Tight-binding study of high-pressure phase transitions in titanium: alpha to omega and beyond

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We use a tight-binding total energy method, with parameters determined from a fit to first-principles calculations, to examine the newly discovered α phase of titanium. Our parameters were adjusted to accurately describe the α-Ti-ω-Ti phase transition, which is misplaced by density functional calculations. We find a transition from ω-Ti to α-Ti at 102 GPa, in agreement with the experimental value of 116 GPa. Our results suggest that current density functional calculations will not reproduce the ω-Ti-γ-Ti phase transition, but will instead predict a transition from ω-Ti to the bcc β-Ti phase.

Structural transformations in titanium have received a great deal of experimental and theoretical attention. This Letter is motivated by a recent experimental study which revealed a previously unsuspected phase transition in titanium at 116 GPa from the ω-Ti phase to a new γ-Ti phase. We have been able to confirm these experiments by performing highly accurate tight-binding calculations of the phase diagram of Ti.

At room temperature the group-IV metals zirconium and hafnium transform under pressure from the ground state hexagonal close packed (hcp) phase to the intermediate pressure phase ω [3] (space group P6/mmm – D1h, Pearson Symbol h3P, Strukturbericht Designation: C32) at 2.2 GPa and 38 GPa, respectively. At 35 GPa [1,2] and 71 GPa respectively, the metals transform from the ω phase to a body centered cubic (bcc) structure. One would logically assume that titanium also follows this transformation sequence, and indeed the transition from hcp α-Ti to ω-Ti takes place at a pressure variously given as 9 GPa [4–6] or 20–90 GPa [7]. However, no room temperature pressure driven transition from α-Ti to β-Ti has been observed, although first-principles calculations predict a transition at 98 GPa. [4] and β-Ti exists at room pressure and temperatures above 1155 K. [7] Recently, however, Vohra and Spencer [4] found that at 116 GPa titanium transforms from the ω phase to a previously unsuspected γ-Ti phase. The new phase has a two-atom body-centered orthorhombic unit cell, space group Cmcm – D14h, Pearson symbol oC4, with the atoms at the points (0, ±b, ±c/4), where a, b, and c are the lengths of the primitive vectors in the full orthorhombic unit cell, and y is an internal parameter.

This crystal structure is observed in various materials, including α-U, the random alloy AgCd, and a metastable form of gallium. [1,4] (The α-U phase has the Strukturbericht designation A20. [1,4,9]) With appropriate choices of the parameters this structure can reproduce several higher symmetry phases. In particular, when b/a = \sqrt{3} and y = 1/6, it becomes the hcp structure, while when b/a = c/a = \sqrt{2} and y = 1/4 the atoms are on the sites of a bcc cell. Wentzcovitch and Cohen [7] used this pathway to describe a possible theoretical model for the hcp → bcc transition in magnesium.

Examination of the γ-Ti structure by first-principles techniques requires a minimization of the total energy with respect to three parameters (e.g., b/a, c/a, and y) at several volumes. This is impractical because of the high computational demand of first principles methods. We have instead chosen to study the α-ω-γ transformation sequence using the much faster NRL tight-binding method. [8,9] This method has been shown to reproduce the ground-state phase, elastic constants, surface energies, and vacancy formation energies of the transition metals. The tight-binding parameters in Ref. [1] were found by fitting to a Local Density Approximation (LDA) database of total energies and eigenvalues for the fcc and bcc structures. The parameters correctly predicted the ground state structures of all of the transition and noble metals, including the hcp metals and manganese. [20] However, upon examination, we found that the titanium parameters from Ref. [1] do not predict the correct position for the ω-Ti phase. In fact, no α-Ti-ω-Ti phase transition is seen.

We therefore developed a new set of tight-binding parameters according to the procedures of Ref. [19], fit to an expanded database of first-principles calculations. In particular, our database includes the fcc, bcc, simple cubic, hcp, and ω structures. The eigenvalues and total energies were generated using the general-potential Linearized Augmented Plane Wave (LAPW) method, [21,22] using the Perdew-Wang 1991 Generalized Gradient Approximation (GGA) [23,24] to density functional theory. We fit our tight-binding parameters to both total energies and band structures, using the parametrization described by equations (7), (8), (9), and (11) of Ref. [19]. The RMS error in fitting the energies for the lowest energy phases (hcp, ω, fcc, and bcc) was less than 1 mRy/atom. The band structure RMS error is about 10 mRy for the occupied bands of the hcp and ω structures. [25]

In agreement with previous calculations, [1,4] our first-principles results show that the ω-Ti phase is slightly lower in energy (about 0.5 mRy/atom) than α-Ti. This
The equilibrium lattice constants of the \( \alpha \) (hcp), \( \beta \) (bcc), and \( \omega \) phases of titanium, as determined by the tight-binding parameters described in the text, \[25\] the LAPW calculations used in the fitting procedure, and experiment. Note that \( \beta \text{Ti} \) is not seen at room temperature. The lattice constant given is extrapolated from alloy data. \[26\] All values are in Bohr.

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\begin{array}{cccccc}
\text{Phase} & \text{TB} & \text{LAPW} & \text{Exp.} \\
\alpha^a & a & c & a & c & a \\
\beta^a & 5.561 & 8.699 & 5.547 & 8.779 & 5.575 & 8.851 \\
\omega^b & 6.118 & 6.118 & 6.137 & 6.137 & 6.206 & 6.206 \\
\end{array}
\]

\[a\] Experimental data from Ref. \[26\]
\[b\] Experimental data from Ref. \[1\]

FIG. 1. Low energy structures of titanium, as determined by the tight-binding parameters described in the text. The \( \gamma \text{Ti} \) phase is described in the text. Over this range of volumes it is degenerate with the hcp (A3, or \( \alpha \text{Ti} \)) structure. The crystal structures are described in full at http://cst-www.nrl.navy.mil/lattice.

We further checked the behavior of our tight-binding Hamiltonian by determining the elastic constants and phonon frequencies in \( \alpha \text{Ti} \), as shown in Tables I and II, respectively. Compared to experiment, we find an RMS error of 22 GPa for the elastic constants, and 32 cm\(^{-1}\) for the phonon frequencies. This is typical of the predictive capability of the tight-binding method for hcp metals. \[19\]

We studied the \( \alpha-\omega-\gamma \) transition path in titanium by fixing the volume of a given phase, and then minimizing the total energy as a function of the other parameters \((c/a) \) for \( \alpha \) (hcp) and \( \omega; b/a, c/a, \) and \( y \) for \( \gamma \)). The pressure was calculated in one of two ways: by differentiating an extended Birch fit, \[11\][12\] and by calculating the pressure by numerical differentiation of the total energy with respect to volume. The enthalpy of each phase, \( H(P) = E + PV \) is then calculated by both methods. In Fig. 2 we show the enthalpy of the \( \omega \text{Ti}, \gamma \text{Ti}, \) and bcc (\( \beta \text{Ti} \)) phases in the transition region. From the plot we see that the \( \omega \text{Ti}-\gamma \text{Ti} \) phase transition takes place at about 102 GPa, compared to the experimental result of 116 GPa. We also see a \( \gamma \text{Ti}-\beta \text{Ti} \) phase transition at about 115 GPa. This is not seen experimentally, but it suggests that we may expect a higher pressure \( \gamma \text{Ti}-\beta \text{Ti} \) phase transition, which would complete the \( \alpha-\omega-\beta \) transition sequence seen in Zr and Hf, albeit with an interloping \( \gamma \text{Ti} \) phase between \( \omega \text{Ti} \) and \( \beta \text{Ti} \). More details of the phase transitions predicted by our Hamiltonian are shown in Table IV.

In the absence of the \( \gamma \text{Ti} \) phase, Fig. 3 shows that
there would be an \( \omega \rightarrow \beta \) phase transition at 110 GPa. This is in good agreement with the prediction made from the LAPW/GGA calculations in our database, 105 GPa, and with the LMTO/GGA prediction of 98 GPa found in Ref. [5].

The behavior of titanium in the \( \alpha \rightarrow \omega \rightarrow \gamma \) phase sequence is explored further in Fig. 3 which shows the lattice parameters \( b/a, c/a \), and \( y \) as a function of the volume. We see that at a volume of about 85 Bohr\(^3\)/atom there is an abrupt change from hcp \( \alpha \) Ti into the lower symmetry \( \gamma \) Ti phase. From this point the structure merges more or less continuously into bcc \( \beta \) Ti at about 70 Bohr\(^3\)/atom. Note, however, that none of these phases is observed in the volume range 74-108 Bohr\(^3\), as this is the region where the \( \omega \) phase is stable.

Finally, we note that our LAPW calculations and other first-principles calculations [3,4] place the \( \omega \) Ti phase slightly lower in energy than the \( \alpha \) Ti phase, leading to a direct transition from \( \omega \) Ti to \( \beta \) Ti at 105 GPa. Hence, the essential difference between the first-principles calculations and our TB model is the ordering of the \( \alpha \) Ti and \( \omega \) Ti phases.

In conclusion, our tight-binding Hamiltonian provides a good description of the low pressure behavior of titanium, and shows the correct \( \alpha \rightarrow \omega \rightarrow \gamma \) transition sequence as reported in recent experiments. Our work suggests that current first-principles density functional calculations, which place the \( \omega \) Ti phase below the \( \alpha \) Ti phase, will also fail to predict the stability of the \( \gamma \) Ti phase under pressure.

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**TABLE IV.** Pressure induced phase transitions in titanium, as determined by the tight-binding parameters described in the text [25] and compared to experiment. [1].

| Transition | Pressure (GPa) | \( \Delta V/V \) (%) | Pressure (GPa) | \( \Delta V/V \) (%) |
|-----------|---------------|-----------------|---------------|-----------------|
| \( \alpha \rightarrow \omega \) | 6 | -0.6 | 9 | -1.9 |
| \( \omega \rightarrow \gamma \) | 102 | -1.3 | 116 | -1.6 |
| \( \gamma \rightarrow \beta \) | 115 | \( \approx 0 \) | none up to 146 GPa | |

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