<table>
<thead>
<tr>
<th>Title</th>
<th>Title: First-principles calculations of the ferroelastic transition between rutile-type and CaCl2-type SiO2 at high pressures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Togo, Atsushi; Oba, Fumiyasu; Tanaka, Isao</td>
</tr>
<tr>
<td>Citation</td>
<td>PHYSICAL REVIEW B (2008), 78(13)</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2008-10</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/84631">http://hdl.handle.net/2433/84631</a></td>
</tr>
<tr>
<td>Right</td>
<td>© 2008 The American Physical Society</td>
</tr>
<tr>
<td>Type</td>
<td>Journal Article</td>
</tr>
<tr>
<td>Textversion</td>
<td>publisher</td>
</tr>
</tbody>
</table>

Kyoto University
First-principles calculations of the ferroelastic transition between rutile-type and CaCl$_2$-type SiO$_2$ at high pressures

Atsushi Togo,$^{1,*}$ Fumiyasu Oba,$^1$ and Isao Tanaka$^{1,2}$

$^1$Department of Materials Science and Engineering, Kyoto University, Sakyo, Kyoto 606-8501, Japan
$^2$Nanostructures Research Laboratory, Japan Fine Ceramics Center, Atsuta, Nagoya 456-8587, Japan

(Received 14 May 2008; revised manuscript received 19 September 2008; published 14 October 2008)

The tetragonal to orthorhombic ferroelastic phase transition between rutile- and CaCl$_2$-type SiO$_2$ at high pressures is studied using first-principles calculations and the Landau free-energy expansion. The phase transition is systematically investigated in terms of characteristic phonon modes with $B_{1g}$ and $A_g$ symmetries, shear modulus, transverse-acoustic mode, rotation angle of the SiO$_6$ octahedra, spontaneous symmetry-breaking and volume strains, and enthalpy. The results show that these physical behaviors at the transition are well described using the Landau free-energy expansion parametrized by the first-principles calculations.

DOI: 10.1103/PhysRevB.78.134106

PACS number(s): 62.50.−p, 62.20.de, 63.20.−c, 61.50.Ks

I. INTRODUCTION

Rutile-type SiO$_2$, which is called stishovite, transforms to CaCl$_2$-type SiO$_2$ upon applying high pressure. The tetragonal ($P4_{2}/mnm$)$\Leftrightarrow$orthorhombic ($Pnma$) transition was found to be consistent with a classical second-order transition. This transition is known as a prototypical pseudoproper ferroelastic transition, which is characterized by strain/order-parameter coupling. The transition is driven by $B_{1g}$ mode softening. However, the strain/order-parameter coupling results in the transition having a nonzero soft-mode frequency. The results indicate on the basis of $B_{1g}$ mode frequency vanishes.8 Karki et al.9–11 employed the Landau free-energy expansion parametrized by the first-principles calculations. In this study, the ferroelastic transition of stishovite is investigated using first-principles calculations and the Landau free-energy expansion.

A unit cell of the tetragonal phase is shown in Fig. 1(a). It is made of two silicon and four oxygen atoms. A silicon atom and six surrounding oxygen atoms form SiO$_6$ tetrahedron. The octahedra on the same $a$-$b$ plane share their apexes and the octahedra along the $c$-axis direction share their edges. From the viewpoint of the octahedral connection, the orthorhombic structure is equivalent to the tetragonal structure. The $B_{1g}$ mode in the tetragonal phase and the $A_g$ mode in the orthorhombic phase show characteristic behavior. These modes correspond to rotational vibrations of the octahedra.

![FIG. 1. (Color online) (a) Unit cell of the rutile-type structure. The dark gray and light gray (red) denote silicon and oxygen atoms, respectively. (b) Polyhedral representation of the $B_{1g}$ ($A_g$) mode of the tetragonal (orthorhombic) structure projected onto the $a$-$b$ plane. The directions of the octahedral rotations are depicted by arrows. The square with dashed lines represents the unit cell. (c) Schematic representation of the tetragonal shear strain. The dashed and solid lines represent the tetragonal and orthorhombic lattices, respectively. The arrows show the shear direction.](image-url)
around the c axis as shown in Fig. 1(b). The directions of the rotations between adjacent octahedra are opposite. These modes involve only displacements of the oxygen atoms parallel to the a-b plane. Above the transition pressure, the octahedra at equilibrium start to rotate and symmetry-breaking spontaneous strain is generated. The shear strain corresponding to the tetragonal to orthorhombic lattice deformation is shown in Fig. 1(c).

II. LANDAU FREE-ENERGY EXPANSION

In this section, the Landau free-energy expansion of stishovite developed by Carpenter and et al.\textsuperscript{12,19} is summarized following Ref. 12. Using the Landau free-energy expansion, excess energy $G$ of the orthorhombic structure relative to the tetragonal structure is expanded by an order parameter and the components of strain, up to fourth and second orders, respectively,

$$G = \frac{1}{2}a(P - P_\zeta)Q^2 + \frac{1}{4}bQ^4 + \lambda_1(e_1 + e_2)Q^2 + \lambda_2(e_1 - e_2)Q$$

$$\quad + \lambda_3\varepsilon_3Q^2 + \lambda_4(e_1^2 - e_2^2) + \lambda_5\varepsilon_5Q^2 + \frac{1}{4}(c_{11}^0 + c_{12}^0)(e_1 + e_2)^2$$

$$\quad + \frac{1}{4}(c_{11}^0 - c_{12}^0)(e_1 - e_2)^2 + c_{11}^0(e_1 + e_2)e_3 + \frac{1}{2}c_{13}^0\varepsilon_3^2$$

$$\quad + \frac{1}{2}c_{44}^0(e_1^2 + e_2^2) + \frac{1}{2}\varepsilon_6^2,$$  

(1)

where $a$ and $b$ are the normal Landau coefficients, $P$ is the applied pressure, $P_\zeta$ is the critical pressure, $Q$ is the driving order parameter, $e_1 - e_6$ are the components of spontaneous strain in Voigt notation, and $\lambda_1 - \lambda_6$ are the strain/order-parameter coupling coefficients. $c_{ij}^0$ are the bare elastic stiffness constants which would be measured in the absence of a transition pressure $P_\zeta$. The pressure dependences of $Q$, $c_{ij}^0$, and $Q$ depend on pressure. The pressure dependences of $a$, $b$, and $\lambda_i$ are expected to be weak, which will be discussed in Sec. IV. Though in fact pressure varies slightly with applying strain,\textsuperscript{22} constant pressure is assumed when the applied strain is small as long as the second-order expansion by strain is valid.\textsuperscript{22}

Equation (1) is rewritten as

$$G = \frac{1}{2}a(P - P_\zeta)Q^2 + \frac{1}{4}b^*Q^4,$$  

(2)

where $P_\zeta$ is the renormalized critical pressure corresponding to the transition pressure, and $b^*$ is the renormalized fourth-order coefficient. The conditions of $Q$, $e_1 - e_2$, $e_1 + e_2$, and $e_3$ at equilibrium are written as

$$\frac{\partial G}{\partial Q} = 0, \quad \frac{\partial G}{\partial (e_1 - e_2)} = 0, \quad \frac{\partial G}{\partial (e_1 + e_2)} = 0, \quad \frac{\partial G}{\partial e_3} = 0.$$  

(3)

e_4, e_5, and $e_6$ are zeros in the cases of tetragonal and orthorhombic symmetries. From these conditions, the phase-transition pressure $P_\zeta$ is obtained as

$$P_\zeta = P_\zeta + \frac{2\lambda_2^2}{a(c_{11}^0 - c_{12}^0)},$$  

(4)

and $b^*$ is given by

$$b^* = b - 2\frac{\lambda_3^2(c_{11}^0 + c_{12}^0) + 2\lambda_4^2c_{33}^0 - 2\lambda_1^2c_{11}^0 + c_{33}^0)}{c_{33}^0(c_{11}^0 + c_{12}^0) - 2c_{13}^0}.$$  

(5)

The symmetry-breaking strain $e_1 - e_2$, nonsymmetry-breaking strain $e_1 + e_2$, and $e_3$ vary with $Q$ as

$$e_1 - e_2 = -\frac{2\lambda_2}{c_{11}^0 - c_{12}^0}Q,$$  

(6)

$$e_1 + e_2 = \frac{2(\lambda_3 e_3^0 - \lambda_2 c_{33}^0)}{c_{33}^0(c_{11}^0 + c_{12}^0) - 2e_3^0}Q^2,$$  

(7)

$$e_3 = \frac{2\lambda_1 e_3^0 - \lambda_3(c_{11}^0 + c_{12}^0)}{c_{11}^0(c_{11}^0 + c_{12}^0) - 2c_{13}^0}Q^2.$$  

(8)

The pressure dependence of the order parameter is given by

$$Q^2 = \begin{cases} 0, & P < P_\zeta, \\ \frac{a}{b^*}(P_\zeta - P), & P > P_\zeta. \end{cases}$$  

(9)

The second derivative of the excess energy $G$ with respect to the order parameter under constant strain conditions at equilibrium is called the inverse order-parameter susceptibility $\chi^{-1}$.\textsuperscript{23,24} This is given by\textsuperscript{12,19,20}

$$\chi^{-1} = a(P - P_\zeta) + 3bQ^2$$

$$= \begin{cases} a(P - P_\zeta), & P < P_\zeta, \\ a\left(\frac{b}{b^*} - 1\right)(P_\zeta - P) + a(P_\zeta - P), & P > P_\zeta. \end{cases}$$  

(10)

Since the squared frequencies of the B_{1g} and A_{g} modes are expected to be proportional to $\chi^{-1}$,\textsuperscript{12} they are also linearly dependent on pressure.

The elastic stiffness constants are given by\textsuperscript{23}

$$c_{ij} = c_{ij}^0 - \chi \frac{\partial G}{\partial e_j} \frac{\partial G}{\partial Q}.$$  

(11)

Therefore, $c_{11}$ and $c_{12}$ in the tetragonal phase are

$$c_{11} = c_{11}^0 - \lambda_2^2 \chi,$$  

(12)

$$c_{12} = c_{12}^0 + \lambda_2^2 \chi.$$  

(13)

The shear modulus in the tetragonal phase $(c_{11} - c_{12})/2$ is obtained from Eqs. (4), (10), (12), and (13) as\textsuperscript{12}

$$\frac{c_{11} - c_{12}}{2} = \frac{c_{11}^0 - c_{12}^0 - P - P_\zeta}{2}.$$  

(14)

Similarly, $c_{11}$, $c_{22}$, and $c_{12}$ in the orthorhombic phase are

$$c_{11} = c_{11}^0 - (4\lambda_2^2 Q^2 + 4\lambda_2 \lambda_3 Q + \lambda_3^2) \chi,$$  

(15)
\[ c_{22} = c_{22}^0 - 4\lambda_2^2Q^2 - 4\lambda_1\lambda_2Q + \lambda_2^2\chi, \quad (16) \]
\[ c_{12} = c_{12}^0 - 2(4\lambda_2^2Q^2 - \lambda_2^2)\chi. \quad (17) \]

From Eqs. (4), (10), and (15)–(17), the shear modulus in the orthorhombic phase \((c_{11} + c_{22} - 2c_{12})/4\) is given by
\[ c_{11} + c_{22} - 2c_{12} = c_{11}^0 - c_{12}^0 \frac{P - P_c^o}{2} \left( P - P_c^o \right), \quad (18) \]
where \(P_c^o\) is the orthorhombic critical pressure, which is defined by
\[ P_c^o = P_e^s + \frac{P_e^s - P_c}{3b/b' - 1}. \quad (19) \]

The elastic stiffness constants are originally defined by
\[ c_{ij} = \Delta \sigma_j / \epsilon_i, \quad (20) \]
where \(\Delta \sigma_j\) are the changes in the components of stress upon applying strain. We use the elastic stiffness constants to describe the formulae instead of the elastic constants used in Ref. 12, since the elastic stiffness constants are formally related to energy by
\[ P_e^o = \frac{\partial^2 E}{\partial \epsilon_i \partial \epsilon_j}, \quad (21) \]
where \(G\) is assumed to be normalized by unit volume. In contrast, the elastic constants \(C_{ij}\) are defined by
\[ C_{ij} = \frac{\partial^2 E}{\partial \epsilon_i \partial \epsilon_j}, \quad (22) \]
where \(E\) is the internal energy per unit volume. Therefore, \(c_{ij}\) and \(C_{ij}\) are not equivalent to \(C_{ij}\) under pressure, and thus the elastic stiffness constants are considered more suitable for use than the elastic constants.

### III. METHOD OF CALCULATION

#### A. Phonon

Phonon calculations were performed using the Parлинski-Li-Kawazoe method as implemented in the FROPHO code. Phonon frequencies were obtained within harmonic approximation by solving the secular equations of dynamical matrices. Force-constant matrices \(\Phi\) are written as
\[ \Phi_{ab}(j') = \frac{F_{a}(j)}{\Delta \mu_{ab}(j' l')}, \quad (23) \]
where subscripts \(a\) and \(b\) denote the Cartesian components, \(j\) and \(j' l'\) denote the \(j\) and \(j'\)th atoms in the \(l\) and \(l'\)th unit cells, respectively. \(F_{a}\) is the \(a\) component of force on an atom and \(\Delta \mu_{ab}\) is the \(b\) component of the atomic displacement from equilibrium position. This method of obtaining the force constants from forces and finite atomic displacements using supercells follows that developed by Parлинski et al. and is explained in the FROPHO manual. In this study, the forces were obtained using first-principles calculations. The dynamical matrices \(D\) are written as
\[ D_{ab}(j,j',k) = \frac{1}{(m_j m_{j'})^{1/2}} \sum_{l'} \Phi_{ab}(j j') \exp\left[i (k \cdot r(j') - k \cdot r(j))\right], \quad (24) \]
where \(\omega\) and \(\text{e}(k, \nu)\) are the phonon frequency and eigenvector, respectively, and \(\nu\) is the label of the solution.

#### B. Computational details

For the first-principles calculations, we employed the plane-wave basis projector augmented wave (PAW) method in the framework of density-functional theory within the generalized gradient approximation in the Perdew-Burke-Ernzerhof form as implemented in the VASP code. A plane-wave energy cutoff of 500 eV was used. To avoid the discontinuity of calculated physical properties, we fixed the fast Fourier transform (FFT) mesh numbers of unit cells to those of the unit cell having the largest volume. The radial cutoffs of the PAW potentials of Si and O were 1.50 and 1.52 Å, respectively. The 3s and 3p electrons for Si and the 2s and 2p electrons for O were treated as valence and the remaining electrons were kept frozen. The Brillouin zones of the tetragonal and orthorhombic unit cells were sampled by \(4 \times 4 \times 6\) \(k\)-point meshes generated in accordance with the Monkhorst-Pack scheme. The total energy was minimized until the energy convergence became less than \(1 \times 10^{-6}\) eV. To obtain the equilibrium structures of unit cells at applied pressures, internal atomic positions were optimized until the residual forces became less than \(1 \times 10^{-7}\) eV/Å. Lattice parameters were optimized until the difference between each component of the specified and calculated stress became less than \(1 \times 10^{-2}\) GPa.

To obtain the force constants for the phonon calculations, atomic displacements of 0.01 Å were employed. Displacements in opposite directions along the \(a\) and \(b\) axes were incorporated in the calculations of force constants to improve the precision.

### IV. RESULTS AND DISCUSSION

#### A. \(B_{1g}\) and \(A_{g}\) modes

The squared phonon frequencies of the \(B_{1g}\) and \(A_{g}\) modes calculated using the \(2 \times 2 \times 3\) supercells as a function of pressure are shown in Fig. 2. As expected from Eq. (10), they are linearly dependent on pressure except at very low pressures. The calculated values of the \(B_{1g}\) mode between 10 and 100 GPa are fitted by a straight line \(\sim -538 P + 51743\) cm\(^{-1}\). The values of the \(A_{g}\) mode between 54 and 120 GPa are fitted by \(1308 P - 46696\) cm\(^{-1}\). The transition pressure \(P_c\) is given by 53.3 GPa where these two lines intersect. This is considered to agree with the transition pressures of experiments 51.6, 6.12, 13.19, 54.1, and \(\sim 50\) GPa. The critical pressure \(P_c\), which is determined from Eq. (10), is the pressure at…
which the frequency of the $B_{1g}$ mode vanishes and is given by the fit as 96.2 GPa. A Raman result gives $P_c$ = 102.3 GPa.\textsuperscript{6,12,13,19} The orthorhombic critical pressure $P^o_c$, which is determined from Eqs. (10) and (19), is the pressure at which the frequency of the $A_g$ mode vanishes and is given by the fit as 35.7 GPa. The Raman result gives $P^o_c$ = 29.3 GPa.\textsuperscript{6,12,13,19} The calculated $P_c$ and $P^o_c$ are different from the experimental values by about 6 GPa. The ratio of the slopes of the squared frequencies was calculated as 2.43, which is greater than the experimental value of 2.27.\textsuperscript{6,12,13,19}

The values of $P_c$, $P_e$, and $P^o_c$ determined in this section are taken as reference values in Secs. IV B–IV F, since the use of $B_{1g}$ and $A_g$ modes is the most unambiguous method of determining these values among those discussed in this study.

![Graph](image)

**FIG. 2.** (Color online) Squared frequencies of the $B_{1g}$ and $A_g$ modes as a function of pressure. The filled and open circles depict the values for the tetragonal and orthorhombic structures, respectively. The solid and dashed lines are the fits to respective values.

### B. Order parameter

The order parameter $Q$ is considered to be proportional to the angle $\phi$ of the octahedral rotation, i.e., $Q \propto |\phi|$. The rotation angle is represented in the following two ways:\textsuperscript{36}

$$\phi = \arctan \left( \frac{b_o(0.5-y)}{a_o(0.5-x)} \right) - 45,$$

and

$$\phi' = 45 - \arctan \left( \frac{b_o y}{a_o x} \right),$$

where $\phi$ and $\phi'$ are the rotation angles, $a_o$ and $b_o$ are the lattice parameters along the $a$ and $b$ axes, respectively, and $x$ and $y$ represent the internal atomic position of an oxygen atom on the face of the unit cell shown in Fig. 1(a) in the reduced coordinates. The difference between $\phi$ and $\phi'$ is obtained from the lengths of Si-O bonds projected onto the $a$-$b$ plane. This difference between $\phi$ and $\phi'$ represents the torsion of the octahedron.

Under constant strain conditions with the tetragonal structure, Eq. (1) reduces to

$$G = \frac{1}{2} a(P - P_c)Q^2 + \frac{1}{4} bQ^4.$$  \hspace{1cm} (28)

If the temperature effect is not considered, $G$ is formally reduced to excess internal energy $E$, which is calculated as the internal energy relative to that at $\phi=0$ with the fixed lattice parameters. The values of $E$ at various pressures were calculated as a function of the rotation angle $\phi$. The rotations are given as atomic displacements along with the eigenvectors of the corresponding $B_{1g}$ modes. As shown in Fig. 3(a), the energy required to rotate the octahedra decreases with increasing pressure. At 100 GPa, the structure at $\phi=0$ is no longer dynamically stable. However, the transition does not occur at the pressure at which the structure at $\phi=0$ becomes dynamically unstable but at the transition pressure $P^*_c$, since the transition pressure is renormalized by the strain/order-parameter coupling given by Eq. (4).

Since $Q \propto |\phi|$, $E$ is represented by the following expansion using $\phi$:

$$E(\phi) = A \phi^2 + B \phi^4 + O(\phi^6),$$  \hspace{1cm} (29)

where $A$ and $B$ are the second- and fourth-order coefficients, respectively, which are proportional to $a(P - P_c)$ and $b$ in Eq. (28), respectively. The odd-order terms disappear due to symmetry. $A$ and $B$ as a function of pressure, determined by fits to $E$, are shown in Fig. 3(b). As expected, $A$ is linearly dependent on pressure and vanishes around the critical pressure obtained in Sec. IV A. $B$ also depends linearly on pressure, hence the same holds for $b$.

Above the transition pressure, the octahedra at equilibrium start to rotate. The squared rotation angles $\phi$ and $\phi'$ as a function of pressure at equilibrium are shown in Fig. 3(c). The rotation angles increase with increasing pressure and nonlinearity is clearly observed. Since the torsion is smaller than that estimated from the lattice strain, it is considered that the rotation occurs to reduce the torsion of the octahedron.

Since the prefactors of pressure in Eq. (10) [$a$ and $a(3b/b^*-1)$] are obtained as constants in Sec. IV A, the coefficient $b^*$ is linearly dependent on pressure. Due to the pressure dependence of $b^*$, the squared order parameter $Q^2$ above the transition pressure in Eq. (9) is formally written as

$$\phi^2 \propto Q^2 = \frac{P - P^*_c}{P - P_c},$$  \hspace{1cm} (30)

where $\alpha$ and $\beta$ are the constant parameters. This represents that the nonlinearity observed in Fig. 3(c) follows the pressure dependence of $b^*$. Using Eq. (30), the transition pressure is obtained by the fit as 53.4 GPa. This agrees well with that obtained in Sec. IV A (53.3 GPa).

### C. Elasticity

As given by Eqs. (14) and (18), the shear moduli of the tetragonal and orthorhombic phases are related to a combination of the bare elastic stiffness constants $(c_{11}^0 - c_{12}^0)/2$. It is expected that the bare elastic stiffness constants can be calculated without relaxing the internal atomic positions. The pressure dependencies of $(c_{11}^0 - c_{12}^0)/2$ with strains of 0.001,
dependent of the amount of strain.

\[ (c_{11} - c_{12})/2 \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]

\[ \phi \]

\[ \phi' \]
The shear strain along the [1 1 0] direction corresponds to a transverse-acoustic (TA) mode with a wave vector along the [1 1 0] direction in the long-wavelength limit (k → 0). Since the group velocity in the long-wavelength limit is proportional to the shear modulus, the group velocity at k → 0 vanishes at the transition pressure as well as the shear moduli.

The group velocity $v_g$ is defined by

$$v_g(k) = \frac{\partial \omega_{TA}(k)}{\partial k},$$

where $\omega_{TA}$ is the phonon frequency of the TA mode. For a small $|k|$, the group velocity at $k \rightarrow 0$ is approximated by $\omega_{TA}(k)/|k|$. To obtain the phonon frequency for small $|k|$, we employed a supercell elongated in the [1 1 0] direction by an $8 \times 1 \times 1$ expansion of the redefined unit cell that is shown in Fig. 5. The redefined unit cell is formed by rotating the original unit cell by 45°. The lattice vectors in the $a$-$b$ plane are redefined along the [1 1 0] and [1 1 0] directions of the original unit cell.

TA-mode phonon branches between the $\Gamma$ and $M$ points calculated using the elongated supercell and the $2 \times 2 \times 3$ supercell at 20, 40, 60, and 80 GPa are shown in Fig. 6(a). The branches at 20 and 40 GPa were calculated using the tetragonal structures and those at 60 and 80 GPa were calculated using the orthorhombic structures. The circles on the solid curves are the $k$ points whose atomic displacements fulfill the boundary condition of the elongated supercells. Therefore, the frequencies are expected to be correct within the approximations used in this study. When the atomic interaction range is sufficiently small compared with the supercell size, reasonable frequencies are obtained even if the $k$ point is not represented exactly by the supercell. Indeed, the phonon branches of the $2 \times 2 \times 3$ supercells at 20 and 80 GPa are analogous to those of the elongated supercells.

However, at 40 and 60 GPa, the branches of the $2 \times 2 \times 3$ supercells are markedly distorted near the $\Gamma$ point. Even in the elongated supercells, an unexpected imaginary frequency appears at 40 GPa. This indicates that the atomic interaction range becomes larger than the supercell size as the pressure approaches the transition pressure.

The squared TA-mode frequencies calculated using the elongated supercell at $k=[1/16,1/16,0]$ as a function of pressure. The filled and open circles show the values for the tetragonal and orthorhombic structures, respectively, and the solid and dashed curves are the fits to the respective values.
The strains $e_1$, $e_2$, and $e_3$ are defined as
\[
e_1 = \frac{a_o - a_t}{a_t}, \quad e_2 = \frac{b_o - a_t}{a_t}, \quad e_3 = \frac{c_o - c_t}{c_t},
\]  
where $a_o$, $b_o$, and $c_o$ are the lattice parameters of the orthorhombic structure and $a_t$ and $c_t$ are those of the tetragonal structure. The lattice parameters as a function of pressure are shown in Fig. 7. $a_o$ and $c_t$ were calculated under the constraints of $P4_2/mnm$ symmetry even above the transition pressure. Since $c_o$ and $\sqrt{a_o \times b_o}$ are smaller than $a_t$ and $c_t$, respectively, the volume of the orthorhombic structure is smaller than that of the rutile structure.

The spontaneous symmetry-breaking strain $e_1 - e_3$ appears above the transition pressure. From Eqs. (4), (6), and (9), the squared symmetry-breaking strain is given by
\[
(e_1 - e_3)^2 = \frac{2a^2(P_o^* - P_o)(P_t^* - P)}{b^2(c_{11}^0 - c_{12}^0)}.
\]  
The squared symmetry-breaking strain as a function of pressure is shown in Fig. 8(a). If we assume that $b^*$ and $c_{11}^0 - c_{12}^0$ are linearly dependent on pressure, as discussed in Secs. IV B and IV C, the values are fitted well by Eq. (33). As a result, the transition pressure is given as 53.4 GPa, which agrees well with that obtained in Sec. IV A (53.3 GPa).

Volume strain $V_s$ is defined as
\[
V_s = \frac{V_o - V_t}{V_t},
\]  
where $V_l$ and $V_o$ are the volumes of the tetragonal and orthorhombic structures, respectively. The volume strain calculated using the lattice parameters as a function of pressure is shown in Fig. 8(b). Since the volume strain is approximated by $e_1 + e_2 + e_3$, from Eqs. (7) and (8), it is given by...
The excess energy $G$ at 0 K is formally calculated by the excess enthalpy of the orthorhombic structure relative to that of the tetragonal structure. The excess enthalpy as a function of pressure normalized by the unit volume of the tetragonal structure is shown in Fig. 9. The values above 54 GPa are fitted by Eq. (36), where $b^0$ is assumed to be linearly dependent on pressure. The transition pressure is obtained as 55.7 GPa by the fit, which is overestimated by ~2 GPa compared with that obtained in Sec. IV A (53.3 GPa). Employing enthalpy to determine the transition pressure is considered to be the most difficult method among those presented in this study.

\[ V_s = \frac{2\mu_1(c_{13}^0 - c_{13}^0) + \mu_3(2c_{13}^0 - c_{11}^0 - c_{12}^0)}{c_{33}(c_{11}^0 + c_{12}^0) - 2c_{13}^0} Q^2. \]  

If we assume that the prefactor of $Q^2$ is constant, the transition pressure is obtained as 53.3 GPa from the fit using Eq. (30). This agrees well with that obtained in Sec. IV A (53.3 GPa).

**V. CONCLUSIONS**

We studied the pseudoproper ferroelastic phase transition of stishovite using first-principles calculations in conjunction with the Landau free-energy expansion. Various phenomena related to the transition, the characteristic behaviors of the $B_{1g}$ and $A_2$ phonon modes, the vanishing shear moduli, the rotation of the octahedra, the spontaneous symmetry-breaking strain and volume strain, and the excess enthalpy were systematically investigated. The physical values predicted by the first-principles calculations are well described by the Landau free-energy expansion. In some cases, the pressure-dependent parameters of the Landau free-energy expansion are required to describe the nonlinear behaviors, as pointed out in Sec. VII of Ref. 12. The present results indicate that the combination of the first-principles calculation and the Landau free-energy expansion is useful for explaining and understanding the physical phenomena of the ferroelastic phase transition.

**ACKNOWLEDGMENTS**

This work was supported by three programs from the Ministry of Education, Culture, Sports, Science and Technology of Japan: the Grants-in-Aid for Scientific Research (A), Priority Area on “atomic scale modification” (No. 474), and the global COE program.
FIRST-PRINCIPLES CALCULATIONS OF THE...

PHYSICAL REVIEW B 78, 134106 (2008)