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

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Abstract. – We use a tight-binding total-energy method, with parameters determined from a fit to first-principles calculations, to examine the newly discovered γ 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 γ Ti at 102 GPa, in good 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 [1–4] and theoretical [5–10] attention. This letter is motivated by a recent experimental study [1] 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 hexagonal close-packed (hcp) phase to the ω phase [2] (space group $P6/mmm-D_{6h}^1$, Pearson Symbol $hP3$, *Strukturbericht* Designation: $C32$) at 2.2 GPa [2] and 38 GPa [4], respectively. At 35 GPa [11, 12] and 71 GPa [4], respectively, the metals transform from the ω phase to a body-centered cubic (bcc) structure. In titanium the transition from hcp α Ti to ω Ti takes place at a pressure between 2 and 9 GPa [1, 2]. No pressure-driven transition from ω Ti to β Ti has been observed, although first-principles calculations predict a transition at 98 GPa [5, 10]. Recently, however, Vohra and Spencer [1] found a transition from the ω phase to a previously unsuspected γ Ti phase at 116 GPa. The new phase has a two-atom body-centered orthorhombic unit cell, space group $Cmcm-D_{2h}^{17}$, Pearson symbol $oC4$, with the atoms at the points $(0, \pm yb, \pm c/4)$, where y is an internal parameter.

This structure has the same space group and Wyckoff positions as α U, [13] which has *Strukturbericht* designation $A20$ [14, 15]. With appropriate choices of parameters this structure can reproduce several higher-symmetry phases: 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. This pathway has been used to describe a possible theoretical model for the hcp \rightarrow bcc transition in magnesium [16].

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 [17, 18]. 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. [18] 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 [19]. However, upon examination, we found that the titanium parameters from ref. [18] 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. [18], 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 [20, 21], using the Perdew-Wang 1991 Generalized Gradient Approximation (GGA) [22, 23] to density functional theory. We fit our tight-binding parameters to both total energies and band structures, using the parametrization described by eqs. (7), (8), (9), and (11) of ref. [18]. 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 [24].

In agreement with previous calculations [5–8], our first-principles results show that at equilibrium ω Ti is slightly lower in energy (about 0.5 mRy/atom) than α Ti. This implies a -5 GPa α Ti- ω Ti phase transition. We have adjusted our tight-binding parametrization to shift the ω Ti phase equilibrium upwards by 0.8 mRy/atom. This produces an α Ti- ω Ti phase transition at 6 GPa, in good agreement with experiment. As we shall see, this has important consequences for the ω Ti- γ Ti phase transition.

We have tested the fit in a variety of ways. Table I shows the equilibrium lattice constants for α -, β - and ω Ti, as determined by our tight-binding parameters, our first-principles LAPW calculations, and experiment [1, 25]. The TB agreement with experiment is comparable to that achieved by the first-principles calculations. We also examined the behavior of a variety of crystal structures using our tight-binding parameters. Figure 1 shows the energy/volume

TABLE I – *The equilibrium lattice constants of the α (hcp), β (bcc), and ω phases of titanium, as determined by the tight-binding parameters described in the text [24], the LAPW calculations used in the fitting procedure, and experiment. Note that β Ti is not seen at room temperature. The lattice constant given is extrapolated from alloy data. [25] All values are in Bohr.*

Phase	TB		LAPW		Exp.	
	a	c	a	c	a	c
$\alpha^{(a)}$	5.561	8.609	5.547	8.779	5.575	8.851
$\beta^{(a)}$	6.118	6.118	6.137	6.137	6.206	6.206
$\omega^{(b)}$	8.675	5.268	8.644	5.348	8.689	5.333

^(a) Experimental data from ref. [25].

^(b) Experimental data from ref. [1].

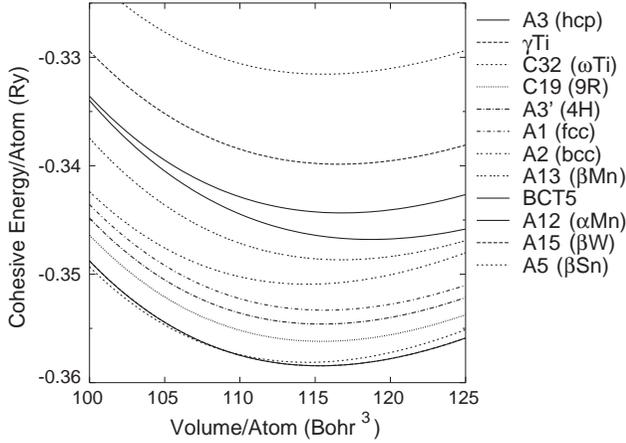


Fig. 1 – Low-energy structures of titanium, as determined by the tight-binding parameters described in the text. The γ Ti phase is described in the text. Over this range of volumes it is degenerate with the hcp (A3, or α Ti) structure. The crystal structures are described in full at <http://cst-www.nrl.navy.mil/lattice/>.

behavior of a number of low-energy structures. As expected, the observed phases (α Ti and ω Ti) are followed by close-packed stacking fault phases (9R, 4H, and fcc).

We further checked the behavior of our tight-binding Hamiltonian by determining the elastic constants and high-symmetry [26, 27] phonon frequencies of α Ti, as shown in tables II and III, respectively, where our calculations are compared to experiment [28, 29]. The results are typical of the predictive capability of the tight-binding method for hcp metals [18].

We studied the α - ω - γ 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 α (hcp) and ω ; b/a , c/a , and y for γ) using a conjugate-gradient nonlinear least-squares algorithm. Starting with the hcp structure at low pressure, we used the equilibrium parameters obtained at one volume as the starting point for the minimization of the next smaller volume. As a check, we reversed the process and started with the bcc-like lattice parameters at high pressure, and used the equilibrium results from one volume to start the calculation at the next higher volume.

The pressure was calculated in one of two ways: by differentiation of an extended Birch fit [30, 31], 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 ω Ti, γ Ti, and bcc (β Ti) phases in

TABLE II – Elastic constants of α Ti at the experimental volume, as determined from the parameters described in the text and compared to experiment [28]. All values are in GPa.

	TB	Experiment		TB	Experiment
C_{11}	127	162	C_{33}	147	181
C_{12}	81	92	C_{44}	45	47
C_{13}	64	69			

TABLE III – *High-symmetry \mathbf{k} -point phonon frequencies (in cm^{-1}) of αTi at the experimental volume, as determined from the parameters described in the text and compared to experiment [29]. The symmetry notation is from Miller and Love [26, 27].*

		TB	Exp.			TB	Exp.
Γ_3^+		189	185				
Γ_5^+		141	137	M_1^+	LO	259	257
A_1	LA/LO	178	191	M_2^+	TA	56	113
A_3	TA/TO	98	101	M_2^-	TO	171	202
K_1		275	234	M_3^+	TA	99	127
K_4		180	200	M_3^-	TO	192	232
K_5	LA/LO	144	207	M_4^-	LA	200	234
K_6	TA/TO	141	173				

the transition region. From the plot we see that the ωTi - γTi phase transition takes place at about 102 GPa, compared to the experimental result of 116 GPa. We also see a γTi - βTi phase transition at about 115 GPa. This is not seen experimentally, but it suggests that we may expect a higher-pressure γTi - βTi phase transition, which would complete the α - ω - β transition sequence seen in Zr and Hf, albeit with an interloping γTi phase between ωTi and βTi . More details of the phase transitions predicted by our Hamiltonian are shown in table IV.

In the absence of the γTi phase, fig. 2 shows that there would be an ωTi - βTi 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 α -, β -, and γTi phases 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 Bohr³/atom there is an abrupt change from hcp αTi into the lower

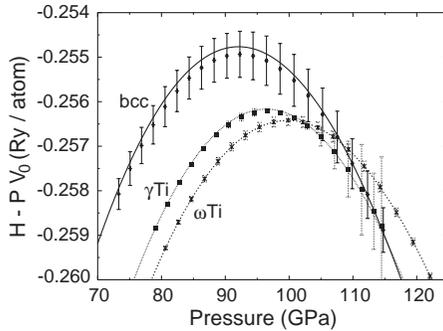


Fig. 2 – The enthalpy for several phases of titanium in the ω - γ transition region. For increased clarity we subtract PV_0 from each enthalpy, where the reference volume $V_0 = 75 \text{ Bohr}^3$. The lines are derived from extended Birch fits [30, 31] to the $E(V)$ data for each phase. Numerical differentiation of $E(V)$ provides the pressure for the points, and a check on the accuracy of the Birch fit. The error bars on the points represent estimates of the uncertainty in the energy and pressure calculations due to the numerical \mathbf{k} -point integration.

TABLE IV – Pressure-induced phase transitions in titanium, as determined by the tight-binding parameters described in the text [24] and compared to experiment [1].

Transition	TB		Experiment	
	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	≈ 0	none up to 146 GPa	

symmetry γ Ti phase. From this point the structure merges more or less continuously into bcc β Ti at about 70 Bohr³/atom. Note, however, that none of these phases is observable in the volume range 74–108 Bohr³, as this is the region where the ω Ti phase is stable.

We note that our LAPW calculations and other first-principles calculations [5–8] place the ω Ti phase slightly lower in energy than the α Ti phase, leading to a direct transition from ω Ti to β Ti at 105 GPa. Hence, the essential difference between the first-principles calculations and our TB model is the ordering of the α Ti and ω Ti phases.

The experimental zero-temperature state of titanium is still uncertain [32]. Accordingly, we refit our titanium parametrization, emphasizing the energy difference between α Ti and ω Ti. With these parameters we found the equilibrium ω Ti phase to be 0.6 mRy/atom below the equilibrium α Ti phase, close to our first-principles result. In this case we find that the ω - γ Ti and ω - β Ti transitions both take place at 113 GPa, and the γ Ti phase is never stable. This is a good indication that the correct sign of the ω - α energy difference crucial to the observation of the γ -Ti phase.

Finally, we note that the differences in zero-point energy between the ω , γ and β phases might be large enough to change the outcome of our calculations. The relevant volume range is between 74 Bohr³, the volume of the ω - γ transition and 70 Bohr³, the volume of the γ - β transition. In this region, as shown in fig. 3, the structural parameters of the γ phase are almost identical to the structural parameters in the β phase. We thus expect little difference in the zero-point energy between these two phases, and little change in the γ - β transition

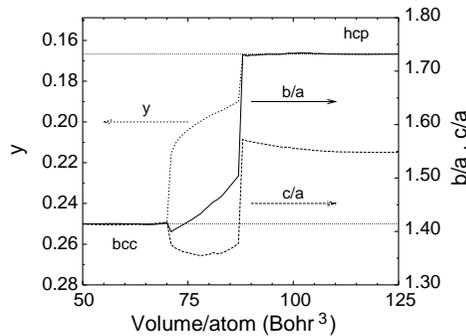


Fig. 3 – The lattice parameters b/a and c/a and the internal parameter y which minimize the total energy of γ Ti as a function volume, using the tight-binding parameters described in the text. The horizontal dotted lines indicate the parameter values needed to achieve an ideal bcc lattice ($y = 1/4$, $b/a = c/a = \sqrt{2}$) and an hcp lattice ($y = 1/6$, $b/c = \sqrt{3}$, arbitrary c/a).

pressure. As for the ω phase, we note that the bcc lattice can be described as a trigonal ω phase (space group $P\bar{1}m1-D_{3d}^3$, *Strukturbericht* Designation: C6), with $c/a = \sqrt{8/3} = 0.613$. This is close to the computed c/a ratio for the hexagonal Ti- ω phase in this volume range, 0.603, and suggests that the zero-point energy difference between the ω and β phases is small. If anything, zero-point motion in the more open ω phase should be higher than in the β phase, which would decrease the ω - γ transition pressure. We conclude that the addition of zero-point energy would not significantly change our predictions.

Summarizing, our tight-binding Hamiltonian provides a good description of the low-pressure behavior of titanium, and shows the correct α - ω - γ transition sequence as reported in recent experiments. Our work suggests that current first-principles density-functional calculations, which place the ω Ti phase below the α Ti phase, will also fail to predict the stability of the γ Ti phase under pressure.

* * *

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