

Density-functional study of the pressure-induced phase transitions in Ti at zero Kelvin

Zhi-Gang Mei, ShunLi Shang, Yi Wang, and Zi-Kui Liu

Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, USA

(Received 15 December 2008; published 3 April 2009)

The pressure-induced stable and metastable phase transitions of Ti at 0 K were studied by first-principles density-functional calculations. With the pressure from the equation of state fitting or extracted directly from first-principles calculations, we predicted that the 0 K phase transition sequence of Ti is $\alpha \rightarrow \omega \rightarrow \gamma \rightarrow \beta$, which is different from the theoretic predictions in the literature. We also found that the δ phase is not stable under hydrostatic compression. The obtained stable ($\alpha \rightarrow \omega \rightarrow \gamma \rightarrow \beta$) and metastable ($\alpha \rightarrow \beta$) phase transition pressures are in a good agreement with the experimental results. We found that the equation of state based on different fitting schemes can introduce significant errors in predicting the transition sequence of Ti. Our calculations also show that only under -8.0 GPa, the β phase exhibits magnetism. However, it is energetically not stable with respect to the α and ω phases at low pressures.

DOI: 10.1103/PhysRevB.79.134102

PACS number(s): 61.50.Ah, 61.50.Ks, 61.66.Bi, 62.50.-p

I. INTRODUCTION

In the past few years, group IV transition metals have attracted tremendous interest both scientifically and technologically. The technological importance of these materials is mainly due to their high strength-to-weight ratio and excellent resistance to corrosion.¹ The scientific interest in these materials stems from the fact that they have a narrow d band in the midst of a broad s - p band, which has a critical impact on the electronic properties and the stability of crystal structures. The electron transfer from the s - p band to the d band under pressure plays an important role in the phase stability of these materials.²

Among these elements, Ti is controversial in its phase transitions at high pressures. There are five solid phases of Ti reported in the literature: α (hcp), β (bcc), ω (hexagonal), γ (distorted hcp), and δ (distorted bcc).¹⁻⁸ At room temperature, Ti is known to undergo a phase transition from the α phase to the ω phase at the transition pressure ranging from 2 to 11.9 GPa.¹⁻⁷ X-ray experiment by Xia *et al.*³ showed that the $\alpha \rightarrow \omega$ transition is the only transition at pressures up to 87 GPa. Recently, Vohra and Spencer¹ observed a new phase transition $\omega \rightarrow \gamma$ at 116 GPa by energy-dispersive x-ray-diffraction measurements. Subsequently, Akahama *et al.*² reported another phase transition $\gamma \rightarrow \delta$ at 140–145 GPa using a monochromatic synchrotron x-ray diffraction technique. The γ and δ phases have the same orthorhombic structure, with space group $Cmcm$ and atoms at the $4c$ Wyckoff positions $(0, y, 1/4)$.^{1,2} The only difference is $y=0.11$ for γ (Ref. 1) while $y=0.295$ for δ .² However, as pointed out by the authors themselves, the stability of the δ phase is suspected due to the possible nonhydrostatic condition in the transition,² also by later theoretical studies because of its relative high energy with respect to the β phase.^{9,10} Thus far, the high-pressure β -Ti has not been observed in most of the experiments even under extreme high pressure up to 220 GPa by Akahama *et al.*,² except as claimed by Ahuja *et al.*¹¹ of the observation of the $\omega \rightarrow \beta$ transition in the range of 40~80 GPa using angle-dispersive synchrotron x-ray diffraction.

First-principles density-functional theory (DFT) calculations have also been used to understand the phase stability of

Ti.⁹⁻¹⁵ Ahuja *et al.*¹¹ predicted the transition $\omega \rightarrow \beta$ at 57.5 GPa based on local density approximation (LDA). Joshi *et al.*¹⁰ employed the full-potential linear-augmented-plane-wave method (FLAPW) to study the stability of γ and δ and obtained that the ω phase transforms to the β phase at 93 GPa. Kutepov and Kutepova¹⁵ investigated the crystal structural stability for the five phases (α , β , ω , γ , and δ) of Ti under pressures, using FLAPW method with full geometry optimizations. They found the transition sequence at 0 K to be $\alpha \rightarrow \omega \rightarrow \gamma \rightarrow \delta \rightarrow \beta$. Recently, Verma *et al.*⁹ used augmented plane wave (APW) with local orbital (LO) method and found that $\omega \rightarrow \gamma$ and $\gamma \rightarrow \beta$ transition pressures are 102 and 112 GPa, respectively. However, in all above theoretical investigations except that of Kutepov and Kutepova,¹⁵ fixed ratios b/a and c/a have been used for the total-energy calculations. In the work of Kutepov and Kutepova,¹⁵ however, the enthalpy curve of the δ phase oscillates within the pressure range of 135–145 GPa. Kutepov and Kutepova¹⁵ were themselves skeptical about the authenticity of these oscillations and attributed them to poor Brillouin-zone sampling.¹⁵ In all the above theoretical works, none of them discussed

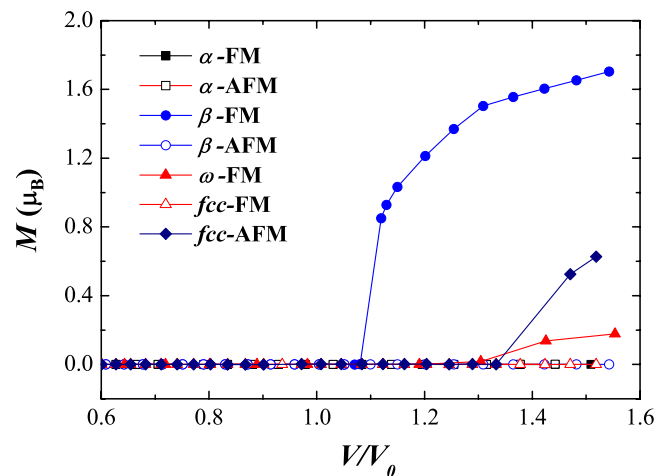


FIG. 1. (Color online) Calculated magnetic moment per atom as a function of volume V/V_0 (where V_0 is the equilibrium volume of ω -Ti) for FM α , β , ω , and fcc, and AFM α , β , and fcc phases.

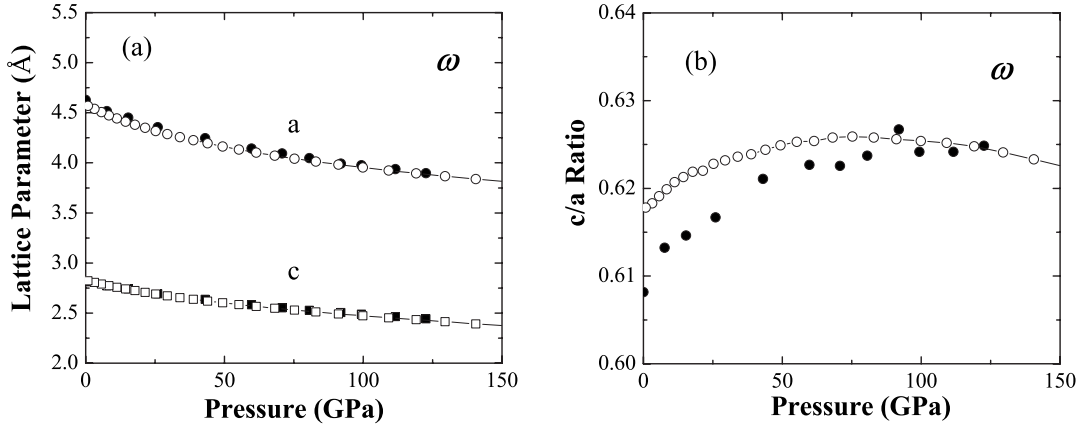


FIG. 2. Calculated lattice parameters and c/a ratio (open symbols) in comparison with the experimental data (filled symbols) of Akahama *et al.* (Ref. 2) for ω -Ti at room temperature.

how the pressures were obtained for the Gibbs free-energy calculations. A common practice is to fit the calculated total-energy versus volume (E - V) data to an appropriate equation of state (EOS), and then obtain pressure by $P = -\partial E / \partial V$. However, EOS fitting can be a significant source of error when the free-energy difference between phases is small. This could be a reason why the δ phase is stable in some predictions^{12,15} while unstable in others⁹ since β , γ , and δ phases have very similar free energies in the phase transition regions.

Under ambient conditions, Ti is a nonmagnetic (NM) metal. Moruzzi and Marcus,¹⁶ however, demonstrated that nonmagnetic transition metals can become ferromagnetic (FM) at large volumes by first-principles calculations. They found that β -Ti undergoes a second-order transition from nonmagnetic to ferromagnetic phase at an expanded volume $V = 1.25V_0$ (V_0 is the calculated equilibrium volume of β). The ferromagnetic and antiferromagnetic (AFM) phase stabilities of Ti have not been fully discussed yet.

With the aim to understand both the magnetic and structural phase stabilities of Ti with respect to pressure, we systematically investigated the structural and magnetic phase transitions through first-principles calculations in the present work. The stability of the high-pressure phases γ and δ was

carefully examined with procedures using both different EOS fittings and direct extraction of pressures from DFT calculations. The rest of the paper is organized as follows. The computational method for first-principles calculations and EOS fitting is described in Sec. II. The discussion of the phase stability of Ti using pressure extracted directly from first-principles calculations or EOS fitting is presented in Sec. III. Finally, the conclusion of this work is given in Sec. IV.

II. COMPUTATIONAL METHOD

Density-functional calculations within the generalized gradient approximation (GGA), as implemented in Vienna *ab initio* simulation package (VASP),^{17,18} were utilized in this study. Perdew-Burke-Ernzerhof (PBE) GGA (Ref. 19) for the exchange-correlation potential was used for all calculations. The all-electron projector augmented plane-wave (PAW) (Refs. 18 and 20) method was adopted. In order to avoid core overlap at high pressure, we treated semicore states $3s$ and $3p$ as valence electrons. To be complete, fcc Ti was also included in our calculations. For obtaining accurate total energy and stress tensor, the plane-wave basis energy cutoff (E_{cut}) was set to 500 eV. Our calculations showed that sys-

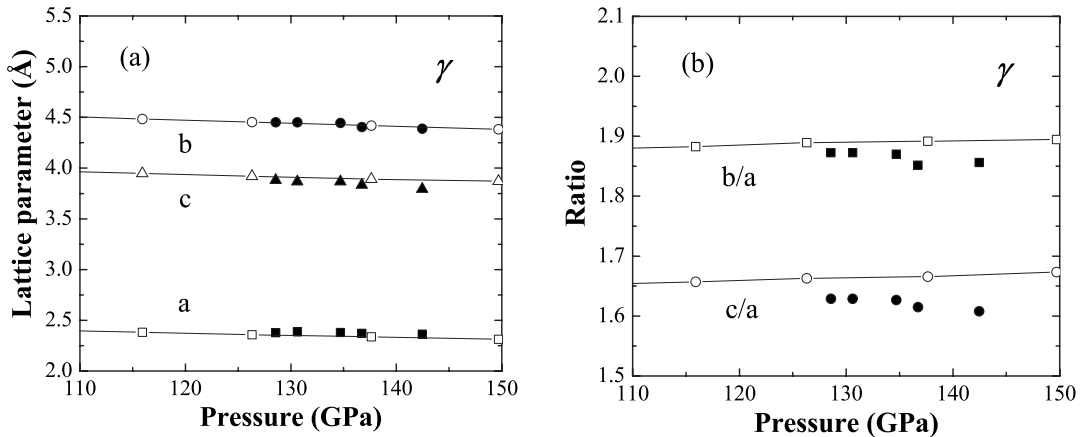


FIG. 3. Calculated lattice parameters and their ratios (open symbols) in comparison with the experimental data (filled symbols) of Akahama *et al.* (Ref. 2) for γ -Ti at room temperature.

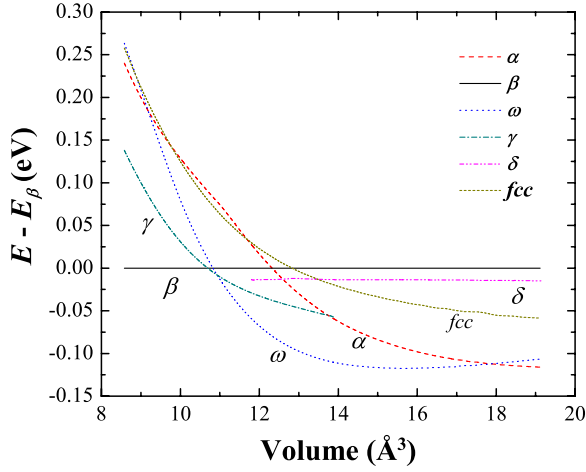


FIG. 4. (Color online) Calculated energy differences for α , β , ω , γ , δ , and fcc phases with respect to β as a function of volume per atom. For γ and δ phases, only the stable parts are shown in the figure.

tems need to be fully relaxed with high accuracy (both large E_{cut} and high k -point sampling) to mimic truly hydrostatic compression. Hence, dense k -point samplings in the first Brillouin zone were adopted, i.e., $27 \times 27 \times 15$ for α -Ti, $25 \times 25 \times 25$ for β -Ti, $17 \times 17 \times 24$ for ω -Ti, $27 \times 27 \times 15$ for γ -Ti, $25 \times 25 \times 15$ for δ -Ti, and $24 \times 24 \times 24$ for fcc Ti. Full geometry optimization at each volume was considered to be completed when the forces exerted on the atoms were less than 10^{-3} eV/Å. A high accurate static calculation using the tetrahedron method with Blöchl corrections²¹ and with an energy convergence criterion of 10^{-8} eV/cell was performed after the completion of the structure relaxation.

The commonly used procedure for studying pressure-induced transition is to compare the Gibbs free energy G as a function of pressure. The most stable phase has the lowest G . In order to get the pressure, different EOSs could be used to fit the E - V data. The widely used EOSs are the Birch-Murnaghan (BM) equation of state²² and the Vinet equation of state.²³ The Vinet EOS is more accurate for high com-

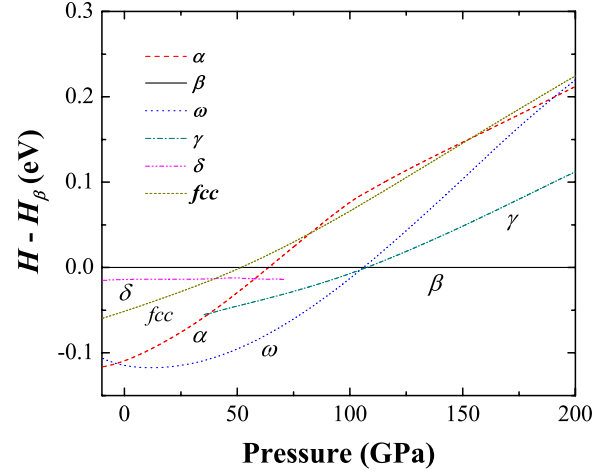


FIG. 5. (Color online) Calculated enthalpy differences of α , β , ω , γ , δ , and fcc phases with respect to β as a function of pressure. For γ and δ phases, only the stable parts are shown in the figure.

pressible materials. The third-order Birch-Murnaghan (BM3) EOS can be expressed as

$$E(V) = \sum_{n=0}^3 a_n V^{-2n/3}, \quad (1)$$

where V is the volume of the unit cell. The E - V expression for the Vinet EOS is much more complicated than that of the BM EOS and can be found elsewhere.²³ The minimum-energy volume (V_0) is found by minimizing energy with respect to volume. The bulk modulus $B_0 = -V_0(\partial P/\partial V)_0$ is computed from the definition $B(V) = V(\partial^2 E/\partial V^2)$. Its first and second pressure derivatives (B'_0 and B''_0) are defined by $B'_0 = (\partial B/\partial P)_{P=0}$ and $B''_0 = (\partial^2 B/\partial P^2)_{P=0}$, respectively. However, EOS fittings can introduce errors to G or even change phase transition sequence when the free-energy difference is small. On the other hand, we can extract pressure (stress) directly from the first-principles calculations. To obtain accurate stress, the structures should be fully relaxed with high accu-

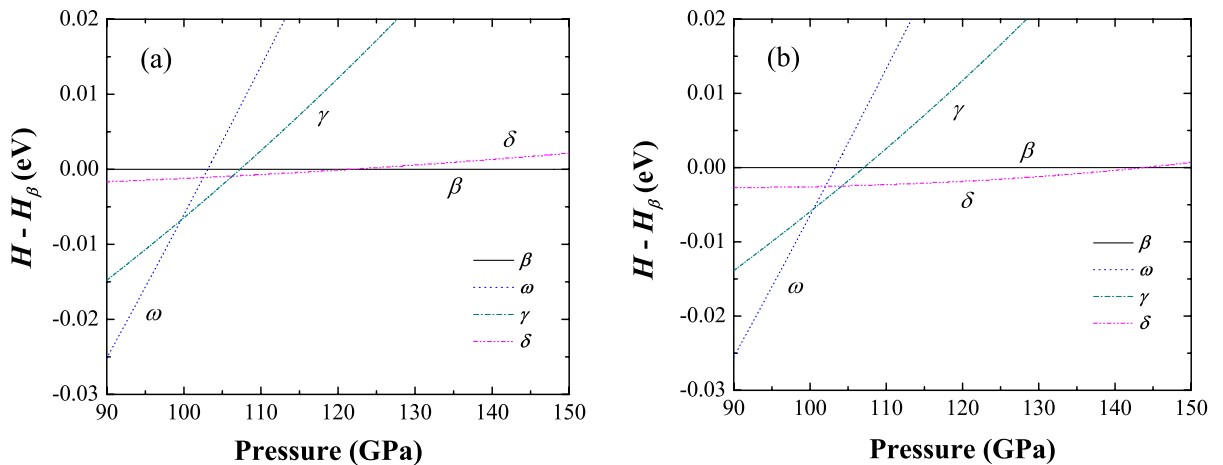


FIG. 6. (Color online) Calculated enthalpy differences of Ti phases with respect to β as a function of pressure using different EOSs fitting: (a) Vinet EOS; (b) third-order Birch-Murnaghan EOS.

TABLE I. Optimized structural parameters and bulk modulus (B_0) of Ti in different structures.

Structure	Space group		Unit cell (Å)			Positional parameters	B_0 (GPa)
			a	b	c		
α	$P6_3/mmc$	This work	2.939	2.939	4.650	$2c: 1/3, 2/3, 1/4$	110
		Experiment	2.920	2.920	4.717 ^a		117 ± 9 ^c
			2.957	2.957	4.685 ^b		
β	$Im\bar{3}m$	This work	3.255	3.255	3.255	$2a: 0,0,0$	106
		Experiment	3.31	3.31	3.31 ^d		87.7 ^d
ω	$P6/mmm$	This work	4.575	4.575	2.828	$1a:0, 0, 0; 2d:1/3, 2/3, 1/2$	118
		Experiment	4.588	4.588	2.837 ^a		138 ± 10 ^c
			4.598	4.598	2.822 ^b		
γ	$Cmcm$	This work	2.380	4.485	3.915 ^e	$4c: 0, 0.108, 1/4$ ^e	96
		Experiment	2.388	4.484	3.915 ^f		143.7 ^b
			2.382	4.461	3.876 ^g		

^aReference 13.^bReference 1.^cReference 7.^dLattice constants were estimated at 1173 K, and bulk modulus was evaluated from elastic constants (Ref. 8).^eStructural parameters estimated at 115 GPa.^fStructural parameters estimated at 118 GPa (Ref. 1).^gLattice constants estimated at 130 GPa (Ref. 2).

racy, although being computationally demanding. Both of these methods are utilized in this work.

III. RESULTS AND DISCUSSION

We calculated the total energies of NM α , β , ω , γ , δ , and fcc phases. The total energies of FM α , β , ω , and fcc, and AFM α , β , and fcc phases were also calculated to explore the magnetic behaviors of Ti. In Fig. 1, we show the calculated magnetic moments of FM and AFM α , β , ω , γ , δ , and fcc phases as a function of reduced volume V/V_0 (V_0 is the equilibrium volume of ω -Ti) at 0 K. It can be seen that the FM- β phase first begins to exhibit magnetism at a volume larger than $1.12V_0$, which is equivalent to a negative pressure of -8.0 GPa. However, this FM- β phase is not stable with respect to the α and ω phases at low pressures. Therefore, we only consider the NM α , β , ω , γ , δ , and fcc phases in this work.

To benchmark our high-pressure calculations, we compared the calculated lattice parameters of ω and γ with experimental results (see Figs. 2 and 3). Table I also lists the optimized structural parameters and bulk modulus (B_0) of Ti with different structures. The predicted lattice parameters of the ω and γ phases compare well with the experimental values. For the δ phase, however, the fully relaxed lattice parameters a and c are quite different from the experimental results of Akahama *et al.*² In fact, the δ phase is not stable any more above the pressure of 71.8 GPa. The fully relaxed structure shows that it has transformed to a bcc structure with $a/b=c/b \approx \sqrt{2}$ and $y \approx 0.25$ in the orthorhombic coordinates.²

The total energies of α , β , ω , γ , δ , and fcc (relative to that

of β) by direct VASP calculations as a function of volume per atom are depicted in Fig. 4 (All the volumes in the present paper are in terms of per atom). The ω phase has the lowest energy at its equilibrium volume, consistent with most theoretical predictions.^{9,12,15} Our calculations show that there is a small interval of stability for γ , while δ is not stable in the entire volume region. This result is in agreement with the work of Verma *et al.*⁹ but contrary to the calculations of Kutepov and Kutepova.¹⁵ Similar to the work of Kutepov and Kutepova,¹⁵ the E - V curve of γ coincides with that of α as γ becomes unstable at volumes larger than 14 \AA^3 when fully relaxed, and the E - V curve of δ coincides with that of β as δ becomes unstable at volumes smaller than 11.5 \AA^3 when fully relaxed. As a result, these two parts of E - V curves for the γ and δ phases are not shown in Fig. 4. Consistent with the above crystal structure analysis, the δ phase is stable only under pressure lower than 71.8 GPa. Above this pressure, it transforms to a bcc structure under hydrostatic pressure. Thus our calculation results indicate that the δ phase found by experiment probably exists only under nonhydrostatic compression. As for the γ phase, it transforms to a hcp structure at pressure lower than 32.8 GPa with $b/a \approx \sqrt{3}$ and $y \approx 0.167$ in the orthorhombic coordinates.¹

At 0 K, Gibbs free energy is equal to enthalpy H , expressed as $H=E+PV$. Figure 5 shows the relative enthalpies of Ti phases as a function of pressure with β as the reference phase, using pressures calculated directly by VASP. Consistent with the results of the E - V data, the most stable phase at 0 K under ambient pressure is ω , not α which is the most stable phase at room temperature as reported by experiments.¹⁻³ This can be interpreted as the entropy from the thermal population of phonon states that stabilizes the α phase at room temperature.²⁴ Our calculated $\omega \rightarrow \gamma$ phase

TABLE II. Calculated transition sequence and pressures of Ti.

Phase transition	Transition pressure (GPa)		
	Expt.	Theory	This work
$\alpha \rightarrow \omega$	2–11.9 ^a	–3 ^b	–3.7
$\alpha \rightarrow \beta$ ^c	50 ^d		63.7
$\omega \rightarrow \gamma$	116 ± 4 ^e	98 ^b , 102 ^f , 106.3 ^g	104.9
$\gamma \rightarrow \delta$	140–145 ^h	106 ^b , 134.9 ^g	
$\delta \rightarrow \beta$		136 ^b , 160.8 ^g	
$\gamma \rightarrow \beta$		112 ^f	107.3

^aReferences 1–6.^bReference 15.^cThe $\alpha \rightarrow \beta$ is a metastable phase transition.^dTransition pressure estimated from Ref. 25.^eReference 1.^fReference 9.^gReference 12.^hReference 2.

transition pressure is 104.9 GPa, which is lower than the experimentally observed pressure of 116 ± 4 GPa. In the subsequent phase transition, γ transforms to β at the pressure of 107.3 GPa. The δ phase is not stable in comparison with the β phase. We also calculated the total energy of δ using the experimental a/b and c/b ratios, which has higher energy than that of β at any pressures. Thus, there are only three phase transitions at 0 K for Ti, namely, $\alpha \rightarrow \omega$, $\omega \rightarrow \gamma$, and $\gamma \rightarrow \beta$. The calculated transition pressures are listed in Table II. Table III lists the calculated equilibrium volume (V_0), the bulk modulus (B_0), and the first and second pressure derivatives of bulk modulus (B'_0 and B''_0) with different EOSs. From Fig. 5, we can also obtain a metastable phase transition $\alpha \rightarrow \beta$ at 63 GPa, which is comparable to the extrapolated value 50 GPa from the experimentally determined phase diagram.²⁵

Our 0 K phase transition sequence is different from the results by Kutepov and Kutepova¹⁵ and Hao *et al.*¹² Kutepov

and Kutepova¹⁵ predicted that the δ phase is stable between 106–136 GPa while Hao *et al.*¹² showed that the δ phase is stable between 134.9–160.8 GPa using the Vinet EOS fitting, although Kutepov and Kutepova¹⁵ did not mention how they calculated the pressure. To explore the origin of the differences, we used Vinet EOS to fit our calculated E - V data of all the phases using data in the whole pressure range. The result shows that the δ phase is stable between 106–122 GPa, as shown in Fig. 6(a). These transition pressures are a little lower than those of the results of Hao *et al.*¹² We also found that the δ phase is stable between 104–144 GPa using BM3 EOS, as shown is Fig. 6(b), which is very close to the results of Kutepov *et al.*¹² However, our direct VASP calculations show that the δ phase is not stable in the whole pressure region and becomes bcc when relaxed at high pressures. Thus, one has to be very careful in using any EOS fitting in predicting the phase transition sequence of Ti.

IV. CONCLUSIONS

We investigated the phase stability of Ti by first-principles DFT calculations. Only under a large negative pressure, –8.0 GPa, does the β phase exhibit magnetism, though not stable in comparison with the α and ω phases. The 0 K phase transition sequence of Ti is predicted to be $\alpha \rightarrow \omega \rightarrow \gamma \rightarrow \beta$ with increasing pressure. The obtained stable and metastable phase transition pressures are in a good agreement with the experimental results. Under hydrostatic compressions, the γ phase is stable in the pressure range of 104.9–107.3 GPa. Total-energy calculations with full relaxation indicate that the δ phase relaxes into the bcc structure at high pressures. We also found that highly accurate DFT calculation is critical in obtaining the correct phase transition sequence of Ti and extreme care should be taken when the EOS is fitted. To verify the stability of γ and δ phases, more experiments with truly hydrostatic compression will be helpful.

ACKNOWLEDGMENTS

The authors want to thank Clive A. Randall for his long-

TABLE III. Calculated equilibrium volume per atom V_0 ($\text{\AA}^3/\text{atom}$), bulk modulus B_0 (GPa), and first and second pressure derivatives of bulk modulus (B'_0 and B''_0) with different EOSs.

Structure	EOS	V_0 ($\text{\AA}^3/\text{atom}$)	B_0 (GPa)	B'_0	B''_0 (GPa^{-1})
α	BM3	17.46	110	3.3	–0.033
	Vinet	17.41	116	3.1	–0.029
β	BM3	17.28	103	3.3	–0.036
	Vinet	17.26	105	3.2	–0.035
ω	BM3	17.09	118	3.4	–0.031
	Vinet	17.09	119	3.3	–0.032
γ	BM3	17.61	96	3.5	–0.038
	Vinet	17.59	96	3.6	–0.047
δ	BM3	17.39	98	3.4	–0.037
	Vinet	17.34	102	3.3	–0.038

term collaboration. This work is funded by the National Science Foundation (NSF) through Grant No. DMR-0510180. First-principles calculations were carried out on the LION clusters at the Pennsylvania State University supported in

part by the NSF (Grants No. DMR-9983532, No. DMR-0122638, and No. DMR-0205232) and in part by the Materials Simulation Center and the Research Computing and Cyber infrastructure unit.

-
- ¹Y. K. Vohra and P. T. Spencer, *Phys. Rev. Lett.* **86**, 3068 (2001).
²Y. Akahama, H. Kawamura, and T. Le Bihan, *Phys. Rev. Lett.* **87**, 275503 (2001).
³H. Xia, S. J. Duclos, A. L. Ruoff, and Y. K. Vohra, *Phys. Rev. Lett.* **64**, 204 (1990).
⁴A. Jayaraman, W. Klement, and G. C. Kennedy, *Phys. Rev.* **131**, 644 (1963).
⁵Y. Akahama, H. Kawamura, and T. L. Bihan, *J. Phys.: Condens. Matter* **14**, 10583 (2002).
⁶A. Kutzar, *Pis'ma Zh. Eksp. Teor. Fiz.* **35**, 91 (1982).
⁷D. Errandonea, Y. Meng, M. Somayazulu, and D. Häusermann, *Physica B* **355**, 116 (2005).
⁸H. Ogi, S. Kai, H. Ledbetter, R. Tarumi, M. Hirao, and K. Takashima, *Acta Mater.* **52**, 2075 (2004).
⁹A. K. Verma, P. Modak, R. S. Rao, B. K. Godwal, and R. Jeanloz, *Phys. Rev. B* **75**, 014109 (2007).
¹⁰K. D. Joshi, G. Jyoti, S. C. Gupta, and S. K. Sikka, *Phys. Rev. B* **65**, 052106 (2002).
¹¹R. Ahuja, L. Dubrovinsky, N. Dubrovinskaia, J. M. Osorio Guillen, M. Mattesini, B. Johansson, and T. Le Bihan, *Phys. Rev. B* **69**, 184102 (2004).
¹²Y. J. Hao, L. Zhang, X. R. Chen, Y. H. Li, and H. L. He, *Solid State Commun.* **146**, 105 (2008).
¹³F. Jona and P. M. Marcus, *Phys. Status Solidi B* **242**, 3077 (2005).
¹⁴C. Bercegeay and S. Bernard, *Phys. Rev. B* **72**, 214101 (2005).
¹⁵A. L. Kutepov and S. G. Kutepova, *Phys. Rev. B* **67**, 132102 (2003).
¹⁶V. L. Moruzzi and P. M. Marcus, *Phys. Rev. B* **38**, 1613 (1988).
¹⁷G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
¹⁸G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
¹⁹J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
²⁰P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
²¹P. E. Blöchl, O. Jepsen, and O. K. Andersen, *Phys. Rev. B* **49**, 16223 (1994).
²²F. Birch, *Phys. Rev.* **71**, 809 (1947).
²³P. Vinet, J. H. Rose, J. Ferrante, and J. R. Smith, *J. Phys.: Condens. Matter* **1**, 1941 (1989).
²⁴S. P. Rudin, M. D. Jones, and R. C. Albers, *Phys. Rev. B* **69**, 094117 (2004).
²⁵E. Y. Tonkov and E. G. Ponyatovsky, *Phase Transformations of Elements Under High Pressure* (CRC, Boca Raton, 2005), p. 224.