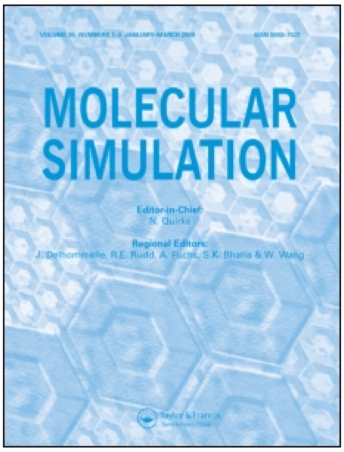

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Molecular Dynamics Simulation of the Structural and Physical Properties of the Four Polymorphs of TiO_2

Masanori Matsui[a]; Masaki Akaogi[b]
[a] Chemical Laboratory, Kanazawa Medical University, Ishikawa, Japan [b] Department of Chemistry, Faculty of Science, Gakushuin University, Tokyo, Japan

To cite this Article Matsui, Masanori and Akaogi, Masaki(1991) 'Molecular Dynamics Simulation of the Structural and Physical Properties of the Four Polymorphs of TiO_2', Molecular Simulation, 6: 4, 239 — 244
To link to this Article: DOI: 10.1080/08927029108022432
URL: http://dx.doi.org/10.1080/08927029108022432

Molecular Simulation, 1991, Vol. 6, pp. 239–244
Reprints available directly from the publisher
Photocopying permitted by license only

MOLECULAR DYNAMICS SIMULATION OF THE STRUCTURAL AND PHYSICAL PROPERTIES OF THE FOUR POLYMORPHS OF TiO_2

MASANORI MATSUI

Chemical Laboratory, Kanazawa Medical University, Uchinada, Ishikawa 920-02, Japan

and MASAKI AKAOGI

Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-5 Mejiro, Toshima-ku, Tokyo 171, Japan

(*Received May 1990, accpeted June 1990*)

The structural and physical properties of the four TiO_2 polymorphs [rutile, anatase, brookite and TiO_2 II (α-PbO_2 structure)] have been calculated by means of molecular dynamics simulation with quantum corrections. The potential model used is composed of the pairwise additive Coulomb, dispersion and repulsion interactions. Energy parameters were determined to reproduce the observed crystal structures of rutile, anatase and brookite, and the measured elastic constants of rutile. Overall, the simulation is successful in reproducing a wide range of properties of the four polymorphs, including the crystal structures, volume compressibilities, volume thermal expansivities, and enthalpy relationships between them.

KEY WORDS: Molecular dynamics, titanium (IV) oxide, polymorph, crystal structure, volume compressibility, thermal expansivity.

INTRODUCTION

Titanium (IV) oxide naturally occurs in the three polymorphic forms: rutile, anatase and brookite. Of these, rutile, most common in nature, is generally considered to be the stable phase under the ambient conditions, with both anatase and brookite being metastable with respect to rutile [1,2]. Under high pressure, each of the three phases transforms to another dense phase (called TiO_2 II) with the α-PbO_2 structure [3,4]. Each transformation is the reconstructive type which allows TiO_2 II to exist metastably at the ambient conditions. In addition, shock compression experiments suggest that there exists a super-dense phase with the fluorite or the distorted fluorite structure [3,5].

The purpose of this paper is to reproduce or to predict the structural and physical properties of the four TiO_2 polymorphs (rutile, anatase, brookite, and TiO_2 II) by means of the molecular dynamics (MD) simulation with quantum correction.

High pressure and high temperature behavior of TiO_2 has also been of considerable interest to researchers in geophysics [6,7], since TiO_2 is a model relevant to stishovite (SiO_2) which is among the important mineral phases stable under the very high pressures prevailing in the earth's deep mantle.

SIMULATION METHOD

Crystal Structures

Rutile and anatase are both tetragonal with space group $P4_2/mnm$ and $I4_1/amd$, respectively, and brookite and TiO_2 II are both orthorhombic with space group *Pbca* and *Pbcn*, respectively. In each of the four structures Ti ions are coordinated by six O ions, and O ions are surrounded by three Ti ions. Each TiO_6 octahedra shares four edges in anatase, three edges in brookite, and two edges both in rutile and TiO_2 II; the structural difference between rutile and TiO_2 II may be described such that the edge sharing octahedra run vertically parallel to the *c*-axis in rutile, whereas form zigzag chains along the *c*-axis in TiO_2 II [8].

Potential Model

Following our previous investigations [9,10], the potential energy for a lattice configuration is approximated to be the sum of pairwise interatomic interactions in the form:

$$V_{ij} = q_i q_j r_{ij}^{-1} - C_i C_j r_{ij}^{-6} + f(B_i + B_j) \cdot \exp\,[(A_i + A_j - r_{ij})/(B_i + B_j)], \qquad (1)$$

where the terms represent Coulomb, dispersion, and repulsion interactions, respectively. Here r_{ij} is the interatomic distance between atoms i and j, and q_i, A_i, B_i, and C_i are the effective charge, repulsive radius, softness parameter, and van der Waals coefficient of the atom i, respectively. The quantity f is a standard force of 4.184 kJ $Å^{-1}$ mol^{-1}. The effective charge $q_0 (= -q_{Ti}/2)$ was transferred from the value obtained by Traylor *et al.* [11] using the observed phonon-dispersion relations of rutile. The value of C_0 was fixed at that developed previously for the modeling of magnesium silicates [9,10]. The remaining energy parameters were adjusted to reproduce the observed elastic constants of rutile [12,13], as well as by using least-squares fitting to the observed crystal structures of rutile [14,15], anatase [15,16], and brookite [8]. The observed structure of TiO_2 II was not included for the least-squares fitting, since it was obtained based on powder X-ray data, with limited accuracy of the atomic coordinates [4]. The optimized energy parameters, used for the present simulation, are listed in Table 1.

MD Simulation with Quantum Correction

The MD simulations of the TiO_2 polymorphs were carried out using the constant-temperature MD method proposed by Nosé [17] and the constant-pressure MD technique described by Parrinello and Rahman [18], in a similar manner as our previous investigations [10,19]. The parameters Q and W, which determine the time scale of the temperature and volume fluctuations [17,18], were set at 10 kJ mol^{-1} $(ps)^2$ and 80 g mol^{-1}, respectively, throughout. Periodic boundary conditions were used

Table 1 Energy parameters[a] used for the simulation

	q	A	B	C
Ti	+2.196	1.1823	0.077	22.5
O	−1.098	1.6339	0.117	54.0

[a] Unit: q in $|e|$, A and B in Å, and C in $Å^3$ $kJ^{1/2}$ $mol^{-1/2}$.

with the MD basic cells composed of 96 ($4\mathbf{a}_1 \times 4\mathbf{a}_2 \times 6c$, containing 576 atoms), 32 ($4\mathbf{a}_1 \times 4\mathbf{a}_2 \times 2c$, 384 atoms), 18 ($2\mathbf{a} \times 3\mathbf{b} \times 3\mathbf{c}$, 432 atoms), and 48 ($4\mathbf{a} \times 3\mathbf{b} \times 4\mathbf{c}$, 576 atoms) unit cells for rutile, anatase, brookite, and TiO_2 II, respectively. The Newtonian equations of motion were solved by a fifth-order predictor-corrector algorithm with a time increment of 1.0 fs. In each MD run, after a sufficient long period of aging, a 5000-steps (5 ps) MD run was carried out to simulate time-averages of structural properties. Equilibrium structures were calculated directly from such averages, while their pressure and temperature derivatives were obtained by a numerical linear interpolation.

The classical mechanics description of atoms in solids is approximately valid only at high temperature limit. We, therefore, included quantum correction terms to the MD simulated properties, using the Wigner-Kirkwood expansion of the free energy of Planck constant h, with the same technique described in our recent paper [19]. We included only the first nonvanishing term with the order h^2, and neglected all the higher-order terms (the second nonvanishing term is of the order h^4).

RESULTS AND DISCUSSION

In our MD simulation the basic cell is treated as a triclinic lattice (space group $P1$), with all the atomic coordinates in the basic cell being treated as independent variables, so that the simulation can examine the stability of crystal lattices. In all the MD simulations studied here we found no significant deviations of the calculated struc-

Table 2 Observed and calculated structural data, volume compressibilities, and volume thermal expansivities of the four TiO_2 polymorphs ($P = 0$ GPa). Calculated values include the quantum corrections (quantum minus classical) which are given in square brackets.

	rutile		*anatase*		*brookite*		*TiO_2 II*	
	Obs	*Calc*	*Obs*	*Calc*	*Obs*	*Calc*	*Obs*	*Calc*
Cell parameters, molar volume, and mean Ti–O distance at 300 K								
a/Å	4.59[a]	4.51 [0.007]	3.78[b]	3.78 [0.005]	9.17[c]	9.19 [0.014]	4.52[d]	4.55 [0.007]
b	4.59	4.51 [0.007]	3.78	3.78 [0.005]	5.45	5.41 [0.008]	5.50	5.40 [0.009]
c	2.96	3.02 [0.004]	9.51	9.65 [0.033]	5.14	5.17 [0.011]	4.94	4.96 [0.008]
$V/(cm^3\ mol^{-1})$	18.80	18.50 [0.08]	20.51	20.75 [0.12]	19.33	19.35 [0.10]	18.45	18.31 [0.09]
⟨Ti-O⟩/Å	1.96	1.95 [0.003]	1.95	1.96 [0.003]	1.96	1.96 [0.003]	1.96	1.96 [0.003]
Volume compressibility/TPa^{-1} at 300 K								
β	4.7–4.8[e]	4.3 [−0.08]	—	6.1 [−0.15]	—	5.1 [−0.11]	4.0[f]	4.5 [−0.09]
Volume thermal expansivity/(10^{-5} K^{-1}) at 500 K								
α	2.8[g]	2.0 [−0.6]	2.5[g]	1.4 [−0.8]	2.4[h]	1.9 [−0.6]	—	1.9 [−0.6]

[a] Ref.[14]. [b] Ref.[16]. [c] Ref.[8]. [d] Ref.[4]. [e] Refs.[12,13,21]. [f] Ref.[20]. [g] Ref.[15]. [h] Observed value between 298–898 K, Ref.[8].

tural parameters from the corresponding observed structures of the four TiO_2 polymorphs.

Table 2 summarizes the simulated structural and physical properties of the four TiO_2 polymorphs, together with the measured values for comparison. In Table 2 we also list the contributions of the quantum corrections to the simulated properties. The quantum correction to the volume thermal expensivity is very important except at very high temperatures; at 500 K for example, the magnitudes of the quantum corrections to the classical MD values reach 23%, 36%, 24%, and 24% for rutile, anatase, brookite, and TiO_2 II, respectively, as can be seen in Table 2. In contrast, the quantum effect is found to have a very small influence on the volume compressibility, with the correction being only 2% at 300 K for each of the four polymorphs (Table 2). More detailed discussion on the quantum contributions to the structural and physical properties of crystals is given in our recent investigations [19].

In each of the four polymorphs, the simulated structure at 300 K and 0 GPa reproduces the observed one quite accurately. The largest error in the cell parameters is within 2% for each polymorph. The mean Ti–O distance $\langle$ Ti–O $\rangle$ is correct within 0.01 Å for each polymorphs, with the absolute deviations in the individual Ti–O distance being less than 0.05 Å, 0.02 Å, 0.06 Å, and 0.06 Å, for rutile, anatase, brookite, and TiO_2 II, respectively (note that the observed atomic coordinates in TiO_2 II are determined using powder X-ray data [4], so they are not very certain). The measured molar volumes are in the order of TiO_2 II < rutile < brookite < antase; the same is true for our calculated values.

Quite recently we have obtained the volume compressibility of TiO_2 II at room temperature by means of volume compression experiment using synchrotron X-ray data [20], and accurate experimental data are presented for the volume compressibility of rutile at room temperature [12,13,21], while no measured compressibility data are available either for anatase or for brookite. As can be seen in Table 2, the errors of our calculated volume compressibilities at 300 K and 0 GPa are about 10% for rutile, and 12% for TiO_2 II; similar magnitudes of error might be expected in the predicted volume compressibilities for anatase and brookite, listed in Table 2.

The volume thermal expansivities have been measured for rutile [8,15], anatase [15], and brookite [8], while no experimental data is reported for TiO_2 II. The simulated volume thermal expansivities at 500 K and 0 GPa are 2.0, 1.4, and 1.9 $\times$ 10^{-5} K^{-1} for rutile, anatase, and brookite, respectively, which are significantly too small when compared with the experimental values at 500 K of 2.8, 2.5, and 2.4 $\times$ 10^{-5} K^{-1}. Additional investigations are required to improve the potential model for TiO_2.

By calorimetric experiments, Navrotsky and coworkers [1,22] have reported the transformation enthalpies of TiO_2 II and anatase to rutile at room temperature to be $-3.2(7)$ and -5.2 kJ mol^{-1}, respectively; so the enthalpies are measured to increase in the order rutile < TiO_2 II < anatase at room temperature. At 971 K, the enthalpies of transformation of brookite and anatase to rutile have been determined using solution calorimetry by Mitsuhashi and Kleppa [23] as $-0.7(4)$ and $-3.3(8)$ kJ mol^{-1}, respectively. Since specific heat differences among polymorphs are usually small, the enthalpy trend measured at 971 K, rutile < brookite < anatase, may be expected to be same as that at room temperature. Our simulated transformation enthalpies of anatase, brookite, and TiO_2 II to rutile at 300 K are -29.1, -17.3, and -3.5 kJ mol^{-1}, respectively; the quantum correction to the enthalpy is estimated to be 0.4 kJ mol^{-1} for each of the four polymorphs. The simulated enthalpy relationship among the four polymorphs at 300 K, rutile < TiO_2 II < brookite < anatase, is consistent with the two measured enthalpy sequences remarked above, i.e. rutile $<$ TiO_2 II $<$ anatase by Navrotsky and coworkers [1,22], and rutile $<$ brookite $<$ anatase by Mitsuhashi and Kleppa [23]. The simulation has predicted the enthalpy of TiO_2 II smaller than that of brookite. Hopefully, further experiments to establish the enthalpy relation between brookite and TiO_2 II will be undertaken.

Acknowledgments

The authors are grateful to Y. Matsui for his support and helpful discussions, and to S. Nosé for kindly providing the original MD program that was modified for the present calculations. The computations were carried out using the FACOM VP-400E computer at the Kyoto University Data Processing Center. This work was supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

[1] A. Navrotsky and O.J. Kleppa, "Enthalpy of the anatase-rutile transformation", *J. Amer. Ceram. Soc.*, **50**, 626 (1967).
[2] J.C. Jamieson and B. Olinger, "Pressure-temperature studies of anatase, brookite, rutile, and TiO_2 (II): a discussion", *Amer. Mineral.*, **54**, 1477 (1969).
[3] R.G. McQueen, J.C. Jamieson and S.P. Marsh, "Shock-wave compression and X-ray studies of titanium dioxide", *Science*, **155**, 1401 (1967).
[4] P.Y. Simons and F. Dachille, "The structure of TiO_2 II, a high-pressure phase of TiO_2", *Acta Crystallogr.*, **23**, 334 (1967).
[5] K. Kusaba, M. Kikuchi, K. Fukuoka and Y. Syono, "Anisotropic phase transition of rutile under shock compressions", *Phys. Chem. Minerals*, **15**, 238 (1988).
[6] L.-G. Liu, "A fluorite isotype of SnO_2 and a new modification of TiO_2: implications for the earth's lower mantle", *Science*, **199**, 422 (1978).
[7] Y. Syono, K. Kusaba, M. Kikuchi and K. Fukuoka, "Shock-induced phase transitions in rutile single crystal", in High-Pressure Research in Mineral Physics, M.H. Manghnani and Y. Syono, eds, Terra Sci. Pub. Co., Tokyo, 1987, pp. 385–392.
[8] E.P. Meagher and G.A. Lager, "Polyhedral thermal expansion in the TiO_2 polymorphs: refinement of the crystal structures of rutile and brookite at high temperature", *Canad. Mineral.*, **17**, 77 (1979).
[9] M. Matsui, M. Akaogi and T. Matsumoto, "Computational model of the structural and elastic properties of the ilmenite and perovskite phases of $MgSiO_3$", *Phys. Chem. Minerals*, **14**, 101 (1987).
[10] M. Matsui, "Molecular dynamics study of $MgSiO_3$ perovskite", *Phys. Chem. Minerals*, **16**, 234, (1988).
[11] J.G. Traylor, H.G. Smith, R.M. Nicklow and M.K. Wilkinson, "Lattice dynamics of rutile", *Phys. Rev.* **B3**, 3457 (1971).
[12] M.H. Manghnani, E.S. Fisher and W.S. Brower, Jr., "Temperature dependence of the elastic constants of single-crystal rutile between 4 and 583 K", *J. Phys. Chem. Solids*, **33**, 2149 (1972).
[13] I.J. Fritz, "Pressure and temperature dependences of the elastic properties of rutile (TiO_2)", *J. Phys. Chem. Solids*, **35**, 817 (1974).
[14] S.C. Abrahams and J.L. Bernstein, "Rutile: normal probability plot analysis and accurate measurement of crystal structure", *J. Chem. Phys.*, **55**, 3206 (1971).
[15] K.V.K. Rao, S.V.N. Naidu and L. Iyengar, "Thermal expansion of rutile and anatase", *J. Amer. Ceram. Soc.*, **53**, 124 (1970).
[16] M. Horn, C.F. Schwerdtfeger and E.P. Meagher, "Refinement of the structure of anatase at several temperatures", *Z. Krist.*, **136**, 273 (1972).
[17] S. Nosé, "A unified formation of the constant temperature molecular dynamics methods", *J. Chem. Phys.*, **81**, 511 (1984).
[18] M. Parrinello and A. Rahman, "Polymorphic transitions in single crystals: a new molecular dynamics method", *J. Appl. Phys.*, **52**, 7182 (1981).
[19] M. Matsui, "Molecular dynamics study of the structural and thermodynamic properties of MgO crystal with quantum correction", *J. Chem. Phys.*, **91**, 489 (1989).

[20] In preparation.
[21] L.-C. Ming and M.H. Manghnani, "Isothermal compression of TiO_2 (rutile) under hydrostatic pressure to 106 kbar", *J. Geophys, Res.*, **84**, 4777 (1979).
[22] A. Navrotsky, J.C. Jamieson and O.J. Kleppa, "Enthalpy of transformation of a high-pressure polymorph of titanium dioxide to the rutile modification", *Science*, **158**, 388 (1967).
[23] T. Mitsuhashi and O.J. Kleppa, "Transformation enthalpies of the TiO_2 polymorphs", *J. Amer. Ceram. Soc.*, **62**, 356 (1979).