The high-pressure stability of Ni$_2$In-type structure of ZrO$_2$ with respect to OII and Fe$_2$P-type phases: A first-principles study

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Abstract: The density-functional theory is used to investigate the stability of the Ni$_2$In-type hexagonal structure with the space group: $P6_3/mmc$ at high pressures and compared to the orthorhombic OII and Fe$_2$P-type phases of zirconia (ZrO$_2$). The calculations showed that the high-pressure phase transition sequence in ZrO$_2$ is as follows: OII $\rightarrow$ Fe$_2$P $\rightarrow$ Ni$_2$In, which is consistent with the recent measurements that are observed in Fe$_2$P as a post-OII phase of ZrO$_2$. We obtained a very small volume change across OII $\rightarrow$ Fe$_2$P transition, whereas an appreciable volume change is found across the Fe$_2$P $\rightarrow$ Ni$_2$In transition. The compressibility of Ni$_2$In phase is found to be high as compared to the other two high-pressure phases.

1. Introduction
The transition-metal dioxide zirconia (ZrO$_2$) is involved in many industrial applications [1–7] due to its important properties. As a result of the bonding nature of this dioxide, ZrO$_2$ has received an obvious attention regarding its structural and mechanical properties, where many experimental (e.g., Refs. [8–13]) and theoretical (e.g., Refs. [8, 11, 14–17]) studies have focused on investigating the high-pressure behavior of ZrO$_2$ including the determination of the EOS of its various polymorphs, phase stability, and mechanical strength. At ambient temperature, the well-known high-pressure phase transition sequence [8, 12, 14, 15, 18, 19] is as follows: MI $\rightarrow$ OI $\rightarrow$ OII, where MI has a monoclinic structure (space group: $P2_1/c$) and both OI and OII have an orthorhombic structure (space groups: $Pbca$ and $Pnma$, respectively). Recent measurements and calculations have confirmed the discovery of Fe$_2$P-type structure (Hexagonal, space group: $P6_2m$) as a post-OII phase for ZrO$_2$ at ultrahigh pressures [11], and thus, the most recent high-pressure sequence becomes as follows: MI $\rightarrow$ OI $\rightarrow$ OII $\rightarrow$ Fe$_2$P (Fig. 1). We should mention that Fe$_2$P-type structure has been also discovered as a post-OII phase in the similar dioxides TiO$_2$ [20] and HfO$_2$ [21]. Recently, after this discovery, another theoretical study [16] has proposed a new hexagonal phase (Ni$_2$In-type structure) of ZrO$_2$ (Fig. 1) to be the most stable phase at pressures greater than 380 GPa. However, in this work [16], the transition to Ni$_2$In phase is claimed to likely occur from OII phase rather than Fe$_2$P phase, indicating that this study [16] suggests the following transition sequence: MI $\rightarrow$ OI $\rightarrow$ OII $\rightarrow$ Ni$_2$In. In fact, ignoring Fe$_2$P phase from the high-pressure phase transition sequence is not consistent with the recent experimental and theoretical studies [11, 20, 21] that have confirmed the phase stability of Fe$_2$P as a post-OII phase. Thus, the reasonable expectation is that any new proposed phase transition in ZrO$_2$ should occur from the experimentally observed Fe$_2$P phase.

In our study, we use DFT calculations to test the stability of Ni$_2$In-type structure at high pressures with respect to OII and Fe$_2$P phases. The main goal in this work is to investigate the upper part of high-pressure phase transition sequence of ZrO$_2$ in an effort to better understand the high-pressure phase diagram of this dioxide.
2. Theoretical Methods

To investigate the high-pressure phase transitions and the EOSs within the three ZrO\textsubscript{2} phases, we used density-functional theory (DFT) [22] based static first-principles computations. The projector-augmented wave (PAW) formalism [23, 24] was used to treat the interactions between the atoms having a core radii of 2.500 Bohr for hafnium Hf (with the valence configuration of 4\textit{s}^24\textit{p}^65\textit{s}^24\textit{d}^2) and 1.520 Bohr for oxygen O (with the valence configuration of 2\textit{s}^22\textit{p}^4). The generalized gradient approximation (GGA) [25] was used to treat the electronic exchange and correlation effects. We performed our calculations using the VASP software package [26–29] with an energy cutoff of 600 eV and Γ-centered \textit{k}-point meshes [30]. For all phases, total energies and pressures were converged to better than ~0.1 meV/atom and ~0.1 GPa, respectively. The Brillouin zone integration was performed using the following \textit{k}-point meshes for the ZrO\textsubscript{2} phases: 4x8x4 for OII, 6x6x10 for Fe\textsubscript{2}P, and 10x10x8 for Ni\textsubscript{2}In. For a fixed volume, all internal degrees of freedom and unit-cell parameters of the structure were optimized simultaneously during the geometry optimizations. The ground-state energy for each phase was determined for 13-20 volumes. Up to highest pressure achieved in our calculations, all ZrO\textsubscript{2} phases remain insulators.

3. Results and Discussion

3.1. Bulk modulus determination

To study the compressibility of the three phases, we used Birch-Murnaghan (BM-) EOS to determine the bulk modulus for each phase. In the third-order BM-EOS [31], the pressure \(P\) is given by

\[
P(V) = \frac{3}{2} K_0 \left[ \left( \frac{V}{V_0} \right)^{7/3} - \left( \frac{V}{V_0} \right)^{5/3} \right] + \frac{3}{4} K_0 \left( \frac{V}{V_0} \right)^{5/3} \left( \frac{V}{V_0} \right)^{2/3} - 1 \]  \quad \text{Eqn. (1)}

Figure 1: Crystal structures of ZrO\textsubscript{2} phases. The larger dark spheres represent the Zr atom, while the smaller light spheres represent the O atom.
where $V$ is the volume at pressure $P$, $V_0$ is the zero-pressure volume, $K_0$ is the zero-pressure bulk modulus, and $K_0'$ is the first pressure derivative of the bulk modulus at zero pressure. From the thermodynamic relationship: $P(V) = -\frac{\partial E}{\partial V}$, the total energy $E$ in the third-order form of BM-EOS is written as

$$E(V) = \frac{9K_0V_0}{2}\left[\frac{1}{2}\left(\frac{V}{V_0}\right)^\frac{2}{3} - 1\right]^2 + (K_0' - 4)\left[\frac{1}{2}\left(\frac{V}{V_0}\right)^\frac{2}{3} - 1\right] + E_0$$  

Eqn. (2)

Where $E_0$ is the total energy at zero pressure. One can obtain the second-order BM-EOS by substituting $K_0' = 4$ in Eqns. 1 and 2. The EOS parameters for each ZrO$_2$ phase were obtained by fitting the total energy as a function of volume to the second- and third-order BM-EOS [31] (Table I). We determined the EOSs for the three phases and summarized them in Table I. We note that our bulk modulus ($K_0$) for both OII and Fe$_2$P phases is in excellent agreement with previous studies [8, 11, 16]. On the other hand, our computed $K_0$ for Ni$_2$In phase is ~16% less than previous results [16]. However, we should note that BM-EOS is sensitive to both $V_0$ and $K_0'$ [31], where $K_0$ decreases with increasing $V_0$ and/or $K_0'$. Although our $K_0$ value (200 GPa) of Ni$_2$In is less than the previously reported one (239 GPa) [16], $V_0$ (31.81 Å$^3$) and $K_0'$ (4) are greater than the reported values [16] of $V_0$ (29.21 Å$^3$) and $K_0'$ (3.86). The EOS calculations show that the change in $K_0$ across the phases is as follows: OII $\rightarrow$ Fe$_2$P ($K_0$ increases) and Fe$_2$P $\rightarrow$ Ni$_2$In ($K_0$ decreases), in agreement with previous studies [8, 11, 16]. In details, using the second-order BM-EOS, $K_0$ increases by ~5.8% across OII $\rightarrow$ Fe$_2$P and decreases by ~26% across Fe$_2$P $\rightarrow$ Ni$_2$In. This clearly indicates that Ni$_2$In-ZrO$_2$ phase is noticeably more compressible than OII and Fe$_2$P phases.

**Table I:** Theoretical EOSs of various ZrO$_2$ phases using the second- and third-order BM-EOS [31].

For comparison, we list other theoretical results [8, 11, 16]. 1σ uncertainties are given in parentheses.

| Phase | Equation of state | Reference |
|-------|-------------------|-----------|
|       | $V_0$ (Å$^3$) | $K_0$ (GPa) | $K_0'$ | |
| OII   | 31.35 (0.04) | 251 (3) | 4 (fixed) | Ref. [8] |
|       | 30.66 | 258 | 4 (fixed) | Ref. [11] |
|       | 30.78 | 242 | 4.24 | Ref. [11] |
|       | 30.88 | 211 | 4.01 | Ref. [16] |
|       | 31.28 (0.04) | 257 (2) | 4 (fixed) | This work |
|       | 31.44 (0.03) | 234 (3) | 4.43 (0.06) | This work |
| Fe$_2$P | 30.34 | 272 | 4 (fixed) | Ref. [11] |
|       | 30.43 | 260 | 4.18 | Ref. [11] |
|       | 30.17 | 248 | 3.76 | Ref. [16] |
|       | 30.94 (0.03) | 272 (2) | 4 (fixed) | This work |
|       | 31.03 (0.01) | 255 (1) | 4.31 (0.01) | This work |
| Ni$_2$In | 29.21 | 239 | 3.86 | Ref. [16] |
|       | 31.81 (0.13) | 200 (5) | 4 (fixed) | This work |
|       | 32.18 (0.03) | 151 (2) | 5.10 (0.04) | This work |

To explain the noticeable compressibility in Ni$_2$In phase, we have investigated the change in the lattice parameters ($a$ and $c$) of this phase with increasing pressure. Figure 2 clearly shows that up to a few tens
of GPa, the c/a ratio sharply decreases as pressure increases. This indicates that at relatively low pressure the lattice parameter $a$ is much more incompressible than the parameter $c$, which likely explains the low $K_0$ value of Ni$_2$In phase.

Figure 2: c/a ratio for Ni$_2$In-ZrO$_2$ phase as a function of pressure. The lattice parameter $a$ is more incompressible than the parameter $c$, especially at low pressures.

3.2. Phase stability
Figure 3 shows the change in enthalpy of Fe$_2$P and Ni$_2$In phases with respect to OII phase. Our calculated transition pressures are as follows: across OII $\rightarrow$ Fe$_2$P is 94 GPa (99 GPa) using the second-(third-) order BM-EOS [31], and across Fe$_2$P $\rightarrow$ Ni$_2$In is 317 GPa (311 GPa) using the second- (third-) order BM-EOS [31]. Although our calculated transition pressure across OII $\rightarrow$ Fe$_2$P of $\sim$26-30% is less than previously reported results [11, 16], this transition is consistent with the recent measurements and calculations, where Fe$_2$P is observed to be the post-OII phase in ZrO$_2$ [11] and in the similar dioxide TiO$_2$ [20], and thus, any high-pressure phase transition to a new structure should occur from Fe$_2$P phase. However, a recent theoretical study [16] has concluded that the transition to Ni$_2$In phase is likely to occur from OII phase and not from Fe$_2$P phase which is not consistent with the recent experimental and theoretical results [20, 11]. These studies have obviously shown that Fe$_2$P phase is more stable at high pressures compared to OII phase. On the other hand, our high-pressure phase transition sequence for ZrO$_2$ (OII $\rightarrow$ Fe$_2$P $\rightarrow$ Ni$_2$In) is in reasonable agreement with previous experimental studies [20, 11] as we propose the transition to Ni$_2$In to occur from Fe$_2$P rather than from OII. Even though Ni$_2$In-ZrO$_2$ phase has not been experimentally observed yet, likely due to the extreme pressure-temperature conditions required to stabilize it, our calculations show that it is the most stable phase of ZrO$_2$ at ultra-high pressures in agreement with previous calculations [16].
Figure 3: Change in enthalpy with respect to OII phase versus pressure of one ZrO$_2$ formula unit. The transition pressures from OII to Fe$_2$P (left) and from Fe$_2$P to Ni$_3$In (right) using a second- (dashed curve) and third- (solid curve) order BM-EOS [31] are given.

3.3. Volume change across transitions
In this section we discuss the volume decrease across each transition of the phase sequence OII $\rightarrow$ Fe$_2$P $\rightarrow$ Ni$_3$In. Figure 4 shows the volume of each ZrO$_2$ phase as a function of pressure as well as the volume decrease across each transition. Our calculations predict a small volume decrease of ~0.4% across OII $\rightarrow$ Fe$_2$P, while we predict a large volume change of ~3.6% across Fe$_2$P $\rightarrow$ Ni$_3$In. However, we should note that the coordination number (CN) across the transition OII $\rightarrow$ Fe$_2$P remains unchanged, which explains the small volume decrease across this transition. On the other hand, the Fe$_2$P $\rightarrow$ Ni$_3$In transition is associated with a CN increase from 9 to 11, and therefore, a large volume decrease is found as expected. This large volume decrease is consistent with previous studies on ZrO$_2$ [8] and similar dioxides TiO$_2$ [32] and HfO$_2$ [33] that have shown a large volume collapse when the transition across the phases is associated with a CN increase.
Figure 4: Pressure versus volume of one ZrO₂ formula unit using the third-order BM-EOS [31]. The dotted line represents the OII phase, and the solid line represents the Fe₂P phase, whereas the dashed line represents the Ni₂In phase. The volume change at the transition pressure is shown (upper inset: across Fe₂P → Ni₂In, lower inset: across OII → Fe₂P).

4. Conclusions
In summary, using DFT calculations, we investigated the stability of Ni₂In phase at high pressures with respect to OII and Fe₂P phases for ZrO₂. Our calculations showed that the predicted high-pressure phase sequence across these phases is as follows: OII → Fe₂P → Ni₂In, where Ni₂In phase is stable at pressures greater than ~317 GPa. Furthermore, we computed BM-EOS for the three phases, and found that the compressibility of Ni₂In phase is obviously high when compared to the other two high-pressure phases. Finally, we have predicted a very small volume change across OII → Fe₂P and a noticeably large volume change across Fe₂P → Ni₂In transition.

Acknowledgements
This work was completed utilizing the Holland Computing Center of the University of Nebraska.

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