TiO₂ 的相变和热力学性质

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摘要: 利用第一性原理平面波赝势密度泛函理论方法对 TiO₂ 从金红石结构到萤石结构的相变进行了理论研究, 并且通过准谐德拜模型分别得到了金红石和萤石结构 TiO₂ 的热力学性质. 计算结果与实验值以及其它理论计算的结果都符合得很好, 通过吉布斯能的计算得到 TiO₂ 从金红石结构到萤石结构的相变压强为 47.74 GPa, 并成功地获得了相对体积(V/V_0)、德拜温度(Θ)和热容(C_V)随压强(p)和温度(T)的变化关系.

关键词: 密度泛函理论; TiO₂; 热力学性质; 相变; 准谐德拜模型

中图分类号: O641; O642; O643

Phase Transition and Thermodynamic Properties of TiO₂

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Abstract: The phase transition of TiO₂ from the rutile structure to the fluorite structure under pressure was investigated by the first principles plane-wave pseudopotential density functional theory method. The thermodynamic properties of the rutile and fluorite structures for TiO₂ were obtained by the quasi-harmonic Debye model. The results obtained are in good agreement with the experimental data and other theoretical results. We found that the rutile-to-fluorite transition of TiO₂ occurred at 47.74 GPa from the Gibbs energy calculations. Moreover, the dependence of the relative volume (V/V_0), the Debye temperature (Θ) and the heat capacity (C_V) on the pressure (p) as well as the heat capacity (C_V) on the temperature (T) were also successfully obtained.

Key Words: Density functional theory; TiO₂; Thermodynamic property; Phase transition; Quasi-harmonic Debye model

Titanium dioxides (TiO₂) is an interesting compound because of its wide applications in catalysis, as sensor material and coatings, and thus has been actively investigated for a long time^[1–3]. TiO₂ occurs in nature in three different phases which, in order of abundance, are rutile, anatase, and brookite. The rutile phase is widely used as a white pigment and opacifier. The anatase phase finds applications in, among others, photocatalysts and nanostructured solar cells. The rutile and anatase phases have been widely studied in recent years. The rarer mineral brookite is not used commercially; this, coupled with its relatively complicated structure, has led to few studies of its proper-

ties^[4–8].

At elevated pressures TiO₂ has a rich phase diagram with a series of structural phase transformations. Rutile TiO₂ is particularly attractive because it is expected to undergo a sequence of phase transformations with increasing pressure similar to that experienced by stishovite SiO₂ in the Earth's mantle, but at more readily accessible pressures. Great interest in the high-pressure phases has also been stimulated by the recent discovery of the ultrahard TiO₂ phase. Very high-pressure experiments have suggested that TiO₂ transforms to a cubic structure at room temperature and pressures in excess of about 60 GPa^[9–10]. Recently, *in*

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situ X-ray diffraction experiments at a pressure of 48 GPa and temperatures between 1900 and 2100 K a stable cubic phase of TiO₂^[11–12] was found, it has been suggested that this phase has the fluorite structure^[2] characterized by the *Fm3m* space group. This phase can be stabilized under high pressure and is the hardest known oxide material; its discovery has stimulated much interest in potential applications of pressure-stabilized phase^[13].

In this work, we also focus on the pressure-induced phase transition of TiO₂ from rutile structure to fluorite structure by using the plane-wave pseudopotential density functional theory (DFT)^[14–15] method. Moreover, we obtain the thermodynamic properties of the rutile and fluorite structures through the quasi-harmonic Debye model^[16], which allows us to obtain all thermodynamics parameters of a solid from the energy–volume data.

1 Theoretical method

In our electronic structure calculations, we adopt the exchange correlation interaction by using the Perdew Wang (1991) version exchange-correlation function under the generalized gradient approximation (PW91-GGA)^[17–18] together with the ultra-soft pseudopotentials^[19–20]. Because it is important to ensure that the ground state energy is converged within a specified tolerance in terms of the iterations for selfconsistency, the convergence tests are first made carefully to determine the needed minimum of *k*-points for the Brillouin-zone sampling and cut-off energy for the used plane-wave basis set in the DFT calculations. According to the result tested, the electronic wavefunctions are expanded in a plane wave basis set with an energy cut-off of 700 eV. Pseudo atomic calculations are performed for Ti 3s²3p⁶ 3d²4s² and O 2s²2p⁴. For the Brillouin-zone sampling, we use 5×5×6 and 8×8×8 *k*-point Monkhorst-Pack meshes^[21–22] for the rutile and fluorite phases, respectively, where the self-consistent convergence of the total energy is 10^{−6} eV·atom^{−1}. All the total energy electronic structure calculations are implemented through the CASTEP code.

2 Thermodynamic properties

To investigate the thermodynamic properties of TiO₂, we here apply the quasi-harmonic Debye model, in which the non-equilibrium Gibbs function $G^*(V; p, T)$ takes the following form:

$$G^*(V; p, T) = E(V) + pV + A_{\text{vib}}(\Theta(V); T) \quad (1)$$

where $E(V)$ is the total energy per unit cell for TiO₂, pV corresponds to the constant hydrostatic pressure condition, p is the pressure, V is the volume, $\Theta(V)$ is the Debye temperature, the vibrational Helmholtz free energy A_{vib} can be written as^[23–24]

$$A_{\text{vib}}(\Theta; T) = nkT \left[\frac{9}{8} \frac{\Theta}{T} + 3 \ln(1 - e^{-\Theta/T}) - D(\Theta/T) \right] \quad (2)$$

where $D(\Theta/T)$ represents the Debye integral, n is the number of atoms per formula unit. For an isotropic solid, Θ is expressed by^[23]

$$\Theta = \frac{\hbar}{k} [6\pi^2 V^{1/3} n]^{1/3} f(\sigma) \sqrt{\frac{B_s}{M}} \quad (3)$$

where M is the molecular mass per unit cell, B_s is the adiabatic bulk modulus, which is approximated by the static compressibil-

ity^[25]

$$B_s \cong B(V) = V \frac{d^2 E(V)}{dV^2} \quad (4)$$

$f(\sigma)$ is given by Refs.[26–27], the Poisson σ is taken as 0.25^[28]. Therefore, the non-equilibrium Gibbs function $G^*(V; p, T)$ as a function of $(V; p, T)$ can be minimized with respect to volume V

$$\left(\frac{\partial G^*(V; p, T)}{\partial V} \right)_{p, T} = 0 \quad (5)$$

By solving Eq.(5), one can get the thermal equation of state (EOS) $V(p, T)$. The heat capacity C_V is taken as

$$C_V = 3nk \left[4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right] \quad (6)$$

Through the quasi-harmonic Debye model, one could calculate the thermodynamic parameters of TiO₂ at any pressures and temperatures from the calculated E – V data at $T=0$ K and $p=0$ GPa.

3 Results and discussion

For both the rutile phase and the fluorite phase of TiO₂, we take a series of constant-pressure *ab initio* simulations to obtain the total energy E and the corresponding primitive cell volume V . The calculated equilibrium lattice constants, zero-pressure bulk modulus B_0 , its pressure derivation B'_0 from the Birch-Murnaghan equation of state (EOS) and the corresponding literature data^[1–5,7,11–13,29–35] are listed in Table 1. It is demonstrated that our calculated results are in satisfactory agreement with the experimental data^[11,31,33–35] and other theoretical results^[1–5,7,12–13,29–30,32].

An estimate of the transition pressure between the rutile and the fluorite structures of TiO₂ may be obtained from the usual condition of equal Gibbs energies, i.e., the pressures, at which the Gibbs energies $G=E+pV+A$, of both phases are the same. Fig.1 shows the Gibbs energy as a function of the pressure at 2000 K. It is found that the transition pressure from rutile structure to the fluorite structure is about 47.74 GPa when the temperature is 2000 K. This result agrees well with the *in situ* X-ray diffraction experiments value of 48 GPa and temperatures between 1900 and 2100 K^[11–12], and shows a larger discrepancy with the other high-pressure experiments value of 60 GPa^[9–10], which maybe results from two important respects: one is that they adopted the experimental data of TiO₂ at room temperature, but we used the experimental data of TiO₂ at 2000 K in our calculation, and the other may be due to the GGA used in our calculation. To our knowledge, it is the first time that the transition pressure from rutile to fluorite phase of TiO₂ has been obtained theoretically. No other theoretical data are available for our comparison. In the following, we investigate the transition pressure at various temperatures (0, 200, 400, 600, 800, 1000, 1200, 1400, 1600, 1800, 2000, 2200, 2400, 2600, and 2800 K), shown in Fig.2. It is noted that the transition pressure (p_t) increases almost linearly with applied temperatures. By fitting these data to 3 third-order polynomials in temperature, we obtain the following relationship:

$$p_t = 45.25794 + 6.14254 \times 10^{-4} T + 5.01984 \times 10^{-7} T^2 - 9.22784 \times 10^{-11} T^3 \quad (7)$$

Using the quasi-harmonic Debye model described above, we

Table 1 Lattice constants, bulk modulus and its pressure derivation of the rutile and fluorite structures of TiO_2 at 0 GPa and 0 K

		This work (GGA)	Calculated method	Calculated value	Experimental value
rutile	a/nm	0.46259	MS-Q ^[1]	0.45866	0.459366 ($T=298\text{ K}$) ^[31]
			GGA ^[2]	0.4656	0.4593 ($T=295\text{ K}$) ^[33]
			LDA ^[3]	0.45997	0.4587 ($T=15\text{ K}$) ^[33]
			LCAO-GGA ^[4]	0.4627	
			PBE ^[5]	0.4681	
			GGA ^[29]	0.4623	
			LDA ^[30]	0.4653	
	c/nm	0.29572	MS-Q ^[1]	0.29581	0.259868 ($T=298\text{ K}$) ^[31]
			GGA ^[2]	0.2968	0.2959 ($T=295\text{ K}$) ^[33]
			LDA ^[3]	0.29806	0.2954 ($T=15\text{ K}$) ^[33]
			LCAO-GGA ^[4]	0.2981	
			PBE ^[5]	0.3005	
			GGA ^[29]	0.2987	
			LDA ^[30]	0.2965	
	B_0/GPa	222.07	MS-Q ^[1]	229	216 ($T=298\text{ K}$) ^[31]
			LCAO-HF ^[4]	239±10	230±20 ^[34]
			GGA ^[12]	215±1	211±7 ^[35]
			B3LYP ^[12]	224±8	
	B'_0	4.3545	LDA ^[3]	4.736	6.76 ($T=298\text{ K}$) ^[31]
			GGA ^[12]	5.35±0.16	
			LDA ^[30]	4.63	
fluorite	a/nm	0.47380	MS-Q ^[1]	0.46886	0.4516 ($p=48\text{ GPa}$, $T=1900\text{--}2100\text{ K}$) ^[11]
			HF ^[4]	0.4794	
			LDA ^[4]	0.4748	
			LDA ^[13]	0.4743	
	B_0/GPa	281.55	MA ^[1]	269	202±5 ($T=300\text{ K}$) ^[11]
			PW-LDA ^[7]	282	
			PW-LDA ^[32]	287	
	B'_0	4.2690	PBE ^[5]	4.41	1.3±1 ($T=300\text{ K}$) ^[11]

Fig.1 Gibbs energy as a function of pressure for TiO_2

Fig.2 Transition pressure (p_t) as a function of temperature

have investigated the thermodynamic properties of the rutile structure of TiO_2 over a range of pressures from 0 to 47.74 GPa, and those of the fluorite structure of TiO_2 over a range of pressures from 47.74 to 100 GPa. For these pressures, we here only consider the rutile structure and fluorite structure of TiO_2 . In Fig. 3, we present the relative volume–pressure diagram of the rutile and fluorite structures for TiO_2 at various temperatures. From

Fig.3(a), it is easily seen that, as the pressure p increases, the relative volume V/V_0 decreases at a given temperature for two structures, and the values of relative volume V/V_0 at higher temperatures are smaller than those at lower temperatures at the same pressure. The relative volume of the rutile structure is less than that of the fluorite structure at the same pressure and temperature. It suggests that the rutile structure is more compress-

Fig.3 Relative volume–pressure diagrams of the rutile and fluorite structures for TiO₂ at various temperatures
(a) Supposing that there exists no phase transition, (b) the phase transition between the rutile and fluorite structures occurs at 47.74 GPa.

Table 2 Heat capacity C_V and Debye temperature Θ over a wide range of temperatures and pressures for the rutile and fluorite structures of TiO₂

T/K	Thermodynamic property	p/GPa					
		0	20	40	60	80	100
			rutile			fluorite	
400	$C_V/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	60.79	56.66	53.30	49.12	46.78	44.69
	Θ/K	834.12	972.41	1081.11	1215.31	1290.73	1359.03
800	$C_V/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	71.13	69.75	68.56	67.00	66.06	65.17
	Θ/K	810.28	956.02	1068.38	1203.52	1280.42	1349.89
1200	$C_V/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	73.27	72.60	72.03	71.28	70.81	70.37
	Θ/K	782.49	937.29	1053.68	1189.72	1268.17	1338.86
1600	$C_V/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	74.01	73.62	73.28	72.85	72.58	72.32
	Θ/K	751.12	917.09	1038.05	1175.09	1255.20	1327.12
2000	$C_V/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	74.36	74.09	73.87	73.59	73.41	73.24
	Θ/K	715.05	895.60	1021.70	1159.94	1241.69	1314.99
2400	$C_V/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	74.54	74.34	74.18	73.99	73.86	73.74
	Θ/K	671.52	872.65	1004.65	1144.30	1227.83	1302.44

ible than the fluorite structure for TiO₂. Considering that the rutile-to-fluorite phase transition of TiO₂ occurs at the pressure of 47.74 GPa, we thus obtain the relative volume–pressure diagrams of the rutile and fluorite structures for TiO₂ at various temperatures Fig.3(b). For the rutile and fluorite structures of TiO₂ at ambient temperature 0 and 300 K, our result agrees with the other theoretical results^[5,12]. It seems that the variations in volume with pressure are trivial for the two polymorphs, because of their toughness and high melting points, and we believe that they can be used as a kind of coating material for supersonic aircrafts. By fitting these data to third-order polynomials in p , we obtain the following relations at $T=2000$ K:

$$V/V_0 = \begin{cases} 0.99982 - 0.00662p + 9.21534 \times 10^{-5}p^2 - 6.88425 \times 10^{-7}p^3 & (p \leq 47.74 \text{ GPa, rutile}) \\ 0.97919 - 0.00344p + 1.77703 \times 10^{-5}p^2 - 4.64612 \times 10^{-8}p^3 & (p \geq 47.74 \text{ GPa, fluorite}) \end{cases} \quad (8)$$

In Table 2, we list the heat capacities at different temperatures (400, 800, 1200, 1600, 2000, 2400 K) and different pressures (0, 20, 40, 60, 80, 100 GPa). It is found that, for the rutile structure, when the applied pressure is from 0 to 40 GPa, the heat capacity decreases by 12.32%, 3.61%, 1.69%, 0.99%, 0.66%, 0.48%, and the Debye temperature increases by 29.61%, 31.85%, 34.66%, 38.20%, 42.89%, 49.61% at the temperatures of 400, 800, 1200,

1600, 2000, 2400 K, respectively. Correspondingly, for the fluorite structure, when the pressure increases from 60 to 100 GPa, the heat capacity decreases by 9.02%, 2.73%, 1.28%, 0.73%, 0.48%, 0.34%, and the Debye temperature increases by 11.83%, 12.16%, 12.54%, 12.94%, 13.37%, 13.82%, respectively. By fitting these data to third-order polynomials in T , we obtain the following relations at the low temperature.

$$\text{rutile: } C_V = -0.90354 + 0.46767T - 5.01557 \times 10^{-4}T^2 + 1.78647 \times 10^{-7}T^3 \quad (p=0 \text{ GPa}, 0 \text{ K} \leq T \leq 1200 \text{ K}) \quad (9)$$

Fig.4 Heat capacity of the rutile and fluorite structures of TiO₂ at various pressures and temperatures

$$C_V = -2.93094 + 0.38028T - 3.23652 \times 10^{-4}T^2 + 9.0325 \times 10^{-8}T^3 \quad (p=30 \text{ GPa}, 0 \text{ K} \leq T \leq 1200 \text{ K}) \quad (10)$$

$$\text{fluorite: } C_V = -4.06149 + 0.30522T - 1.78325 \times 10^{-4}T^2 + 2.02786 \times 10^{-8}T^3 \quad (p=60 \text{ GPa}, 0 \text{ K} \leq T \leq 1200 \text{ K}) \quad (11)$$

$$C_V = -4.39952 + 0.26534T - 1.04884 \times 10^{-4}T^2 + 1.40388 \times 10^{-8}T^3 \quad (p=90 \text{ GPa}, 0 \text{ K} \leq T \leq 1200 \text{ K}) \quad (12)$$

As temperature increases, the heat capacity C_V nearly approaches to the Dulong-Petit result $9N_A k_B$ ($\approx 74.85 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) (as shown in Fig.4) which is followed to all solids at high temperature.

4 Conclusions

In summary, we investigate the transition phase of TiO_2 from the rutile structure to the fluorite structures by the *ab initio* plane-wave pseudopotential density functional theory method using package CASTEP. It is found that the rutile-to-fluorite phase transition occurs at 47.74 GPa according to the usual condition of equal Gibbs energy. Through the quasi-harmonic Debye model, we have successfully obtained the dependences of the relative volume V/V_0 on the pressure p , the Debye temperature Θ and heat capacity C_V on the pressure p , and the heat capacity C_V on the temperature T . It is shown that when the temperature is constant, the Debye temperature increases almost linearly with applied pressures, while the heat capacity shows an opposite trend.

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