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Crystal structures of Ti under high pressure: Theory

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The crystal structures of a few phases of Ti such as hcp, bcc, ω (hexagonal phase) γ (distorted hcp), δ (distorted bcc), and bcc under pressure have been studied by means of first-principles total-energy calculations in a generalized gradient approximation. Our calculations are different from calculations by Joshi *et al.* [Phys. Rev. B **65**, 052106 (2002)] in that we have performed the full geometry optimization for hcp, ω, γ, and δ phases at each volume considered. The experimental phase sequence hcp$\rightarrow\omega\rightarrow\gamma\rightarrow\delta$ has been obtained, though our 0-K transition pressures are little lower than the experimental ones obtained at 300 K. The phase transition $\delta\rightarrow$bcc was obtained at 136 GPa in contradiction to the experimental stability of δ phase up to the highest studied pressure 216 GPa. Our calculations have also shown that at the pressures higher than 170 GPa, the δ phase' parameters change in such a manner that structure obtained is bcc. This fact suggests that the δ structure observed in experiments at pressures 170 GPa and higher maybe is a consequence of nonhydrostatic stresses present in the experiments. Similar conclusion has been reached in the above-mentioned work by Joshi *et al.*

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Group IV transition metals titanium, zirconium, hafnium, and their alloys have tremendous scientific and technological interest. The implication of these materials in scientific area stems from the fact that they have a narrow d band in the midst of a broad sp band, which has an impact on their electronic and superconducting properties. The electronic transfer between the broad sp band and the narrow d band is the driving force behind many structural and electronic transitions in these materials.[1–4] The technological interest in these materials is connected with their high strength, light weight, and corrosion resistance. The mechanical properties of these metals and alloys can be greatly improved by controlling the crystallographic phases present. Pressure is a very important variable in causing phase transformations in these elements.

It is well known that the titanium group of elements all have the hcp crystal structure at room temperature and zero pressure. At high-temperature and zero pressure, they transform to the bcc structure before reaching the melting temperature. At room temperature and under pressure, they undergo a crystallographic phase change into the so-called ω structure. At even higher pressures, both Zr and Hf have been observed to transform to the bcc structure. In Ti, various room-temperature experiments have shown a transition from hcp to the ω phase at the pressure of 11.9 GPa,[5] 2–7 GPa,[6] 2.9–7.5 GPa,[7] 8 GPa,[8,9] 9 GPa,[10] or 7.4 GPa.[11,12] The ω phase has an interesting crystal structure, a hexagonal lattice with three atoms per unit cell. The atomic positions are at $(0,0,0)$, $(\frac{1}{3},\frac{2}{3},c/2a)$, and $(\frac{2}{3},\frac{1}{3},c/2a)$, where the c/a ratio is ~ 0.62. Thus, the symmetry of the crystal is high and there are 24 point-group operations. The ω phase has remained stable up to 87 GPa, the highest studied pressure in the Ref. 8. A few years later, Vohra *et al.*[10] have investigated the structural stability of Ti at the pressures up to 146 GPa and transition $\omega\rightarrow\gamma$ has been found at 116±4 GPa. The proposed γ phase structure belongs to the orthorhombic lattice

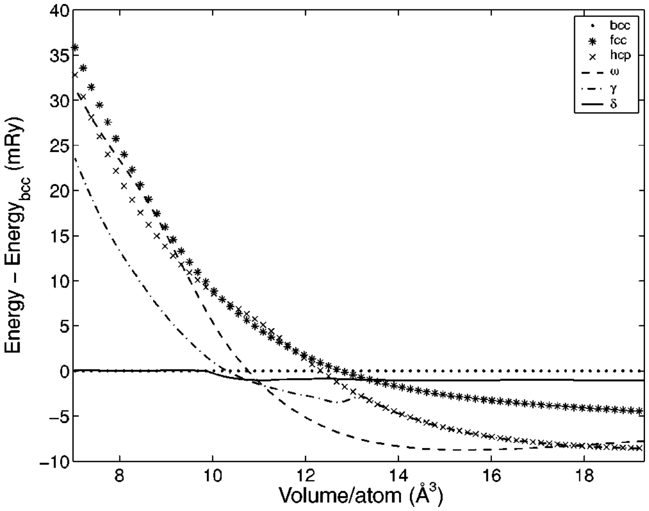

FIG. 1. Calculated energy differences of the structures with respect to the bcc phase as a function of volume.

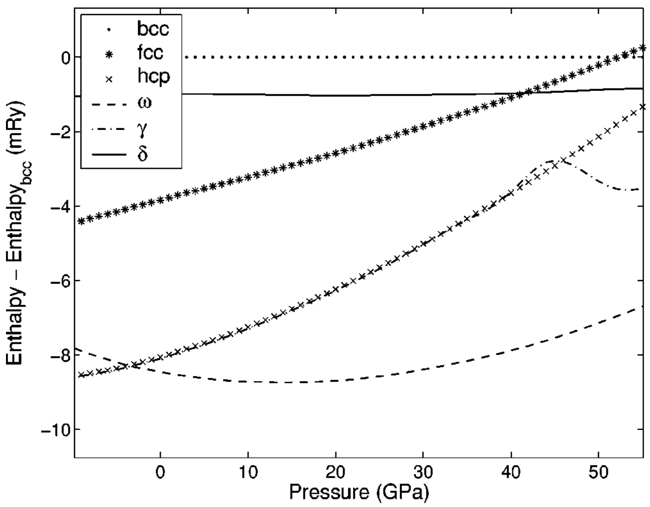

FIG. 2. Enthalpy of the titanium's structures relative to the enthalpy of bcc phase at low pressures.

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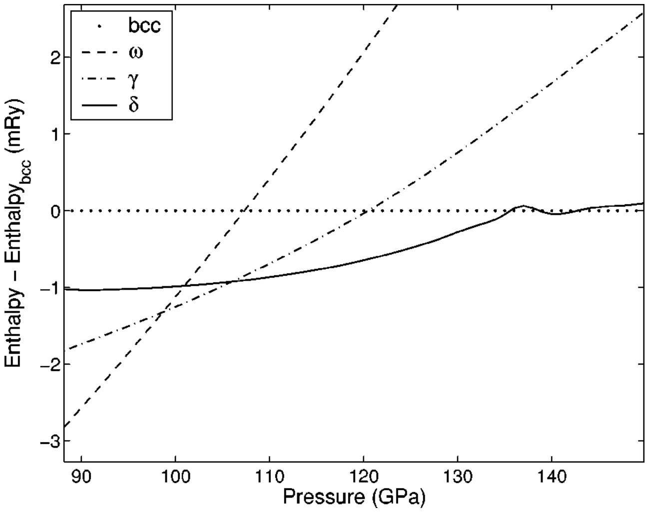

FIG. 3. Enthalpy of titanium's structures relative to enthalpy of bcc phase at high pressures.

space group: *Cmcm*. The choice of four atoms/cell gives a volume of 10.48 Å^3/atom at volume compression V/V_0 of 0.59. Cell parameters at 118 GPa are $a=2.388\pm0.005$ Å, $b=4.484\pm0.009$ Å, and $c=3.915\pm0.008$ Å. The four atoms occupy positions $(0,y,1/4)$, $(0,-y,3/4)$, $(1/2,y+1/2,1/4)$, and $(1/2,1/2-y,3/4)$ with internal parameter $y=0.10(1)$. The measured volume decreases on transformation from the ω phase to the γ phase at 120 GPa is $\triangle V/V=-1.6\%$. The γ phase has remained stable up to 146 GPa, the highest studied pressure in the Ref. 10. Recently, Akahama *et al.*[11] have reached the compression up to pressure 216 GPa. In their work, the transition $\omega\rightarrow\gamma$ have been observed at 124–130 GPa and the transition from γ to new δ phase has been observed at 140–145 GPa. Proposed δ phase structure belongs to the same orthorhombic lattice space group: *Cmcm*, and Ti atoms also occupy the same positions as in the γ phase. The lattice and positional parameters of the δ phase at 178 GPa are $a=3.8610(7)$, $b=2.6296(6)$, and $c=3.6323(4)$ Å. The internal parameter y is equal to 0.295(9). The δ phase has remained stable up to pressure 216 GPa.[11]

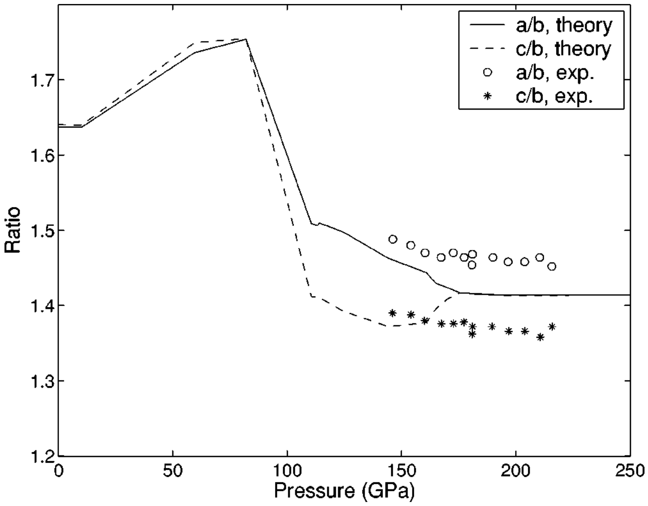

FIG. 4. The pressure dependence of the lattice parameters a/b and c/b for the δ phase. The experimental data are from Refs. 11 and 12.

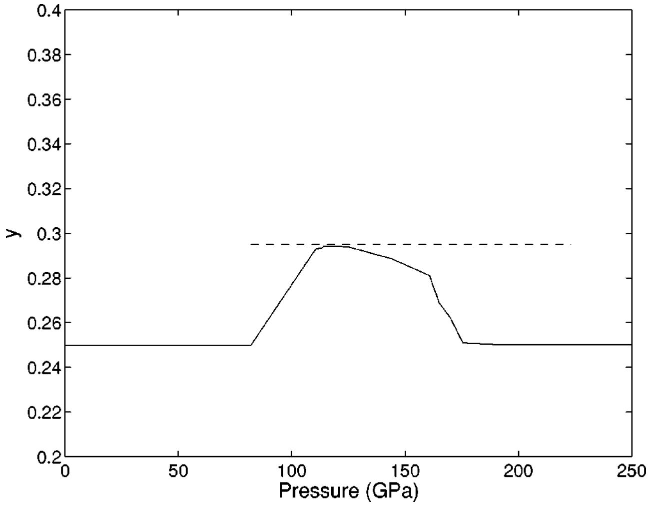

FIG. 5. The pressure dependence of the internal parameter y for the δ phase. The broken horizontal line is the experimental value of the parameter y at 178 GPa.[11]

In the theoretical work by Ahuja *et al.*,[13] the stability of the structures hcp, ω, and bcc of Ti, Zr, and Hf has been investigated. In the case of titanium, the ω phase (not hcp) has been found to be the most stable at $P=0$. This fact has been explained by the authors of Ref. 13 as a temperature effect. Further, the transition $\omega\rightarrow$bcc has been found at 57.5 GPa, that was in disagreement with the experimental data, reported by Xia *et al.*[8] The calculations in the Ref. 13 were based on the local-density approximation. As we think, this fact was a main reason for some discrepancies between the

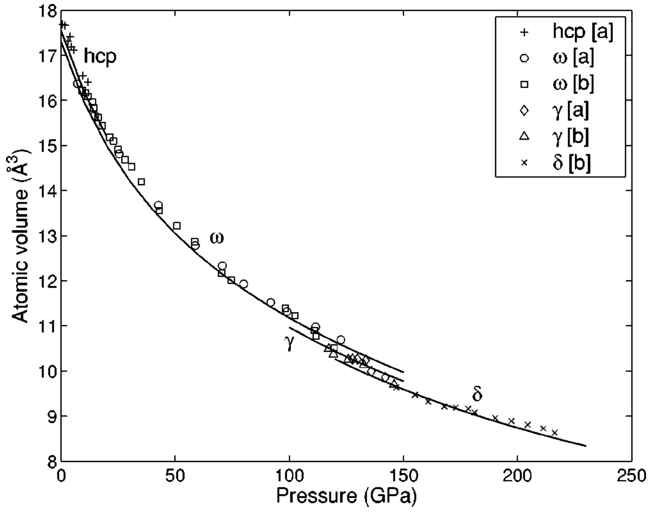

FIG. 6. Comparison of the calculated isotherm with the experimentally observed isotherms of Ti at 300 K. The theoretical results for all the phases have been drawn by solid line. Theoretical lines for bcc and δ phases are indistinguishable on the picture. Symbols belong to the experimental data (see legend). ([a] Ref. 10, [b] Ref. 11.)

TABLE I. The transition pressures and structural parameters for Ti. The structural parameters are given for the intervals of stability of the phases.

	Transition pressure (GPa)		Structural parameters	
Structure, transition	Theory	Experiment	Theory	Experiment
hcp			$c/a=1.58$	
hcp→ω	-3	2–11.9		
ω			$c/a=0.617-0.627$	$c/a=0.608-0.625$
$\omega\rightarrow\gamma$	98	112–130		
γ			$b/a=1.877-1.884$	$b/a=1.84-1.86$
γ			$c/a=1.625-1.629$	$c/a=1.61-1.63$
γ			$y=0.106-0.108$	$y=0.10-0.11$
$\gamma\rightarrow\delta$	106	140–145		
δ			$a/b=1.46-1.50$	$a/b=1.46-1.49$
δ			$c/b=1.38-1.41$	$c/b=1.37-1.40$
δ			$y=0.29-0.295$	$y=0.295-0.30$
δ→bcc	136	>216		

results obtained in Ref. 13 and the experimental ones.

In another theoretical work by Joshi *et al.*,[14] the calculations of structural stability for four phases (γ, δ, ω, and bcc) of Ti in the generalized gradient approximation have been performed. The authors of Ref. 14 have found the transition ω→bcc at 93 GPa. Their conclusions about stability γ and δ phases were: The ω phase transforms to a bcc structure directly without intermediate γ phase and the δ phase is not at all stable at any compression. However, some restrictions in these calculations took place. Namely, the fixed ratios b/a and c/a have been used.

Therefore, in the present work we aim at the same goals as the authors of Ref. 14, but we have used the full geometry optimization for all the structures that have been considered. We have studied the hcp, fcc, ω,γ,δ, and bcc structures up to pressures 800 GPa.

Total energy calculations have been performed with the full-potential linearized-augmented-plane-wave method supplemented by local orbitals (FLAPW+LO).[15] The generalized gradient approximation[16] has been used for the calculation of exchange-correlation energy. We have performed the optimization of a parameter c/a for hcp and ω phases. The parameters b/a, c/a, and y have been optimized for γ and δ structures. The optimization has been performed at each volume considered. Since very small energy differences between some phases are presented in the pressure interval 100–130 GPa, we took care about the total energy convergence in such parameters as a number of basis functions and a number of points in Brillouin's zone. In all the cases, the convergence about 0.1 mRy has been achieved.

The total energy of the different structures of Ti (relatively to the total energy of bcc structure) as a function of relative volume is presented in Fig. 1. As it can be seen there are intervals of stability of γ and δ phases. Thus, there are some differences with respect to the results of the work by Joshi *et al.*,[14] where the γ phase had been obtained as a metastable structure and δ phase had been obtained as an unstable at all compressions. (The curve of the γ phase is coincided with the curve of the hcp phase at volumes from ambient one to approximately 13 Å^3 in Fig. 1. It is due to the geometry optimization: at these volumes, the γ phase parameters have such values, that the structure is hcp.)

The transition pressures have been found by comparison of enthalpy of different structures (at $T=0$, enthalpy is equal to the free Gibbs' energy: $H=E+PV$). The relative enthalpy of titanium's structures is presented in Figs. 2 and 3 for low and high pressures, accordingly. Some oscillations of the δ-phase's curve in the pressure interval 135–170 GPa are due to a finite number of points in Brillouin's zone used for calculations. In this interval of the pressures, the δ phase's total energy is very sensitive to the sampling of Brillouin zone because of very fast change of the δ structure's parameters (see Figs. 4 and 5). Four transitions have been obtained in our calculations: hcp→ω, $\omega\rightarrow\gamma$, $\gamma\rightarrow\delta$, and δ→bcc. Table I contains the transition pressures and parameters of the structures presented.

Despite of the fact, that there are some improvements in describing of the experimental data, some discrepancies are still remain. And if a little underestimated pressures for the first, second, and third transitions can be attributed to the inaccuracies in the calculations or to the thermal effects, the presence of the transition δ→bcc in our calculation and the absence of it in the experimental works[11,12] up to 216 GPa is worthy. In this connection, it is interesting to look at the optimal lattice parameters of the δ phase obtained in our calculations as a function of pressure. In Fig. 4, the parameters a/b and c/b are presented. The internal parameter y is presented in Fig. 5.

There exist some interval of pressures in which the calculated parameters are close to the experimental ones. But at the pressures higher than 170 GPa, the δ phase parameters change in such a manner that structure obtained is bcc (for the bcc structure $a/b=c/b=\sqrt{2}$ and $y=0.25$). Thus, quite possible, that the wide interval of the δ structure's stability[11,12] may be is a consequence of a nonhydrostatic stress in experiments, as had already been pointed out by Joshi *et al.*[14]

In Fig. 6, we compare our theoretical 300-K isotherms with the experimentally observed isotherms for Ti. The thermal correction to our $T=0$ results was consisted in taking into account the lattice vibrations via Debye model with Debye's temperatures obtained from $T=0$ isotherms in according to Ref. 17. As it can be seen from Fig. 6, there is a close accordance between the calculated and experimental isotherms. Especially, it is necessary to note the accordance at high pressures. This fact can also be interpreted as an evidence for the presence of the bcc structure at the pressures 150 GPa and higher.

In summary, we have reproduced the experimental trends of a crystallographic sequence: hcp$\rightarrow\omega\rightarrow\gamma\rightarrow\delta\rightarrow$bcc with pressure for Ti. For all the transitions, the calculated pressures agree well with the experimental ones, although small differences exist. Some of the disagreements between experiment and theory might be due to the thermal effects. As in the Ref. 13, our calculations predict Ti to have the ω phase at $P=0$ and $T=0$, whereas the room-temperature experiments show that the structure is hcp at $P=0$. However, extrapolating the experimental phase boundary between the hcp and ω structures actually gives the ω phase stable at $T=0$. Further, at high pressures, our conclusion is coincided with the one given in Ref. 14: quite possible, that the transition to bcc structure takes place at the pressures lower than 200 GPa and more independent experiments with truly hydrostatic environment in DAC's are needed to clear the structural sequence of Ti.

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