On high pressure $\beta \rightarrow \omega$ phase transition in Ta and Zr-Nb

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Abstract. Transition from $\omega$ (hexagonal) to $\beta$ (bcc) phase under pressure is well established in group IVB elements. It is interesting, however, to explore if pressure induced $\beta$ to $\omega$ transformation is possible. In shock wave experiments $\omega$ phase has been observed in polycrystalline Ta samples retrieved from shock pressure of $\sim$ 45 GPa (Hsiung and Lassila 1998), and also, in $\beta$ stabilized Zr-Nb (Nb 20% by weight) quenched from shock pressure of $\sim$ 15 GPa (Dey et al. 2004). In static pressure measurements, on the other hand, $\beta$ to $\omega$ transition is neither found in Ta up to 170 GPa (Cynn et al. 1998), nor in Zr-Nb up to 8 GPa. Structural stability of $\beta$ and $\omega$ phases has been examined under hydrostatic compression up to 243 GPa in Ta and up to $\sim$ 18 GPa in Zr-Nb from first principles electronic band structure calculations. In agreement with experiments, present theoretical calculations suggest that the $\beta$ phase is energetically favourable over $\omega$ phase at ambient conditions and remains stable throughout the compression range of calculations. Further, the calculation of activation barrier between $\beta$ and $\omega$ phases at various pressures indicate that the $\omega$ phase is always unstable structure in Ta, however, the same phase is metastable Zr-Nb.

1. Introduction
The pressure induced $\omega \rightarrow \beta$ phase transition in Group IV transition metals is well established [1-5]. The $\omega$ and $\beta$ phases are simple hexagonal and bcc structure, respectively. Further, this observed structural transition under pressure has been associated to the pressure induced increase in $d$-electron population due to $sp-d$ electron transfer [6, 7]. It is interesting, however, to explore if pressure induced $\beta$ to $\omega$ transformation is possible. From electron microscopy measurements carried out on polycrystalline sample of elemental solid Ta retrieved from shock pressure of $\sim$ 45 GPa, Hsiung and Lassila [8] have reported the occurrence of $\beta \rightarrow \omega$ phase transition in this metal. However, in high pressure x-ray diffraction measurements carried out on Ta in diamond anvil cell (DAC) experiments, Cynn et al. [9] have reported no $\beta \rightarrow \omega$ transition up to $\sim$ 170 GPa. Subsequent, high pressure experimental studies using DAC by Dawaele et al. [10] up to 100 GPa and by Ling Yun et al. [11] up to 133 GPa also support experimental observation of Cynn et al. [9]. Similarly, in Zr-Nb (Nb 20% by weight) samples retrieved from shock pressure of $\sim$ 15 GPa, Dey et al. [12] have reported the occurrence of $\beta \rightarrow \omega$ phase transition in $\beta$ stabilized phase of this alloy. However, this transition has not been observed under static loading at 8 GPa [12]. Later from theoretical calculations using WIEN97 code Gupta et al. [13] have demonstrated that $\beta$ phase indeed remains a low energy structure as compared to $\omega$ phase under hydrostatic pressure.

In the present work, we have carried out $ab$-initio electronic band structure calculations on Ta and Zr-Nb alloy (i) to explore the possibility of pressure induced $\beta$ to $\omega$ transition in these materials
and (ii) to determine the equation state at 300 K. Further, in order to examine whether \( \omega \) phase is thermodynamically unstable or metastable, we have determined the activation barrier between \( \beta \) and \( \omega \) phases at various hydrostatic pressures. The calculations on Zr-Nb, though, are already been done by Gupta et al [13], we have further refined these by using more advanced version of WIEN code [14].

2. Theoretical Procedure

The total energy calculations have been performed as a function of hydrostatic compression on \( \beta \) and \( \omega \) phase of Ta and Zr-Nb employing full potential linearized augmented plane wave (FP-LAPW) method (WIEN2K package) [14] within generalized gradient approximation (GGA) [15] for exchange - correlation energy. The plane wave cut-off parameter \( R_{\text{Kmax}} \) is fixed at 8 for both the cases; however, a grid of 5000 k points and, 3000 k points respectively was used for sampling of the full Brillouin zone in Ta and Zr-Nb. The muffin tin radius used for both the structures was 2.0 a.u. in Ta and 2.2 a.u. in Zr-Nb. In Ta being a high Z metal; calculations have been performed both without and with spin orbit coupling (SOC). The total energy calculations for \( \beta \) and \( \omega \)-phase in Ta were performed on AlB \(_2\) type structure with one atom at the site \( \text{Al} \) \((0,0,0)\) and two atoms at site \( \text{B} \) \([(1/3,2/3,1/2+\delta),(2/3,1/3,1/2-\delta)]\). It may be noted that \( \delta = 1/6 \) for \( \beta \)-phase and \( \delta = 0 \) for ideal \( \omega \)-phase. For \( 0 < \delta < 1/6 \) the symmetry is trigonal and structures are termed as non-ideal \( \omega \). In case of Zr-Nb alloy the calculations were carried out on hexagonal super lattice \( \text{(space group P6/mmm)} \) and the \( c/a \) ratio of the super cell is twice as compared that for the normal \( \omega \) cell. The unit cell of the super lattice contain total six atoms located on three inequivalent sites \( '4h', 'a' \) and \( 'b' \) \( \text{(international Table of Crystallography, Vol. 2)} \). The site \( '4h' \) \([(2/3, 1/3, 1/4-\delta), (1/3, 2/3, 1/4+\delta), (2/3, 1/3, 1/4-\delta), (1/3, 2/3, 1/4+\delta)]\) and \( 'a' \) \((0, 0, 0)\) are occupied by Zr atoms, however, the site \( 'b' \) \((0, 0, 1/2)\) is occupied by Nb atom. In this structure the Zr-Nb alloy contained 17.5\% of Nb by weight, which is closer to the composition of Zr-20Nb sample used in the experiment. Again \( \delta = 0 \) corresponds to ideal \( \omega \) phase and \( \delta = 1/12 \) \( \text{(displacement along c axis by 1/12 of C} \omega \text{, the lattice parameter of super lattice)} \) corresponds to \( \beta \) phase. Here, for \( 0 < \delta < 1/12 \) the structures are non-ideal \( \omega \). For further clarity the ideal \( \omega \) cells used for calculations on Ta and Zr-Nb are shown in figure 1.

The 300 K isotherm is determined by adding finite temperature corrections to 0 K calculations using the procedure followed by Wallace [16] and Joshi et al.[17].

![Figure 1](image1.png)

**Figure 1.** Omega lattice used for calculations on Ta (left) and Zr-Nb (right) alloy.

3. Results and Discussions

**Tantalum**

Figure 2 displays the total energy of \( \beta \) and \( \omega \) phases relative to \( \beta \) phase for tantalum as a function of hydrostatic compression. The relative total energies have been plotted for both with and without considering SOC. It is clear from the figure that for both the cases the \( \beta \) phase is energetically
Table 1. The comparison of various physical quantities for $\beta$ of Ta at ambient conditions. The values outside and inside the brackets for the present work are determined using calculations excluding and including SOC, respectively.

|                | Theory other sources | Theory present work | Experimental |
|----------------|----------------------|---------------------|--------------|
| $V_0 (Å^3/\text{atom})$ | 18.016 [18] 18.31 [19] 18.337 [23] 18.245 [24] | 18.238 (18.4) | 18.039 [9], 18.033 [10] 18.005 [11] |
| $B_0 (\text{GPa})$ | 194 [18] 192 [19] 190 [23] 193 [24] | 193 (195.9) | 194.7 [9] 194 [10] 192.6 [11], 196 [20] |
| $B_0'$ | 3.74 [18] 3.81 [23] 3.88 [24] | 3.63 (4.03) | 3.4 [9], 3.25 [10] 3.58 [11] |
| $\gamma_0$ | 1.31 (1.51)* 1.65 (1.84)** | 1.69 [21], 1.63 [22] |

*Values determined using Dugdale- Macdonald relation; ** values determined using Slater’s relation

favourable over $\omega$ phase throughout the compression range, indicating no $\beta \rightarrow \omega$ transition up to ~ 243 GPa, which is in agreement with the experimental observations [9-11]. Further, difference in total energy of $\omega$ phase with $\beta$ is more or less independent of SOC. In figure 3 we compare the theoretically determined equation of state with experimental data [9-11] and other theoretical works [18, 19]. The present theoretical 300 K isotherm determined from calculations carried out without SOC agrees well
with experimental data [9-11] and molecular dynamic (MD) simulations [18] throughout the compression range. However, that derived from calculations including SOC though compares well with experiments [9-11] and MD simulations [19] up to ~ 60 GPa, it starts deviating systematically above this pressure. Further, our theoretical isotherm determined from calculations without SOC is softer than that reported from earlier FP-LAPW calculations [19], however the same agrees well with the later if SOC is taken into account. In Table 1 we compare various physical quantities derived from theoretical isotherm to that obtained experiments[9-11, 20-22] and those available from other theoretical sources [18, 19, 23, 24]. The Gruneisen parameter ($\gamma_0$) is determined using $B_0'$ in both the Dugdale- Macdonald approximation and Slater’s approximations.

Additionally, in order to examine whether $\omega$ phase is thermodynamically unstable or metastable, we have determined the activation barrier between $\beta$ and $\omega$ phases at various hydrostatic pressures. In figure 4 we show total energy with respect to $\beta$ phase along the path of transition in Ta at various pressures. It is clear from this figure that the $\omega$ phase is always an unstable phase. The occurrence of this transition under shock compression suggests that the shear stresses present in shock compression could stabilize even a phase unstable under hydrostatic conditions.

**Figure 4.** Total energy of ideal and non ideal $\omega$ structures relative to $\beta$ phase in Ta as a function of $\delta$, the displacement along c axis of B atoms from the 0.5c$_{\omega}$

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**Figure 5.** Total energy of $\beta$ and $\omega$ phases relative to $\beta$ phase for Zr-Nb.

**Figure 6.** Total energy of ideal and non ideal $\omega$ structures relative to $\beta$ phase in Zr-Nb as a function of $\delta$, the displacement along c axis of B atoms from the 0.25C$_{\omega}$ where C$_{\omega}$ is the lattice parameter of super lattice as displayed in figure 1.
Figure 5 displays the total energy of ideal ω phase relative to that of β phase as a function of volume under hydrostatic compression for Zr-Nb alloy. As depicted in figure, like tantalum, in Zr-Nb also, the β phase is favourable over ω phase throughout the compression range under hydrostatic loading. The zero pressure volume and, bulk modulus and its pressure derivative at this volume for β phase was determined to be 22.06 (Å³)/atom, 113 GPa and 5.64, respectively.

Finally, to determine the activation barrier between β and ω phase, we performed total energy calculations as a function of δ for various compressions. It may be noted that as mentioned in previous section, in case of Zr-Nb the displacement δ along c-axis is normalized with respect to the corresponding lattice parameter of super lattice. As shown in figure 6, for all compressions the total energy shows the two minima corresponding to stable β phase and metastable ω phase. At zero pressure, the local minimum occurs for δ = 0, however, at 7.5 GPa and 15 GPa it shifts to rumpled ω with δ ~–0.02 and δ ~–0.04, respectively. The activation barriers of ~1.1 mRy/atom at zero pressure increases to ~ 1.5 mRy/atom at 15 GPa. The β to ω transition in Zr-Nb is possible, only if the available energy during compression is sufficient to overcome the activation barrier. The detection of ω phase in shock treated samples suggests that this activation barrier might have been overcome due to shear stress present in the shock loading.

Summary

To summarise, our analysis highlights the role of shear stresses in stabilizing the structures which, under hydrostatic condition are metastable or even unstable. It supports the viewpoint of Joshi et al.[5] who proposed that the occurrence of metastable γ and δ phases in Ti at Mbar pressures is related to the presence of shear stresses in DAC experiments.

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