High-pressure phases of titanium: First-principles calculations

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We investigate through first-principles calculations the controversial observation of the high-pressure orthorhombic (γ and δ) phases of titanium. Our calculations predict the transition sequence ω-γ-β under pressure, and reveal that the δ phase is elastically unstable under isotropic compression. We attribute its observation to nonhydrostatic stresses present in the diamond-anvil cell experiments. We find the γ phase to be stable in the 102–112 GPa pressure range, with the upper limit of this pressure range increasing under nonhydrostatic conditions.

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I. INTRODUCTION

The Group IV transition metals, titanium, zirconium, and hafnium, have been studied extensively, both theoretically and experimentally, over a wide range of pressures and temperatures in order to understand their phase diagrams and the underlying mechanisms of phase transformations. These materials are technologically important due to their mechanical strength, stiffness, resistance to degradation with rise in temperature, light weight, and corrosion resistance. As the mechanical properties in general, and especially their strength, depend upon the crystallographic phase, studies of these metals' structural stability have been vigorously pursued. The existence of narrow *d* bands overlapping with broad *s-p* bands is responsible for the structural and electronic transitions observed as thermodynamic conditions are varied; this is mainly due to uneven shifts in the relative energies of the occupied *d* and *s-p* electron bands. Applying pressure is one of the most direct ways of inducing and controlling the structural transitions, and hence there have been extensive high-pressure studies on these metals.[1–12]

Among these, Ti is the element for which high-pressure structural understanding is highly controversial. Recent experimental findings of the orthorhombic phases in Ti (Refs. 1–4) were unexpected, as earlier theoretical simulations had predicted an ω (AlB_2-type)-β [body centered cubic (bcc)] transition similar to those observed, and corroborated by theoretical calculations, in Zr and Hf.[5–7] Also, different experiments reported the α-ω transition at various pressures throughout the range 2–11.9 GPa for Ti.[8–11] More controversial yet is the occurrence and transition pressures of the γ and δ phases, both having orthorhombic structures. So far, the high-pressure β phase has not been found in most of the experiments-except as claimed by Ahuja *et al.* of the observation of the ω-β transition in the range 40 to 80 GPa;[11] all other experiments document the stability of the ω phase at pressures up to at least 100 GPa.[1–4] Also, theoretical calculations predict various transition pressures for the β phase, occurring either directly from the ω phase [57.5 GPa,[5] 80 GPa,[11] 93 GPa (Ref. 7)] or via the δ phase [136 GPa (Ref. 12)]. Moreover, there is disagreement on the influence of temperature on the stability of the γ phase,[7,13] mainly because the enthalpy differences among different phases in the relevant pressure region are quite small.

Accuracy limitations of the methods employed for the computations, inappropriate values of a few parameters used, and insufficient sampling of the Brillouin zone (BZ) for different structures[12] might all have contributed to the incompatible inferences of the different studies. Among these inconsistencies is the assertion by some investigators that no orthorhombic phase occurs at all at high pressures,[7,11] in contradiction to Kutepov and Kutepova[12] who predicted—using the full potential linear augmented plane wave (FP-LAPW) method—the stability of the γ and δ phases before the occurrence of β phase at higher pressure. Kutepov and Kutepova also obtained reasonably good agreement with the experimental data regarding all the structural transitions[1–4] of Ti, but the nature of their total energy curves in the γ phase near 13 $Å^3$/atom volume (40–55 GPa pressure range; see Fig. 1 of Ref. 12) and that of the enthalpy curve in the δ phase in the 135–145 GPa range (see Fig. 2 of Ref. 12) appear to be unusual. Some of the oscillations they see could indicate multiple minima in the total energy versus volume curves, which are unusual for electronic structure calculations pertaining to isotropic compression except for the occurrence of electronic transitions such as Mott-type delocalization effects.[14] The authors of Ref. 12 are themselves skeptical about the authenticity of these oscillations, and attribute them to poor Brillouin-zone (BZ) sampling. The fact that the β phase has not been observed at their predicted pressure ($\sim$136 GPa) in recent experiments, even after repetition,[1–4] indicates that further high-pressure investigations of Ti are useful—especially as it is argued that nonhydrostatic conditions in the experiments hinder the observation of the β structure, which is thus manifested as the δ phase distortion.[2–4,12] Hence, with the aim to resolve the prevailing discrepancies in the high-pressure behavior of Ti, especially at Mbar pressures where orthorhombic phases have been reported, we carried out extensive first-principles electronic-structure calculations that include efforts to mimic the anisotropic stress conditions present in diamond-anvil cell (DAC) experiments.[1–4]

II. DETAILS OF CALCULATIONS

Total-energy calculations as a function of volume were carried out using the first-principles augmented plane-wave (APW) with local orbitals (LO) method as implemented in the WIEN2K computer code.[15] Structural relaxation of the γ and δ phases was performed employing the VASP code (Vienna *Ab Initio* Simulation Package[16–18]), and the generalized gradient approximation (GGA) was employed for exchange-correlations contributions.[19] For all the structures, the WIEN2K total energy calculations were performed using $R_{MT}=1.8$ a.u. and $R_{MT}K_{max}=10$, where R_{MT} is the radius of the muffin-tin sphere and K_{max} controls the energy cutoff of the plane-wave basis set in the APW expansion of the electron states. For consistent numerical accuracy, it is necessary to keep R_{MT} fixed in the high-pressure studies, so that the cutoff energy for the plane-wave expansion does not change with compression.[20] For the full Brillouin-zone (FBZ) sampling, we used 2000, 3000, and 6000 k points respectively for ω, orthorhombic, and β phases. Convergence with respect to the number of k points in the BZ was checked for accuracy to be consistent with the numerical value of 0.01 mRy/atom achieved for the energy convergence. The VASP calculations were performed with the plane-wave basis energy cutoff, $E_{cut}=450$ eV, $17\times17\times17$ mesh for FBZ sampling, and with projector augmented-wave (PAW) pseudopotential, which includes nonlinear core corrections and accounts for core-core overlap. The semicore states $3s$ and $3p$ were included among the valence electrons. These types of PAW potentials have been tested and found suitable for high-pressure studies.[18,21]

The experimental values of the axial ratio (c/a) of the ω phase vary under compression from 0.614 to 0.638 up to 112 GPa pressure.[1] However, we performed the calculations at a fixed value of $c/a=0.624$,[22] as the variation in axial ratio in this phase over the pressure region of our study (100–150 GPa) is known to produce insignificant change in the structural energy.[5,7] The γ phase has orthorhombic structure, with space group *Cmcm* and atoms at the $4c$ Wyckoff positions $(0,y,1/4)$ with $y=0.11$.[2] The lattice-parameter ratios for the γ phase were taken as $a/b=0.5340$ and $c/b=0.8689$, as per the data at 130 GPa of Ref. 2. The δ phase has the same structure and space group, the only difference being that the value of y in the $4c$ Wyckoff position is 0.295.[2] The a/b and c/b ratios in our calculations for the δ phase were fixed at the values of 1.468 and 1.381, again in view of the data of Ref. 2 at 178 GPa. We maintained the same lattice-parameter ratios for other compressions for these two orthorhombic phases.

III. RESULTS AND DISCUSSION

We calculated the 0 **K** total energies of ω, γ, δ, and β phases. As can be seen from Fig. 1, the γ phase becomes energetically more stable than the ω phase at a volume of 10.97 Å^3 per atom (i.e., $V/V_0=0.64$). In the stability region of the γ phase, the β-phase energy is up to 1 mRy/atom higher [1.45 mRy/atom at a compression of 0.631 (i.e. volume of 10.81 Å^3 per atom). The γ phase remains energetically stable up to a volume of 10.61 Å^3 per atom, and on further compression the β phase becomes stable and persists up to the highest volume compression ($V/V_0=0.50$) studied in the present work.

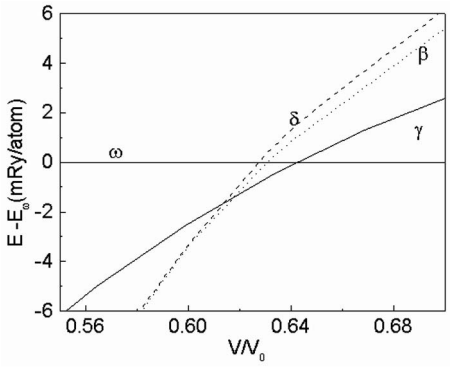

FIG. 1. Total energies of γ, δ, and β phases of Ti with volume compression, shown relative to the ω-phase energy at the same volume. Equilibrium volume V_0 is 17.14 Å^3 per atom.

Using the total energies, we calculated the enthalpies of the ω, γ, and β phases (Fig. 2). The calculated ω to γ phase transition pressure is 102 GPa (10.97 Å^3/atom), which is lower than the experimentally observed transition pressure of 116 (±4) GPa.[1] Subsequent phase transition from γ to β phases occurs at 112 GPa (10.61 Å^3/atom).

This set of calculations reproduces the ω-γ-β sequence under pressure, with no signature of the δ phase although its energy is close to—but slightly higher than—that of the β phase over the pressure range in which it was observed (Fig. 1).

Also, we find that the hcp structure is not a zero-pressure phase, contrary to experimental observation. In fact, we found the zero-pressure phase is ω, which has about 1 mRy per atom lower enthalpy than that of hcp. This is, however, in agreement with other theoretical calculations,[12,23] and is interpreted as temperature (entropy) stabilizing the hcp structure.

While calculating the total energies with the experimental structural parameters for the orthorhombic phases of Ti, we noticed forces as large as 1 eV per Å on atoms in the γ Ti, while in δ Ti these were smaller. We therefore optimized the

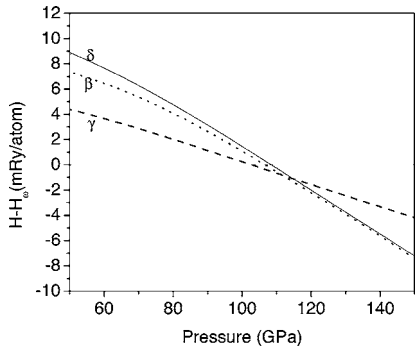

FIG. 2. Enthalpy variation with pressure for β, γ and δ phases, relative to that of ω phase at the same compression, shown as functions of pressure.

structures for these phases, relaxing the a/b, c/b and internal parameter y at each fixed value of the volume, until the forces on the atoms were less than 0.5 meV/Å. We found that δ Ti is not an elastically stable phase at any compression. In fact, at lower compressions (e.g., 16.1, 14.93 Å^3 per atom), it relaxes to the body-centered tetragonal (bct) structure, and at higher compressions (e.g., 10.41, 9.43, 7.00 Å^3 per atom) to the bcc structure. We thus rule out the existence of the δ phase at any compression under truly hydrostatic conditions. The γ phase relaxes to the hexagonal structure at lower compressions (e.g., 17.14, 15.5 Å^3 per atom), but at higher compressions (for volumes lower than 13.86 Å^3 per atom) it is a stable phase, though it could be of higher enthalpy than bcc.

Our results on the δ phase under hydrostatic conditions, are in contrast to those of Kutepov and Kutepova,[12] but in agreement with Joshi *et al.*[7] and Ahuja *et al.*[11] We find from analysis of our electronic-structure results that the calculated atom-projected d density of states at the Fermi level (E_F) for the γ phase is lower in its stability region than those of the β phase. However, this difference decreases with compression, and in the β phase stability region the γ phase acquires a higher atom-projected d density of states at E_F compared to the β phase.[24] This supports Vohra and Spencer's[1] explanation for the γ phase being observed prior to the bcc phase in their experiments.

To get a better insight into the influence of nonhydrostaticity on observations of the δ phase and of the γ phase over a larger pressure range, as previously suggested,[7,12] we carried out further optimization of the orthorhombic structure for two different stress conditions. It is possible to simulate conditions of nonhydrostatic stress by adjusting lattice parameters and relaxing internal coordinates until the desired state of stress is achieved.[25] However, the exact stress conditions are difficult to establish in DAC experiments. Still, we do expect the observed a/b and c/b lattice-parameter ratios[1,2] to mimic the nonhydrostatic stress conditions for the γ and δ phases. It is important to note that these two a/b and c/b values do not correspond to the theoretical equilibrium ratios under hydrostatic compression, and hence represent two different nonhydrostatic stress conditions.

The calculated total energies are shown as a function of the y parameter in Figs. 3(a) and 3(b), allowing us to obtain the most appropriate values under the given nonhydrostatic conditions existing with the chosen (experimental) a/b and c/b ratios. Note that in these two structures the total energy variations with the y parameter and the optimized y values are drastically different. In fact, for the γ phase case at the volume of 17.14 Å^3 per atom (V_0), we find that there is only one minimum at $y=0.1667$ (hcp structure), and a maximum exists at $y=0.25$ (bcc structure) [Fig. 3(a)]. As compression is increased, we see the development of a second minimum around $y=0.25$, and shifting of the minimum at 0.1667 towards 0.11. At a volume of 9.43 Å^3 per atom (about 140 GPa under isotropic compression), the minimum at $y=0.25$ becomes lower in energy. These details indicate the possible existence of the γ phase under suitable stresses over a larger pressure range than quoted earlier (i.e., the range of 10.97–10.61 Å^3 per atom) for isotropic compression.

Similar results for the δ-phase lattice-parameter ratios are shown in Fig. 3(b). At a volume of 17.14 Å^3 per atom we

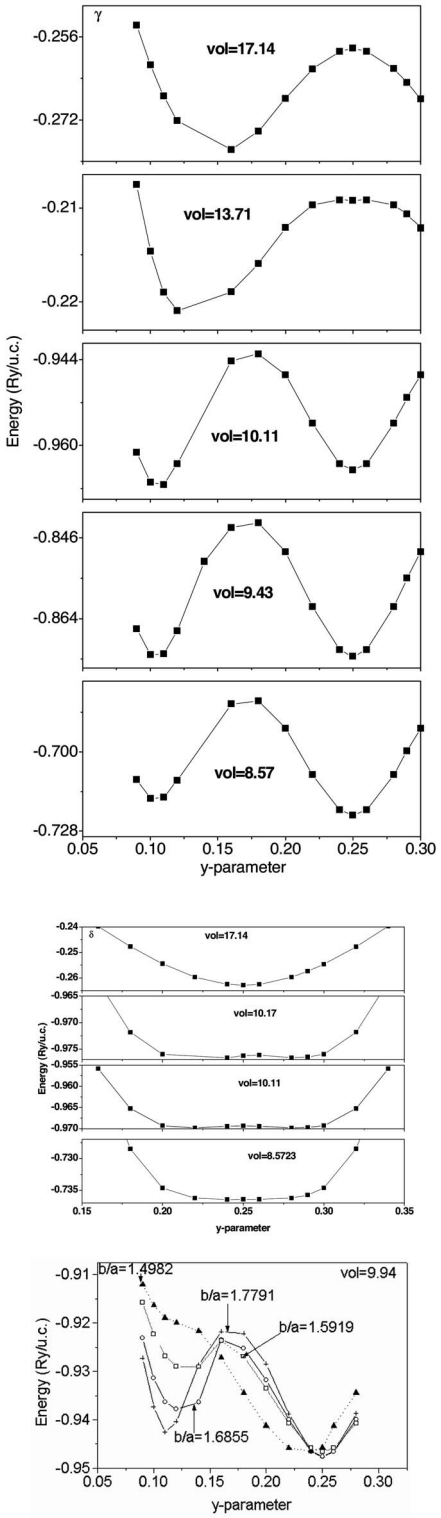

FIG. 3. (a) Total energy variation as a function of the y parameter in the γ phase at different volumes. The values of volumes are given in Å^3 per atom. (b) Total energy variation as a function of the y parameter in the δ phase at different volumes. The volume is given in the unit of Å^3 per atom. (c) Total energy variation as a function of the y parameter in the γ phase for different b/a ratios at a fixed volume of 9.94 Å^3, with c/a fixed at the γ-phase value given in Ref. 2.

TABLE I. Diagonal elements of the stress tensor at two different compressions of Ti.

Volume per atom (Å^3)	Stress components (GPa)	γ phase	δ phase	bcc phase
	s_{xx}	147.9	140.5	140.0
9.43	s_{yy}	153.2	141.5	140.0
	s_{zz}	158.2	142.5	140.0
	s_{xx}	108.1	103.3	102.7
10.287	s_{yy}	110.1	101.4	102.7
	s_{zz}	113.4	103.2	102.7

find only one minimum, at about $y=0.25$ (similar to that in bcc structure), with no other feature. The contrasting behavior of these two stress conditions (corresponding to γ and δ phases) at the volume of 17.14 Å^3 per atom is an indication of the importance of the role played by nonhydrostatic stresses in the experimental observation of these phases, as they differ only in the y parameter, a/b and c/b ratios. A reduction in volume results in widening of the valley around $y=0.25$, and covering the range 0.20–0.30 with a small hump at $y=0.25$ [Fig. 3(b)]. Note that the total energy variation in this range is comparable to the energy difference between bcc and δ phases shown in Fig. 1 at Mbar pressures, indicating the possibility of δ-phase stability under anisotropic stress. The thin margin between the δ and bcc phase stresses is also evident from Table I, which corresponds to a compression at which bcc is stable under hydrostatic conditions but the δ phase is observed due to nonhydrostatic stresses. It can be seen that the experimental lattice-parameter ratios correspond to limited anisotropy in the δ phase at this compression, whereas those for γ phase result in large anisotropic stresses. Table I also verifies that the anisotropies in the γ and δ phases are comparable at lower compressions.

Further, Fig. 3(c) provides some insight into these orthorhombic phases under different stress conditions. Here we show the calculated total energy as a function of the y parameter for different value of b/a, keeping the c/a ratio fixed, at a volume near that of the γ-β transition. We observe not only reduction of the energy barrier with decreasing b/a ratio but also flattening of the minimum around $y=0.25$. Thus, depending on the compression and anisotropy of the stress conditions, either γ [see Fig. 3(a)], or β/δ phase could be observed in an experiment. At the value of 1.4982 for b/a, there is no minimum near $y=0.11$ (indicating the possible occurrence of the δ phase, as discussed earlier). We have also carried out similar calculations for other combinations of b/a and c/a using VASP, and the nature of these curves remains similar to those shown in Fig. 3(c). When

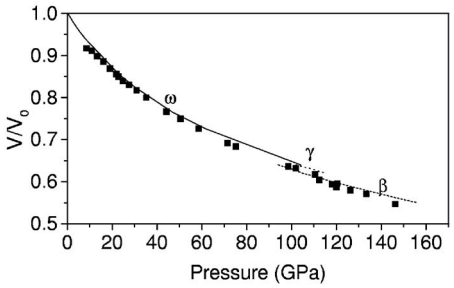

FIG. 4. Pressure variation as a function of V/V_0. V_0 is the respective equilibrium volume in each phase. Filled squares represent the data of Vohra and Spencer (Ref. 1). Zero-point and 300 K lattice-thermal contributions to the pressure are estimated to be about 1 GPa (Ref. 26).

$a/b=c/b=\sqrt{2}$, no hump exists near $y=0.25$ [unlike in Fig. 3(b)] and thus the bcc structure prevails.

Finally, the calculated pressure-volume curve for Ti is in good agreement with the data of Vohra and Spencer[1] (Fig. 4), though slightly on the higher-pressure side possibly due to the fact that we carried out the ω-phase calculations at a fixed c/a ratio.

IV. SUMMARY

We simulated the ω-γ-β high-pressure phase transition sequence in Ti by carrying out total-energy calculations for each phase using the experimentally observed structural parameters. Under hydrostatic compression, the γ phase is found to be stable in the pressure range of 102–112 GPa, and the observed δ phase is energetically unstable. Structural relaxation of the δ phase shows the elastically unstable nature of this phase at all compressions, whereas γ is found to be elastically stable above 100 GPa. The total-energy results for the orthorhombic structure under two different stress conditions demonstrate the potential role played by anisotropic stresses in stabilizing the γ and δ phases. Our calculations also indicate that, although the γ-phase stability region under hydrostatic compression is only about 10 GPa wide (around 107 GPa), it is possible to observe this phase over a larger pressure range under nonhydrostatic situations. These results support previous arguments given for the observation of the δ phase as a manifestation of nonhydrostatic conditions in DAC experiments, and indicate that under truly hydrostatic conditions the bcc phase should be observed. An increase in temperature would shift the conditions toward hydrostatic, explaining why high-pressure-high-temperature experiments did not produce the δ phase of Ti.[11] It is hoped that our work will encourage experiments with more hydrostatic conditions, so that predictions about the relative stabilities of γ and δ phases can be verified.

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