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Effect of pressure on the electronic structure of hcp Titanium

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The effect of pressure on the hexagonal close-packed structure of titanium is investigated. The lattice parameters of the equilibrium structure were determined in terms of the Gibbs free energy using the Epitaxial Bain Path method. When this process was repeated for several pressures, the effect of pressure on the lattice parameters was revealed. The calculated lattice parameters were in good agreement with the experimental and theoretical results. The effects of pressure on parameters depending on the electronic structure such as conductivity and resistivity in the ground state were also investigated up to 30 GPa using density functional theory.

Key words: *effect of pressure, hcp-Ti, Gibbs free energy, lattice parameters, EBP method*

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1. Introduction

At room temperature and ambient pressure, Ti has a hexagonal close-packed structure called the α-phase. The lattice parameters of this structure are $a = 2.957$ Å and $c = 4.685$ Å [1] in which the unit cell has two atoms at (1/3, 2/3, 1/4), (2/3, 1/3, 3/4) and the space group number is 194 ($P6_3/mmc$) with the c/a ratio of ~ 1.59 [2]. Experimental results at room temperature indicate that lattice parameters decrease and the c/a ratio increases with pressure [3]. At ambient temperature and high pressure, it changes to the ω-phase [4, 5]. The lattice parameters of this structures are $a = 4.598$ Å and $c = 2.822$ Å [1, 6] with three atoms per unit cell at (0, 0, 0), (1/3, 2/3, 1/2), (2/3, 1/3, 1/2) and the space group is $P6/mmm$ with the c/a ratio of ~ 0.61 [2]. The $\alpha \rightarrow \omega$ transition in Titanium is a representative example of martensitic transformation. Recently, Trinkel et al. have proposed two pathways for this transformation which are called TAO-1 ("Titanium alpha to omega") and TAO-2. This mechanism is a direct mechanism in which six-atom transformation proceeds without a meta-stable intermediate phase and has small shuffles and strains [7].

The effect of pressure on lattice parameters was investigated using the Epitaxial Bain Path (EBP) method [8, 9]. In this method, the equilibrium structure is determined by minimized Gibbs free energy. As a hexagonal structure is defined by its lattice parameters, the Gibbs free energy $[G \equiv E(a, c) + PV(a, c)]$ should be minimized with respect to a and c. The EBP method is summarized and explained here. At $T = 0$ K, the Gibbs free energy was $G = E + PV$, where P is the pressure, V was the volume per atom and E is the internal energy per atom. At $P \neq 0$, the lattice parameter of $a = a_1$ was chosen and the value of c was varied until one found the values $c = c_1$ and $E = E_1$. The energy of E for the lattice parameters $c = c_i$ ($i = 1, 2, \dots$) with constant a_1 was calculated using Wien2k until c_1 and E_1 values satisfied $(\partial E/\partial c)_a = - \left(Pa_1^2 \sin \gamma \right)/2$, where γ is the angle between a and c. When a suitable value of c_1 was determined, E_1, V_1 and the Gibbs free energy G_1, which is $G_1 = E_1 + PV_1$ were found at pressure P. This process was repeated for several a_i values at the same pressure and G_i was determined. For the equilibrium structure at pressure P, the value giving a minimum G_P was chosen. Thus, by choosing different values of P, the lattice parameters a and c, ratio c/a and the volume were determined directly as the functions of pressure.

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The energy was calculated using Wien2k Package [10], which employs a self-consistent Full-Potential Linearized Augmented Plane wave plus local orbital (FLAPW+LO) method, under the generalized gradient approximation (GGA) with the Perdew-Burke-Emzerh of 96 exchange Correlation functional [11]. Moreover, the following parameters were used: Muffin-tin-radius, $RMT = 2.3$ bohr, Largest vector in the charge-density Fourier expansion, $G_{\max} = 12$ bohr^{-1}, K point $= 4954$, Plane-wave cutoff, $RK_{\max} = 9$, cutoff energy $= -6$ Ryd and charge convergence $= 1 \times 10^{-4}$e (the charge convergence was used in order to optimize parameters in the SCF cycle). Except for K point $= 5599$ and $RMT = 2.247$ bohr, other parameters which were related to the effect of pressure on the electronic structure did not change.

2. Results and discussion

The effect of pressure on the hexagonal close-packed structure of titanium in the ground state was investigated. The Gibbs free energy (figure 1), ratio of c/a (figure 2), lattice parameters a and c (figure 3) and volume (figure 4) were calculated as functions of pressure. The experimental data were obtained using figure 5 in Errandonea et al. [3] via Gate data software. These results were in good agreement with theoretical [8] and experimental studies [3].
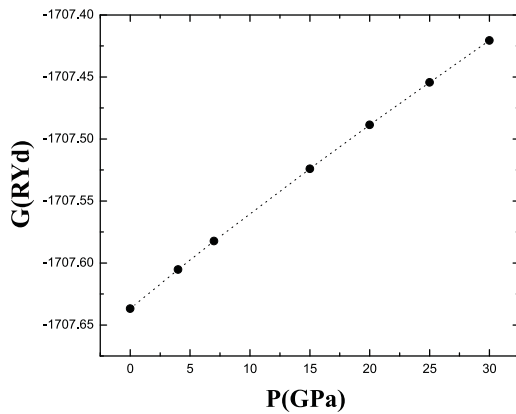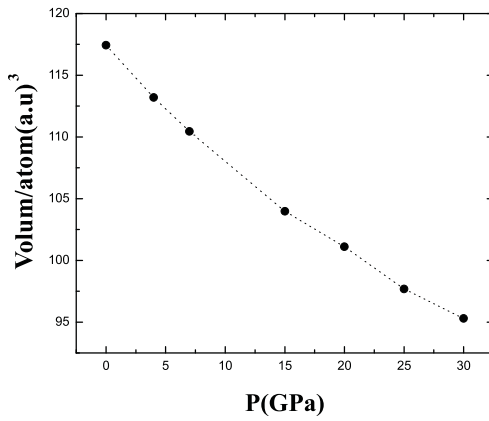

Figure 1. The pressure dependence of the Free energy G.
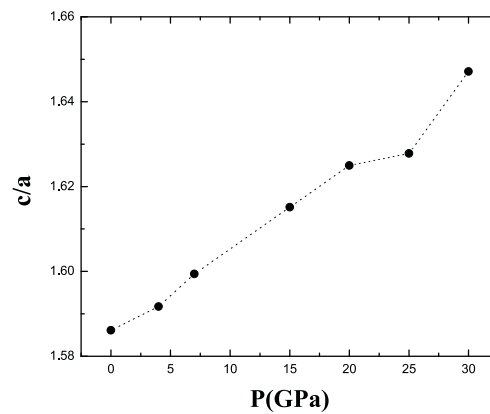
Figure 2. The pressure dependence of ratio c/a.
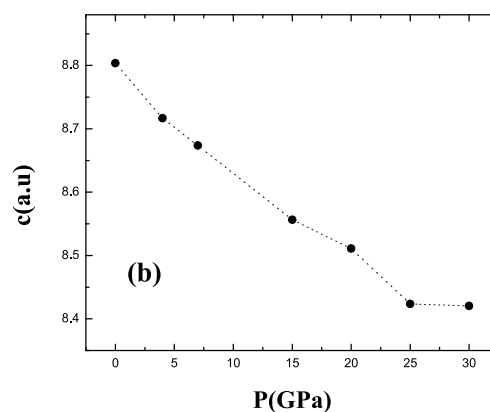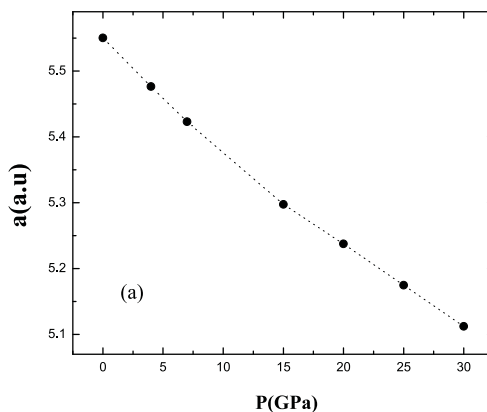
Figure 3. The pressure dependence of (a) lattice parameter a and (b) lattice parameter c.

Figure 4. The pressure dependence of atomic volume.

In order to make a comparison between the results of this study and those of the references [3], only three points of the pressure (0, 4 and 7 Gpa) were chosen which was due to the limitation of the experimental results in which the experimental points were only considered up to 14.5 GPa. These comparisons are tabulated in tables 1 to 3 and shown in figures 5 and 6. As shown in the aforementioned figures, based on the expectations, the lattice parameters decreased and c/a ratio increased with pressure.

In the present study at $T = 0$ K and $P = 0$ GPa, α-phase had the c/a ratio of 1.586 which was in good agreement with the experimental 1.584 [3] and theoretical results 1.611 [8], 1.584 [12] or 1.583 [13] smaller than the ideal value of 1.633 for an hcp crystal. Furthermore, the experimental results showed that the c/a ratio for α-Ti gradually increased from 1.584 at atmospheric pressure to 1.622 at 14.5 GPa [3].

Table 1. Lattice parameter of hcp Ti at zero pressure; estimated deviations with experimental work [3] are indicated.

Lattice parameter	This work	Experimental[a] [3]	Theoretical[b] [8]
a (Å)	2.93693±0.007	2.9575	2.92455
c (Å)	4.65834±0.006	4.68548	4.71120
c/a	1.58613± 0.011	1.58427	1.61091

Table 2. Lattice parameter of hcp Ti at 4 GPa; estimated deviations with experimental work [3] are indicated.

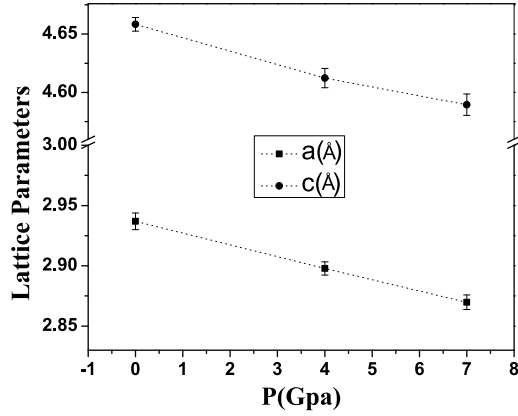| Lattice parameter	This work	Experimental[a] [3]	Theoretical[b] [8]
a (Å)	2.89777±0.005	2.9137	2.88898
c (Å)	4.61230±0.008	4.65088	4.65735
c/a	1.59167±0.003	1.59621	1.61211

Table 3. Lattice parameter of hcp Ti at 7 GPa; estimated deviations with experimental work [3] are indicated.

| Lattice parameter	This work	Experimental[a] [3]	Theoretical[b] [8]
a (Å)	2.86973±0.006	2.88717	2.86523
c (Å)	4.58955±0.009	4.63199	4.62227
c/a	1.59930±0.003	1.60433	1.61323

[a] Experimental values are obtained by Gate Data Software from figure 5 of the reference [3].
[b] Theoretical values are obtained by Gate Data Software from figure 2 of the reference [8].

The α-phase can transform to the ω-phase under pressure. However, it is believed that both structures can coexist in the pressure range studied here [5]. The effect of pressure on lattice

Figure 5. Lattice parameters vs pressure for hcp Ti. Estimated deviations with experimental work [3] are indicated.
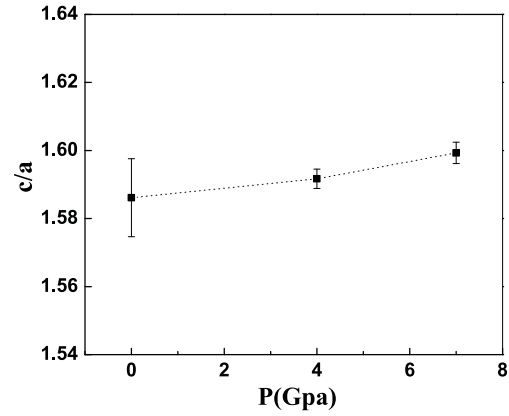
Figure 6. Ratio of c/a parameters vs pressure for hcp Ti. Estimated deviations with experimental work [3] are indicated.

parameters of α-phase in the range of 0–14.5 GPa was also investigated, both experimentally in [3] and theoretically in [8]. These results confirm the possibility of coexistence of both structures in the pressure range of 2–9 GPa and even more.

In fact, the coexistence of these phases has been also reported by experiments within the temperature range from room temperature to around 923 K [14] and by the theory of reconstructive phase transitions [15].

Table 4. Partial charges in the s, p and d bands.

P (GPa)	s	p	d
0	0.31515	0.2767	0.9858
4	0.32471	0.2870	2.0104
7	0.33159	0.2953	2.0426
15	0.34840	0.3125	2.0999
20	0.35676	0.3199	2.1242
25	0.36704	0.3315	2.1744
30	0.37429	0.3371	2.2127

Table 5. Density of states at the Fermi level as a function of pressure.

P (GPa)	$n(E_{\mathrm{F}})$ (States/ev atom)
0	0.8930
4	0.8868
7	0.8500
15	0.8625
20	0.8000
25	0.8158
30	0.7908

Table 6. The pressure dependence of the Fermi energy.

P (GPa)	E_{F} (Ryd)
0	0.56228
4	0.58999
7	0.60881
15	0.65693
20	0.67996
25	0.70925
30	0.73021

Using the lattice parameters and Wien2k, the number of electrons in s, p and d bands (table 4), the Fermi energy (table 5) and the density of states at this energy $n(\varepsilon_{\mathrm{F}})$ (table 6) were calculated for different pressures.
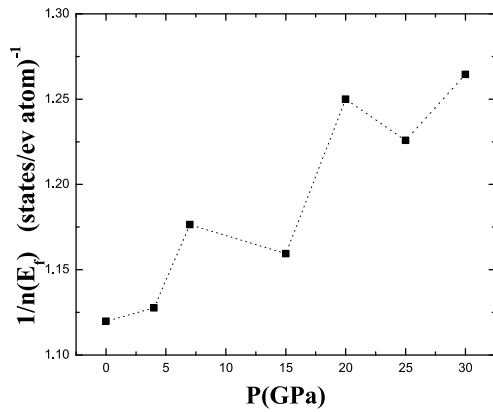
Figure 7. $1/n\left(\varepsilon_f\right)$ as a function of pressure for hcp Ti.

Moreover, the electrical conductivity can be expressed as $\sigma = \mathrm{e}^2 \tau_{\mathrm{F}} v_{\mathrm{F}}^2 n(\varepsilon_{\mathrm{F}})/3$ [16, 17], where v_{F} is velocity at the Fermi energy and τ_{F} is the relaxation time, but $n(\varepsilon_{\mathrm{F}})$ has a greater effect than the latter two parameters. Figure 7 shows $1/n(\varepsilon_{\mathrm{F}})$ as a function of pressure. Because $\rho \propto 1/n(\varepsilon_{\mathrm{F}})$, figure 7 can be taken as a measure of the effect of pressure on electrical resistivity.

According to Matthiessen's rule, total electrical resistivity ρ, due to electron scattering by different factors is given by sum of these factors $\rho = \rho_{\mathrm{Th}} + \rho_{\mathrm{D}} + \rho_{\mathrm{I}}$, where ρ_{Th} is thermal resistivity, ρ_{D} and ρ_{I} are resistivity due to defects and impurities, respectively. The other factor that can scatter electrons is electron-electron (e-e) interaction, which is negligible. At high temperature, the effects of impurities and defects are negligible; thus, $\rho \approx \rho_{\mathrm{Th}}$; at low temperature, ρ_{Th} is less than $\rho_{\mathrm{D}} + \rho_{\mathrm{I}}$, so $\rho \approx \rho_{\mathrm{D}} + \rho_{\mathrm{I}}$. At $T = 0$ K, ions were frozen in fixed positions and electrons do not scatter with phonon ($\rho_{\mathrm{Th}} = 0$). In the present study, pure titanium was investigated. It is chemically and thermodynamically impossible to avoid impurities and defects, so the resistivity at $T = 0$ is not zero ($\rho = \rho_{\mathrm{D}} + \rho_{\mathrm{I}} \neq 0$ where $\rho = \rho_{\mathrm{r}}$ is called residual resistance).

Figure 7 shows that at $T = 0$ K an increase in pressure causes an increase in electrical resistivity, which contradicts the results of P.S. Balog, who investigated the phenomenon at 50–700°C, where ρ was due to electron-phonon interaction. A pressure increase (at constant temperature) leads to a decrease in inter-atomic spacing and atomic vibrational amplitude, causing a decrease in electrical resistivity [18]. However, in the present study, the investigation was carried out at $T = 0$ K and electrical resistivity increased with pressure. According to table 4, an increase in pressure leads to an increase in the number of electrons per volume.

Furthermore, according to table 5, an increase in pressure leads to a decrease in the density of state, thus causing an increase in the electrical resistivity.

According to table 6, an increase in pressure leads to an increase in the width of the valence band. In the formation of molecules, several atoms are arranged beside each other, so atomic orbitals are split and several molecular orbitals are created while the number of orbitals is proportional to the number of atoms. However, if the inter-atomic space is small, atomic orbital splitting is larger. According to the calculations and figure 2, a pressure increase causes a decrease in the lattice constant and inter-atomic space, thus increasing the orbital splitting and width of the valence band.

Table 7. Partial charges in the $p_x + p_y$, p_z; d_{z^2}, $d_{xy} + d_{x^2-y^2}$ and $d_{xz} + d_{yz}$.

P (GPa)	$p_x + p_y$	p_z	$d_{xy} + d_{x^2-y^2}$	d_{z^2}	$d_{xz} + d_{yz}$
0	0.18896	0.08777	0.84783	0.46065	0.67736
4	0.19654	0.09052	0.86045	0.46494	0.68507
7	0.20200	0.09334	0.87419	0.47196	0.69646
15	0.21359	0.09895	0.90120	0.48449	0.71430
20	0.21833	0.10159	0.91282	0.48769	0.72351
25	0.22668	0.10482	0.93479	0.50003	0.73965
30	0.22877	0.10840	0.95242	0.50818	0.75218

Table 7 lists the number of electrons in s, p and d orbitals and the deviation from spherical symmetry is shown in table 8. This deviation for p and d orbitals is given by [19]:

$$\Delta n_d = \left(n_{d_{xy}} + n_{d_{x^2-y^2}}\right) - \frac{1}{2}\left(n_{d_{xz}} + n_{d_{yz}}\right) - n_{d_{z^2}},$$

$$\Delta n_p = \frac{1}{2}\left(n_{p_x} + n_{p_y}\right) - n_{p_z}.$$

Table 8. Deviation from spherical symmetry of the p and d states as a function of pressure.

P (GPa)	Δn_d	Δn_p
0	0.048	2.1528
4	0.052	2.1712
7	0.054	2.1641
15	0.059	2.1585
20	0.063	2.1491
25	0.064	2.1625
30	0.068	2.1104

If Δn_p and Δn_d are close to zero, deviation from spherical symmetry will be just slight. According to table 8, this deviation increases with pressure for d orbitals.

3. Conclusion

The aim of the present study was to investigate the pressure effect on lattice parameters of hcp structure in titanium. The obtained results showed that the c/a ratio of hcp was nearly constant. However, it is believed that both structures can coexist in the pressure range studied. The alpha phase was the most stable phase at ambient conditions and its transformation to the omega phase in the pressure range of 2–9 GPa. Moreover, theoretical and experimental results confirmed the possibility of coexistence of both structures within the pressure range of 2–9 GPa and even more.

Furthermore, effects of pressure on parameters depending on the electronic structure, such as conductivity, resistivity, the Fermi energy and $n(\varepsilon_\mathrm{F})$ in the ground state were also investigated up to 30 GPa using density functional theory. Moreover, an increase in pressure leads to a decrease in the density of state, thus causing an increase in the electrical resistivity.

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Вплив тиску на електронну структуру hcp титану

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Досліджено вплив тиску на гексагональну щільно упаковану структуру титану. Параметри ґратки визначалися в термінах вільної енергії Ґіббса, використовуючи метод епітаксії шляхом Бейна. Коли цей процес повторювався для декількох тисків, було виявлено вплив тиску на параметри ґратки. Обчислені параметри ґратки добре узгоджувалися із теоретичними та експериментальними результатами. Вплив тиску на параметри, такі як провідність та опір в основному стані, в залежності від електронної структури, також було досліджено аж до 30 GPa, використовуючи теорію функціоналу густини.

Ключові слова: *вплив тиску, hcp-Ti, вільна енергія Ґіббса, параметри ґратки, метод ЕВР*