pressures of 27 and 65 GPa respectively, in good agreement with the experimental values of 30 ± 2 and 71 ± 1 GPa respectively.

The $\omega \rightarrow \beta$ transitions at 140, 30 and 71 GPa pressure for Ti, Zr and Hf respectively, do not follow the trend implied by the principle of corresponding state [12]. We have performed

Table 1. Partial d charges for bcc phase.

Elements	V/V_0	${}^a d\text{-}t_{2g}/3$	${}^a d\text{-}e_g/2$	$d\text{-}t_{2g}/3 - d\text{-}e_g/2$
Ti	1.00	0.336	0.328	0.008
	0.63	0.474	0.371	0.103
Zr	1.00	0.356	0.274	0.082
	0.80	0.423	0.321	0.102
Hf	1.00	0.258	0.245	0.013
	0.69	0.398	0.308	0.090

^a Shows average charge per state of this character.

relative stability analysis of ω and β phases in terms of the charge distribution in different d substates. The analysis shows that the $\omega \rightarrow \beta$ transition is related not only to the total d population but also to the distribution of increased d charge, due to pressure-induced s–d transfer, in the different d-substates. In the hexagonal symmetry of the ω phase, the d states decompose into three irreducible representations, d_{z^2} , $d_{x^2-y^2} + d_{xy}$ and $d_{xz} + d_{yz}$. We find that in the ω stability region the dominant contributions are the $d_{xz} + d_{yz}$ character at the Al site and the $d_{x^2-y^2} + d_{xy}$ character at the B site. On increasing pressure, the populations of all the partial d states increase but the increase is largest for the d_{z^2} state. The strong interaction between the d_{z^2} states of the two Al sites (or B sites) results in strong bonding between chains of atoms running parallel to the c axis in the ω phase (equivalently, the (111) direction in the β phase) that destabilizes the ω structure. Therefore, at the Al site, for example, the pressure where the d_{z^2} charge overtakes the $d_{xy} + d_{yz}$ charge decides the onset of the $\omega \rightarrow \beta$ transition. The transition takes place when the initial $d_{z^2}/\{(d_{xz} + d_{yz})/2\}$ charge, with values of 0.78, 0.93 and 0.80 respectively for the three elements, assumes more or less the same value of 1.02–1.05.

In the cubic symmetry, the d states break up into two irreducible representations [13] namely $d\text{-}t_{2g}$ (containing three d substates) and $d\text{-}e_g$ (containing two d substates), where the $d\text{-}t_{2g}$ points to nearest neighbours along the [111] direction and the $d\text{-}e_g$ towards the next-nearest neighbours along [100]. It is the $d\text{-}t_{2g}$ charge, which is responsible for stabilizing the bcc structure, as it gives the strong directional bond along the [111] direction. As can be seen from table 1, we do find that the $d\text{-}t_{2g}$ charge contribution increases on compression towards the transition volume. The difference $d\text{-}t_{2g}/3 - d\text{-}e_g/2$ reaches almost the same value ~ 0.1 for all the three elements at the $\omega \rightarrow \beta$ transition.

In figure 2 we show the equation of state plot for Ti, Zr and Hf at 300 K. The calculated 300 K isotherm compares well with the experimental isotherms [3, 7].

To summarize, our calculated $\omega \rightarrow \beta$ transition pressures in Zr and Hf are in agreement with the experimental ones. In Ti we predict the $\omega \rightarrow \beta$ transition around 102 GPa at 300 K which is lower than that observed by Akahama *et al* [6]. This disagreement in transition pressure value could be associated with the kinetic effects. The occurrence of orthorhombic structure in the experiment of Vohra and Spencer [7] could be associated with the metastability. This is because, as reported by these authors, on decompression from 146 GPa to room pressure a mixture of α and ω phases was obtained due to large shear stress, which causes the partial conversion of $\omega\text{-}\alpha$ (unlike hydrostatic compressions). Therefore we believe that the $\omega \rightarrow \gamma$ transition in the experiment of Vohra and Spencer [7] is shear driven. More experiments under hydrostatic (quasi-hydrostatic) conditions are required to establish the structural sequence in Ti. We have qualitatively correlated the unusual trend of $\omega \rightarrow \beta$ transitions to bonding contributions from different partial d states.

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