High-pressure elasticity of stishovite and the $P4_2/mnm \Rightarrow Pnm$ phase transition

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Abstract. A Landau free energy expansion has been developed to describe the elastic constant variations of stishovite (SiO$_2$) associated with the $P4_2/mnm$ (rutile-type) $\Rightarrow$ $Pnm$ (CaCl$_2$-type) phase transition as a function of pressure. The transition appears to display classical second-order character, with an equilibrium transition pressure which is renormalized by coupling of the soft optic mode with spontaneous strain. Lattice parameter data from the literature show that the symmetry breaking strain is large, while the nonsymmetry breaking strains are small. These have been used to constrain the numerical values of the strain/order parameter coupling coefficients, which in turn have been used to constrain values for the Landau coefficients. When substituted into expressions for all the individual elastic constants, taking values for experimental and calculated values of the bare elastic constants from the literature, a clear view of the pattern of elastic constant variations is produced. Variations of $P$ and $S$ wave velocities derived from the calculated elastic constants for a second-order transition show a dip as the transition point is approached from high pressure and from low pressure but do not show a discontinuity. The velocity anomaly provides a signature for the presence of free silica in the lower mantle.

1. Introduction

The physical properties and structural evolution of SiO$_2$ at high pressures have attracted attention in the geophysical community because stishovite is produced in reactions among mantle materials and might be a component of the lower mantle. Stishovite is also a model material for deep mantle materials in general (see reviews by Cohen [1994], Hemley et al. [1994], and Stixrude et al. [1998]). The possibility of a pressure-induced tetragonal $\Rightarrow$ orthorhombic phase transition in stishovite was suggested by crystal chemical arguments [Nagel and O'Keeffe, 1971] and early, ab initio model calculations [e.g., Hemley et al., 1985; Cohen, 1987]. Experimental indications of the transition were obtained from high-pressure Raman scattering experiments [Hemley, 1987] and powder X-ray diffraction experiments [Tsuchida and Yagi, 1989]. The transition occurs in the vicinity of 50 GPa at room temperature and has now been investigated from both theoretical [Cohen, 1992; Matsui and Isunyuki, 1992; Yamada et al., 1992; Lacks and Gordon, 1993; Lee and Gonze, 1995; Karki et al., 1997a, b; Teter et al., 1998] and experimental perspectives [Tsuchida and Yagi, 1989; Hemley et al., 1994; Kingma et al., 1995, 1996; Andraouit et al., 1998]. The driving mechanism for the transition is the softening of a zone-center optic mode with $B_{1g}$ symmetry, which couples with acoustic modes to produce markedly nonlinear variations of the elastic constants [Cohen, 1992, 1994; Yamada et al., 1992; Lacks and Gordon, 1993; Lee and Gonze, 1995; Kingma et al., 1995; Karki et al., 1997a, b].

The thermodynamic character of the 50 GPa transition has not been determined definitively, but Raman data of Kingma et al. [1995], at least, are consistent with a second-order transition. Ferroelastic phase transitions of this type are expected to conform closely to the precepts of Landau theory due to the role of strain in promoting mean-field behavior (see Carpenter et al. [1998] for discussion and bibliography). As has already been discussed for stishovite [Yamada et al., 1992], Landau free energy expansions provide a convenient and practical means of relating variations of macroscopic physical properties such as strain and elasticity to each other via the order parameter [Salje, 1993; Carpenter and Salje, 1998, and references therein]. Many of the basic concepts behind this approach for phase transitions driven by changing pressure, as opposed to changing temperature, are reviewed by Carpenter [1992] and Carpenter et al. [1998].

In this paper, a Landau expansion is used to generate expressions for the pressure dependence of all the individual elastic constants, $C_{ik}$, of stishovite with increasing pressure through the phase transition. There are just enough data in the literature to permit values for most of the Landau coefficients to be determined, and the resulting parameterization provides a picture of the elastic behavior which depends largely on experimental measurements. Formal expressions for the individual elastic constants reveal the expected form of all the second-order elastic properties and provide a basis for planning more direct determinations of selected $C_{ik}$ values at high pressures or for comparing them with computer-generated model values. Possible geophysical consequences are then examined, given that the elastic anomalies of a second-order phase transition could provide a signature for pure silica if it is present in the lower mantle.
2. Landau Theory

The $P4_{2}/mmm \rightleftharpoons Pnnm$ transition in stishovite is a pseudo-proper ferroelastic transition, in the terminology of Wadsworth [1982]. Following the normal symmetry rules as set out in the tabulations of Stokes and Hatch [1988], the Landau free energy expansion for the transition is

$$G = \frac{1}{2} a (P - P_c) Q^2 + \frac{1}{4} b Q^4 + \lambda_1 (e_1 + e_2) Q^2 + \lambda_2 (e_1 - e_2) Q^2 + \lambda_3 (e_1 - e_2)^2 + \frac{1}{2} \left( C_{11} - C_{12} \right) (e_1 + e_2)^2 + \frac{1}{2} \left( C_{11} - C_{12} \right) (e_1 - e_2)^2 + C_{11} (e_1 + e_2) e_3 + \frac{1}{2} C_{35} e_3^2 + \frac{1}{2} C_{44} (e_1^2 + e_2^2) + \frac{1}{2} C_{66} e_3^2. \quad (1)$$

Here $Q$ is the driving order parameter (related to the soft optic mode), $a$ and $b$ are Landau coefficients, $P_c$ is the critical pressure, $e_1,e_2$ are spontaneous strains, $\lambda_1, \lambda_2, \lambda_3$ are strain/order parameter coupling coefficients, and $C_{ij}$ are the bare (i.e., excluding the influence of the phase transition) elastic constants. This is identical to the expansion described at length for a $422 \rightleftharpoons 222$ transition by Carpenter and Saltz [1998], except that pressure has been substituted for temperature.

A second-order phase transition would occur at $P_c^*$, where

$$P_c^* - P_c = \frac{\lambda_2^2}{\frac{1}{2} \left( C_{11} - C_{12} \right) }. \quad (2)$$

In this case the pressure dependence of the order parameter would be given by

$$Q^2 = \frac{a}{b} \left( P_c^* - P \right). \quad (3)$$

As derived from the reduced expansion

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

where the renormalized fourth-order coefficient, $b^*$, is given by

$$b^* = b \left[ \frac{\lambda_3^2 (C_{11} + C_{12}) + 2 \lambda_2^2 C_{33} - 4 \lambda_1 \lambda_2 C_{13}}{C_{11} + C_{12} - 2 C_{13}} \right]. \quad (5)$$

The strains $e_1, e_3$, and $e_6$ are strictly zero in the orthorhombic phase, while the symmetry breaking strain, $(e_1 - e_2)$, and the nonsymmetry breaking strains, $(e_1 + e_2)$ and $e_3$, vary with $Q$ as

$$e_1 - e_2 = \frac{\lambda_2}{\frac{1}{2} \left( C_{11} - C_{12} \right) } Q, \quad (6)$$

$$e_1 + e_2 = \frac{\lambda_1}{\frac{1}{2} \left( C_{11} + C_{12} \right) } Q^2, \quad (7)$$

$$e_3 = \frac{\lambda_3}{C_{33}} Q^2. \quad (8)$$

The inverse order parameter susceptibility, $\chi^{-1} = \partial^2 G / \partial Q^2$, is given by

$$\chi^{-1} = a (P - P_c) \quad (9)$$

$$\chi^{-1} = \frac{b}{b^*} \left( P_c^* - P \right) + a (P_c^* - P) \quad (10)$$

Variations of the individual elastic constants are obtained by using the standard expression [Slonczewski and Thomas, 1970]

$$C_{ik} = C_{ik}^0 - \sum_{\delta \varepsilon} \frac{\partial^2 G}{\partial e_{\delta} \partial Q} \left( \frac{\partial^2 G}{\partial \varepsilon \partial Q} \right)^{-1} \frac{\partial^2 G}{\partial e_{\delta} \partial Q}. \quad (11)$$

### Table 1. Expressions for the Elastic Constants of Stishovite

<table>
<thead>
<tr>
<th>Tetragonal Structure ($P4_{2}/mmm$)</th>
<th>Orthorhombic Structure ($Pnnm$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11} = C_{22} = C_{11}^0 \rightarrow \lambda_2^2 \chi$</td>
<td>$C_{11} = C_{11}^0 - (4\lambda_1^2 Q^2 + \lambda_3^2 + 4\lambda_1 \lambda_2 Q) \chi$</td>
</tr>
<tr>
<td>$C_{33} = C_{33}^0$</td>
<td>$C_{33} = C_{33}^0 + 4\lambda_2^2 Q \chi$</td>
</tr>
<tr>
<td>$C_{12} = C_{12}^0 \rightarrow \lambda_2^2 \chi$</td>
<td>$C_{12} = C_{12}^0 - (4\lambda_1^2 Q^2 - \lambda_2^2 \chi$</td>
</tr>
<tr>
<td>$C_{13} = C_{23} = C_{13}^0$</td>
<td>$C_{13} = C_{13}^0 - (4\lambda_1 \lambda_2 Q^2 + 2\lambda_2 \lambda_3 Q) \chi$</td>
</tr>
<tr>
<td>$C_{11} - C_{12} = (C_{11}^0 - C_{12}^0) - 2\lambda_2^2 \chi$</td>
<td>$C_{11} - C_{12} = (C_{11}^0 - C_{12}^0) - (2\lambda_2^2 + 4\lambda_1 \lambda_2 Q) \chi$</td>
</tr>
<tr>
<td>$C_{11} + C_{12} = C_{11}^0 + C_{12}^0$</td>
<td>$C_{11} + C_{12} = (C_{11}^0 + C_{12}^0) - (8\lambda_1^2 Q^2 + 4\lambda_1 \lambda_2 Q) \chi$</td>
</tr>
<tr>
<td>$C_{66} = C_{66}^0$</td>
<td>$C_{66} = C_{66}^0 + 2\lambda_4 Q$</td>
</tr>
<tr>
<td>$C_{44} = C_{55} = C_{44}^0$</td>
<td>$C_{44} = C_{44}^0 + 2\lambda_4 Q$</td>
</tr>
<tr>
<td>$C_{55} = C_{55}^0 - 2\lambda_4 Q$</td>
<td>$C_{55} = C_{55}^0 - 2\lambda_4 Q$</td>
</tr>
<tr>
<td>$C_{66} = C_{66}^0 + 2\lambda_6 Q^2$</td>
<td>$C_{66} = C_{66}^0 + 2\lambda_6 Q^2$</td>
</tr>
</tbody>
</table>
Expressions for all the elastic constants obtained by applying (11) to (1) are listed in Table 1. A convenient expression for the critical elastic constant combination \((C_{11} - C_{12})\) in the tetragonal phase may also easily be derived [Fei et al., 1982; Knorr et al., 1986; Carpenter and Salje, 1998] as

\[
(C_{11} - C_{12}) = (C_{44}^0 - C_{12}^0) \left( \frac{P - P_c^e}{P - P_c^*} \right)
\]  

(12)

In the following sections, values for the various coefficients in these equations are determined using experimental data for variations in frequency of the soft mode [Kingma et al., 1995], experimental values of the elastic constants at room pressure and temperature [Weidner et al., 1982], calculated values of the bare elastic constants at high pressures [Karki et al., 1997a], and variations of lattice parameters with pressure through the transition [Andraud et al., 1998]. When dealing with purely elastic effects, it is usual to quote \(C_{44}^0\) values in GPa. These units can be propagated through most of the above equations so that values of the coupling coefficients \(\lambda\) and of the Landau \(b^*\) coefficients are also given in GPa. The Landau \(a\) coefficient is then a dimensionless quantity. Given that 1 Pa = 1 J m\(^{-3}\), it is necessary to multiply through by the molar volume, in m\(^3\) mol\(^{-1}\), when the excess energy is required in J mol\(^{-1}\) rather than joules per unit of volume. Values of \(C_{11}\) and \(a\) are then in J mol\(^{-1}\) and the \(b^*\) coefficient has units of volume.

3. Soft Mode

The soft mode data of Kingma et al. [1995] can be used to determine the value of \((P_c^* - P_c^e)\) as well as to provide some constraints on the possible magnitudes of the nonsymmetry breaking strains. The square of the soft mode frequency is expected to vary linearly with the inverse susceptibility, \(\chi^{-1}\) [see, e.g., Bruce and Cowley, 1981; Dove, 1993], and the Raman data have therefore been plotted as \(\omega^2\) against pressure (Figure 1). For the high-symmetry phase this means that \(\omega^2\) is expected to go linearly to zero at the critical pressure, \(P_c\). A linear fit to the data in Figure 1 gives \(P_c = 102.3\) GPa. For the low-symmetry phase, \(\omega^2\) is expected to recover with a slope which, for a classical second-order transition, should be a factor of 2 greater than the slope of \(\omega^2\) for the high-symmetry phase. From (9) and (10), however, if there is a nonsymmetry breaking strain contributing to renormalization of the fourth-order Landau coefficient and the response of the crystal to changes in \(Q\) (the soft mode) is fast relative to the time required for changes in strain, the ratio of slopes is \(1:2(b^*h^*)\) rather than 1:2. The experimental data yield 1.277, which gives \((b^*h^*) = 1.135\) as \(P \rightarrow P_c^*\). Since \((h^* - b^*)\) depends on the coupling coefficients for the nonsymmetry breaking strains (equation 5), this experimental ratio restricts the range of values permitted for \(\lambda^1\) and \(\lambda_3\), as discussed in section 5. Finally, the trends of \(\omega^2\) for the high-symmetry and low-symmetry phases should meet at the transition pressure, \(P_c^*\). The linear fit in Figure 1 give \(P_c^* = 51.6\) GPa and hence \((P_c^* - P_c^e) = 50.7\) GPa.

4. Bare Elastic Constants

Landau free energy expansions give excess thermodynamic quantities with respect to the properties of the reference (high-symmetry) structure. Thus, as explained in detail by Carpenter and Salje [1998], the bare elastic constants, \(C_{ij}^0\), in (1) refer to the elastic properties of \(P4_2/mnm\) stishovite. For phase transitions which occur in response to changing temperature, it is usually assumed implicitly that the bare elastic constants are independent of temperature to a first approximation. For transitions which occur in response to changing pressure, such an assumption is untenable because of the large changes in elastic properties which occur even in the absence of a phase transition. In the present case, the absolute values and pressure dependences of \(C_{11}^0\), \(C_{12}^0\), \(C_{22}^0\), and \(C_{66}^0\) have been taken from the values calculated at a range of pressures for tetragonal stishovite by Karki et al. [1997a]. These are given in Table 2, and a linear pressure dependence on pressure has been assumed in each case.

The combination of elastic constants \((C_{11} - C_{12})\) has the symmetry properties of the active representation for the phase transition (see Carpenter and Salje [1998] for background information). As a consequence, both the experimental [Weidner et al., 1982] and calculated [Karki et al., 1997a] values of \(C_{11}\) and \(C_{12}\) for the tetragonal form include the influence of the \(P4_2/mnm = Pnm\) phase transition. By substitution in (12), with \(P_c^e = 49\) GPa (see below) and \((P_c^* - P_c^e) = 50.7\) GPa (from above), setting \((C_{11}^0 - C_{12}^0) = 742\) GPa at room pressure and temperature [Weidner et al., 1982] gives \((C_{11}^0 - C_{12}^0) = 492\) GPa. Because \(C_{11}^0\) and \(C_{12}^0\) should have approximately the same positive slope with increasing pressure, \((C_{11}^0 - C_{12}^0)\) has been assumed to be independent of pressure for the present calculations. By way of contrast, \((C_{11} + C_{12})\) has the symmetry properties of the identity representation and is not normally expected to show deviations from \((C_{11}^0 + C_{12}^0)\) in the high-symmetry phase. The values calculated for \(C_{11}\) and \(C_{12}\) by Karki et al. [1997a] have therefore been summed to give the evolution of \((C_{11}^0 + C_{12}^0)\) as 664 + 10.76\(\Delta P\) GPa. Combining \((C_{11} - C_{12})^0\) and \((C_{11} + C_{12})\) gives the evolution of \(C_{11}^0\) and \(C_{12}^0\) specified in Table 2.

[Figure 1: Variation of frequency squared for the soft optic mode through the tetragonal = orthorhombic transition (data from Kingma et al. [1995]). Straight lines through the data intersect at \(P_c^e = 51.6\) GPa; the straight line for tetragonal stishovite extrapolates to zero at \(P_c = 102.3\) GPa. A dashed line for the orthorhombic phase includes the pressure dependence of \(b^*\) but is barely distinguishable from the straight line fit to the data (solid line).]
5. Strain Analysis

The spontaneous strains $e_1, e_3$ are defined in the usual way for a tetragonal $\rightarrow$ orthorhombic transition as

$$e_1 = \frac{a_a - a_o}{a_o}$$

$$e_2 = \frac{b_a - a_o}{a_o}$$

$$e_3 = \frac{c - c_o}{c_o}.$$  \hspace{1cm} (15)

Here, $a, b, c$ are lattice parameters of the orthorhombic phase, while $a_o$ and $c_o$ are the lattice parameters of the tetragonal phase extrapolated into the stability field of the orthorhombic phase. The symmetry-breaking strain is

$$\left(e_1 - e_2\right) = \frac{a - b}{a_o}.$$  \hspace{1cm} (16)

If the nonsymmetry breaking strain ($e_1 + e_2$) is small, the value of the reference parameter $a_o$ can be approximated by

$$a_o = (a \times b)^{0.5}.$$  \hspace{1cm} (17)

The volume strain is given by

$$V_s = V - V_o,$$  \hspace{1cm} (18)

where $V$ is the unit cell volume of the orthorhombic phase and $V_o$ is the volume of the tetragonal phase extrapolated into the orthorhombic stability field. For small strains, $V_s, e_1, e_2,$ and $e_3$ are related to a good approximation by

$$V_s = e_1 + e_2 + e_3.$$  \hspace{1cm} (19)

The high-pressure lattice parameters of Ross et al. [1990], Hemley et al. [1994], Mao et al. [1994], and Andrault et al. [1998] are reproduced in Figure 2a, to which have been added the values of $a_o$ calculated according to (17) for the data of Andrault et al. The symmetry breaking strain has then been calculated using (16) and these values of the reference parameter. As shown in Figure 3, $(e_1 - e_2)^2$ ($\sim Q^2$) is a linear function of pressure between -60 and -100 GPa, which is consistent with the transition being second order in character. Linear extrapolation of the straight line in Figure 3 to zero strain gives a transition pressure, $P_s^*$, of 49.0 GPa. Two data points, at 33.2 and 54.8 GPa, fall below the straight line and, according to Andrault et al., lie within the stability field of the tetragonal phase. However, the strains would be small this close to the transition pressure and, depending on the resolution of the diffractometer used, might give broadening of X-ray diffraction maxima rather than discrete splitting, which could easily be overlooked. In terms of the experimental uncertainties the transition pressures from the soft mode data of Kingma et al. [1995] and from the lattice parameter data of Andrault et al. [1998] are not distinguishable. For internal consistency with the strain calculations the value of 49 GPa has been used for calculations of the elastic constants below.

Real behavior in the close vicinity of the transition point may need further clarification in the light of observations of hysteresis in single-crystal X-ray diffraction measurements [Mao et al., 1994; Hemley et al., (Strain-order parameter coupling in the pressure-induced ferroelastic transition in dense SiO$_2$, submitted to Physical Review Letters, 1999, hereinafter referred to as Hemley et al. (submitted manuscript, 1999))], which indicated that the transition occurred near 58 GPa on
Table 2. Values of Bare Elastic Constants, Transition Pressure, Coupling Coefficients and Landau Coefficients Used to Calculate the Elastic Constants of Stishovite shown in Figure 4

<table>
<thead>
<tr>
<th>Bare Elastic Constants</th>
<th>Landau Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{11} = 578 + 5.38P</td>
<td>P_2^e = 49.0</td>
</tr>
<tr>
<td>C_{12} = 776 + 4.94P</td>
<td>(P_2 - P_1^e) = 50.7</td>
</tr>
<tr>
<td>C_{44} = 86 + 5.38P</td>
<td>\lambda_1 = -8</td>
</tr>
<tr>
<td>C_{55} = 191 + 2.72P</td>
<td>\lambda_2 = 24.62</td>
</tr>
<tr>
<td>C_{11} - C_{12} = 492</td>
<td>\lambda_3 = 17</td>
</tr>
<tr>
<td>C_{44} = 232 + 1.88P</td>
<td>a = -0.04836</td>
</tr>
<tr>
<td>C_{66} = 323 + 3.10P</td>
<td>b = 10.94</td>
</tr>
</tbody>
</table>

All values are given in units of GPa except for a, which is dimensionless.

Compression but near 40 GPa on decompression. Calculated values of \((e_1 - e_2)^2\) from these data have been added to Figure 3 to show the discrepancy.

When describing phase transitions which occur in response to changing temperature, the order parameter is defined as having the value 1 at 0 K. No such limit occurs when pressure is the externally applied variable, and it is a matter of arbitrary choice as to the absolute values assigned to the order parameter. In this case, \(Q = 0.5\) has been chosen for \(P = 100\) GPa; \(Q = 0\) for the high-symmetry phase in the normal manner from the linear fit in Figure 5. \((e_1 - e_2) = -0.050\), which, by inserting \(Q = 0.5\) and \((C_{11} - C_{12}) = 492\) GPa into (6), gives \(\lambda_2 = 24.62\) GPa. From (2), \(a = -0.04856\) is then also obtained. (Note that values of the coefficients are quoted to four significant figures in order to avoid rounding errors and not to imply that they are known to anything like this precision.)

Variations of the c lattice parameter and unit cell volume, \(V_c\), are reproduced in Figures 2b and 2c. The data are not sufficiently precise to indicate whether there is any \(e_3\) strain or excess volume associated with the transition. The calculations of Karki et al. [1997b] suggest that a small reduction of the c parameter occurs in the orthorhombic phase, however, and a small difference between \(c\) and \(c_0\) has therefore been assumed here (\(e_3\) small and negative). It has also been assumed that the volume strain is close to zero, which requires that there is a small and positive strain \((e_1 + e_2)\). Trial values of \(\lambda_1\) and \(\lambda_3\) were propagated in order to find some combination which yielded a symmetry breaking strain which is small but large enough to give \((b/b^*) = 1.135\) at the transition point. From (3), \(b^* = 9.906\) GPa at \(P = 100\) GPa using parameters listed in Table 2, and it was found that \(\lambda_3 = -8\) GPa. \(\lambda_1 = 17\) GPa give the required value of \((b/b^* = 1.6)\) at \(P = P_1^e\). This implies \(b = 10.94\) GPa.

The chosen values of \(\lambda_1\) and \(\lambda_3\) do not represent a unique solution, but they do allow the form of the elastic constants, \(C_{11}, C_{22}, \text{and } C_{33}\) to be displayed (below). At 120 GPa they give \(e_1 = -0.004, (e_1 + e_2) = 0.003, \text{and } V_c = -0.001\). Back-calculation using (13), (14), (15), and (18) and the measured values of the lattice parameters \(a, b, \text{and } c\) yields values for the reference parameters \(a^*, b^*, \text{and } V^*\). These have been added to Figure 2, and it is apparent that such small deviations are at least compatible with the available data given the experimental scatter. A significant increase in resolution of the data will be needed to extract values of the strain coupling coefficients with any more confidence. Finally, the \((e_1 - e_2)^2\) strains were recalculated with the new values of \(a^*\), but the difference from assuming that (17) applies is negligible (Figure 3).

6. Variations of the Elastic Constants

Once values for all the coefficients and bare elastic constants in (1) have been determined, it is only a matter of substituting them into the equations for the individual elastic constants, given in Table 1, to predict the overall elastic behavior of stishovite through the tetragonal = orthorhombic transition. It is worth noting that none of the experimental data discussed above yield values for the coefficients \(\lambda_4\) and \(\lambda_5\), however. In order simply to show the general trends that \(C_{11}, C_{22}, \text{and } C_{66}\) are expected to follow in orthorhombic stishovite, these coupling coefficients have been set arbitrarily to 20 GPa. The resulting variations are all shown in Figure 4. \((C_{11} - C_{12})\) of the tetragonal phase and \(0.5(C_{11} + C_{22} - 2C_{12})\) of the orthorhombic phase both tend to zero in a nonlinear manner as the transition point is approached. \(C_{11} \text{ and } C_{12}\) of the tetragonal phase are individually influenced by the phase transition, as are all the

![Figure 3. Variation of the square of the symmetry breaking strain with pressure. Circles represent strains calculated using the definition of \(a^*\) given by (17) and the data of Andraulf et al. [1998]; crosses represent strains calculated using the alternative variation of \(a^*\) shown by crosses in Figure 2a. The solid straight line is a fit to the data between 60 and 95 GPa, excluding the outlying point at \(\approx 70\) GPa. The extrapolation of this line to zero gives \(P_1^e = \approx 49\) GPa. The dashed line is the calculated variation of \((e_1 - e_2)^2\) using (5) to define \(b^*\). Open squares are from single-crystal X-ray diffraction data [Maw et al., 1994; Hemley et al. (submitted manuscript, 1999)]; D designates measurements of the orthorhombic phase made during decompression.](image-url)
7. Discussion of the Elastic Behavior

The elastic constants for tetragonal stishovite shown in Figure 4 vary in a closely similar manner to the variations calculated by Karki et al. [1997a]. This is in line with the expectation given that the present calculations made use of their results in order to specify the values and pressure dependence of the bare elastic constants. The results for orthorhombic stishovite are different, however. Karki et al. chose orthorhombic parameters with \( a > b \), whereas Andraut et al. [1998] chose \( a < b \), with the consequence that \( C_{11} \) and \( C_{22} \), \( C_{13} \) and \( C_{23} \), and \( C_{44} \) and \( C_{55} \) should be interchanged for a direct comparison of Figure 1 of Karki et al. with Figure 4 of the present study. More significantly, \( 0.5(\bar{C}_{11} + \bar{C}_{22} - 2\bar{C}_{12}) \) is shown here as tending to zero as the transition point is approached from the high-pressure side, whereas the values of Karki et al. show a.

![Figure 4](image1)

**Figure 4.** Variations of the elastic constants given by the expressions in Table 1 and values of the coefficients and bare elastic constants from Table 2.

elastic constants of the orthorhombic phase. Their patterns of evolution follow inevitably from the way that the order parameter for the transition varies with pressure, as well as from the nature and strength of coupling between the order parameter and the spontaneous strains.

Reuss and Voigt bounds and the average of the two for the bulk and shear moduli, \( G \) and \( K \), of a polycrystalline stishovite aggregate have been calculated by substituting the individual \( C_{ij} \) values obtained here into the standard equations listed by Watt [1979]. They are shown in Figure 5a. The Reuss/Voigt averages have then been used to calculate \( P \) and \( S \) wave velocities as a function of pressure through the transition with the usual relationships, taken in this case from Karki et al. [1997a],

\[
V_p = \sqrt{\frac{K + \frac{4}{3}G}{\rho}}
\]

and

\[
V_s = \sqrt{\frac{G}{\rho}}
\]

The density \( \rho \) was calculated using the lattice parameter data of Andraut et al. [1998], and the resulting variations are shown in Figure 5b. Experimental data for \( V_p \) and \( V_s \) measured by Li et al. [1996] at room pressure and at 3 GPa are also shown in Figure 5b. They are ~2% lower than the calculated values. The values of \( G \), \( V_p \), and \( V_s \) from the Reuss/Voigt average all vary continuously through the transition but have a marked softening as the transition point is approached from both the low-pressure and the high-pressure side. The bulk modulus is influenced by the transition to only a very limited extent.

![Figure 5](image2)

**Figure 5.** Variations of bulk properties derived from variations of the individual elastic constants: (a) Bulk modulus \( K \) and shear modulus \( G \). Solid lines are the average of Reuss and Voigt limits; the latter are shown as dotted lines (Voigt limit > Reuss limit). (b) Velocities of (top) \( P \) and (lower) \( S \) waves through a polycrystalline aggregate of stishovite. Circles indicate experimental values obtained by Li et al. [1996] at room pressure and 3 GPa.
discontinuity at $P = P_c^*$. This is then reflected in the continuous evolution shown for acoustic velocities in Figure 5, in comparison with the discontinuity at the transition point shown by Karki et al. The approaches adopted in the two studies are quite different, of course, though the pattern presented here is that of a classical second order phase transition such as has been observed in other materials (e.g., LaP$_2$O$_{14}$ [Errandonea, 1980]). The existence of fluctuations in the vicinity of the transition point, as proposed for example by Yamada et al. [1992], would modify the evolution of elastic properties over a narrow pressure interval about $P_c^*$.

Allowing the bare elastic constants to have a more or less realistic pressure dependence has a few interesting consequences which make the evolution of the order parameter through a pressure-driven phase transition subtly different from what occurs when the transition is caused by changing temperature. The renormalized fourth-order Landau coefficient $b^*$ becomes pressure-dependent once the bare elastic constants are given a pressure dependence (equation (5)). This means that $Q^*$ for a second-order transition is not expected to be exactly linear with pressure in the low-symmetry phase (equation (3)). The linear relationship between $Q$ and the symmetry breaking strain is still expected to apply, however, which means that $(e_1 - e_2)^2$ is itself not expected to vary linearly with pressure. Values of $(e_1 - e_2)^2$ propagated on the basis of the calculated (nonlinear) pressure dependence of $Q^*$ together with the extracted coupling constant, $\lambda_\omega$, and bare elastic constant, $(C_{11}^0 - C_{12}^0)$, have been added to Figure 3 to show that a slightly better representation of the experimental observations at the highest pressures is indeed obtained.

The order parameter susceptibility in the orthorhombic phase (equation (10)) will also have some nonlinearity derived from the pressure dependence of $b^*$. This means that $Q^*$ of the soft mode should recover nonlinearly in the orthorhombic phase. The dashed line above $P_c^*$ in Figure 1 includes this nonlinearity, but the effect is barely detectable over the limited pressure range for which data are available.

Finally, the Landau free energy expansion (equation (1)) gives excess energy as a function of pressure once the coefficients have been determined. Using the values of all the parameters listed in Table 2 yields the excess energy in units of J m$^{-3}$; to convert to J mol$^{-1}$, it is necessary to multiply through by the molar volume of the reference tetragonal state (i.e., using $V_o$). The total excess free energy calculated in this way is shown in Figure 6; it is much smaller than the excess energy given in Figure 4 of Karki et al. [1997b] and ~25% smaller than the excess energy given by Teter et al. [1998].

At worst, the elastic constant variations shown in Figure 4 should at least show the correct general pattern of variations to be expected in stishovite as pressure is increased through the phase transition. At best, the numerical values should be realistic, though the real uncertainties are not easy to evaluate. In principle, the uncertainties are merely those propagated from the experimental determinations of the quantities $C_{ij}^0$, $\epsilon_1^e$, $\epsilon_2^e$, $P_c^*$, and $P_a^*$ (together with $\lambda_\omega$ and $\lambda_\phi$, if these had been determined). Whichever point of view is preferred, the present approach generates explicit functions which can be tested by further experiments or model calculations.

8. Attenuation

In addition to the elastic anomalies described in this paper, materials undergoing a thermodynamically continuous phase transition can display strong attenuation of acoustic waves. Experimental measurements would be needed to quantify the attenuation likely to occur in a polycrystalline aggregate of stishovite held at pressures and temperatures close to the transition point, but some general features can be anticipated. If an acoustic wave propagated through a single crystal of stishovite with its wavevector parallel to the crystallographic [110] direction and displacement vector parallel to [110], the attenuation, $\alpha_\omega$, would be expected to follow a mean-field relationship of the form [Schwabl, 1985; Schwabl and Tauber, 1996]

$$\alpha_\omega \propto \frac{\omega^2}{(T - T_c)^{5/2}}$$

where $\omega_\omega$ is the frequency of the acoustic wave, $T$ is temperature, and $T_c$ would be the transition temperature. Thus, approaching the transition temperature and at the transition point itself, there would be a large attenuation. The temperature interval over which this would occur requires experimental determination, but in the case of some perovskites, attenuation effects following this type of expression (though with different critical exponent) at $T > T_c$ are restricted to a range of the order of or less than ~1 K [e.g., Deorani et al., 1990; Holt and Fossheim, 1981]. Again, experimental data are needed to convert the temperature interval of strong attenuation into a pressure interval, but an equivalently narrow range would be expected. For a polycrystalline aggregate, only those components of an acoustic wave which are resolved into components with $B_1$ symmetry in individual crystals would be attenuated in the manner described by (22). At low acoustic frequencies, such as in the Hertz range, the presence of transformation twins in orthorhombic crystals would result in an additional attenuation. In this case, any acoustic wave, whether longitudinal or transverse, which could cause some displacement of a twin boundary would be attenuated. This effect is less well documented but would be expected to dominate in a small pressure and temperature interval below the transition point where a more or less stable transformation microstructure should occur. In both cases, the extent of
transformation-related attenuation effects in the mantle would, of course, depend on the amount of any stishovite present.

9. Geophysical Implications

We now examine a few of the potential geophysical implications of the above results. The silica content of the mantle has long been central to the question of the composition of the bulk Earth, including the issue of global chemical homogeneity versus heterogeneity of the mantle, both radially (i.e., as a function of depth through the upper and lower mantle) and laterally within this region [see Hemley, 1998]. The existence of free silica would have consequences for a number of geophysical and geochemical questions relating to large-scale structure, dynamics, and thermal state. It is widely accepted on the basis of numerous experimental studies that the lower mantle is composed of (Mg,Fe)SiO₃-perovskite and (Mg,Fe)O-dominated assemblages [Rina, 1998]. Analysis of seismic data for the lower mantle in terms of measured thermoelastic properties of the constituent phases has placed bounds on possible enrichment of silica (in combination with iron) relative to the upper mantle, for example, at the 670-km discontinuity in combination with the formation of (Mg,Fe)SiO₃ perovskite [Jeanloz and Knittle, 1989; Bina and Silver, 1990; Siderude et al., 1992; Fiquet et al., 1998; Bina, 1998]. A recently proposed model for a change in composition at greater depth attempts to satisfy geodynamic, seismological, and mineral thermoelastic considerations as well as the apparent need for isolated geothermal reservoirs [Kellogg et al., 1999; van der Hilst and Karnaon, 1999]. In all such analyses the higher intrinsic density of silica- and iron-enriched assemblages is offset by higher temperatures [e.g., see Siderude et al., 1994]. Enrichment of silica could occur locally (i.e., chemical heterogeneity) and could include the formation of free silica, which may be produced in chemical reactions in the mantle, including those at the core-mantle boundary and D" [Knittle and Jeanloz, 1991; Goarant et al., 1992, Jeanloz and Williams, 1998].

Experiments have established that stishovite is the stable phase of silica at upper to mid-lower mantle pressures. The high sound velocity of stishovite relative to seismic profiles [Weidner et al., 1982] has been taken in part as evidence for the lack of abundant free silica in the lower mantle [e.g., Bina, 1998]. Although there is evidence for hysteresis in the transition pressure, there is no measurable volume discontinuity at the transition, and the equation of state is smooth (negligible change in bulk modulus as discussed above) [Mao et al., 1994, Andraut et al., 1998]. On the other hand, the anomalous softening of both Vp and Vs in the vicinity of the transition complicates, if not invalidates, extrapolations from low pressure. Moreover, the elastic anomaly in stishovite could, in principle, be used as an indicator of the presence of free silica at depth. The velocity anomaly associated with the transition would occur over a depth range of perhaps <50 km, and, moreover, the transition is expected to give rise to a large attenuation.

A pressure of 50 GPa is equivalent to ~1200 km depth. The temperature dependence of the transition has not been measured, but lattice dynamics calculations that reproduce the measured vibrational spectrum predict a weak, positive temperature dependence of the transition pressure (d<TidP> ~ 250 K GPa⁻¹) [Kingma et al., 1993]. This gives a transition pressure of near 60 GPa and a depth of 1500 km at expected lower mantle temperatures of 2000-2500 K. Given the uncertainties in the calculations, seismic structure within the mid-lower mantle (e.g., 1000-1600 km) should be examined. Notably, there is evidence for seismic structure in this depth range [Johnson, 1969; Vinnik et al., 1972; Kawakatsu and Niu, 1994; Le Stoff et al., 1995; Kaneshima and Hellfrich, 1999]. In particular, Le Stoff et al. [1995] report global seismic reflectors at 1200 km. A low-velocity anomaly has recently been reported at 1400-1600 km depth, it has been interpreted as evidence for subducted oceanic crust (chemical heterogeneity) in the lower mantle [Kaneshima and Hellfrich, 1999]. The depth range and thickness of the layer parallel the characteristic properties of the stishovite transition; this suggests that the role of silica should be considered in the interpretation of these results.

Free silica can also form from the breakdown of silicate perovskites within the lower mantle. Experimental reports of the transition in (Mg,Fe)SiO₃ at mid-lower mantle pressures have been controversial. A transition has been reported at ~60 GPa at high temperature [Sasea et al., 1996], which is also close to the phase boundary for the stishovite transformation. Recent studies indicate that silicate perovskite is stable over a wide range of P-T conditions within the lower mantle [Mao et al., 1997; Kesson et al., 1998; Serghio et al., 1998]. The lack of a volume discontinuity for the stishovite transition precludes density as a driving force for the breakdown of perovskite. Moreover, recent experimental data indicate that the solubility of iron in MgSiO₃ increases with increasing pressure and temperature, indicating enhanced stability of perovskite relative to the oxides. On the other hand, there is evidence for the formation of free silica from chemical reactions between perovskite assemblages and iron metal under conditions approaching those of the core-mantle boundary [Knittle and Jeanloz, 1991; Goarant et al., 1997; Jeanloz and Williams, 1998]. Higher-pressure transitions in silica are predicted to occur at these depths (i.e., above 80 GPa) [Karki et al., 1997a, b; Teter et al., 1998]. There is some experimental evidence for such transitions [Dubrovinsky et al., 1997], but other data indicate the persistence of the Pnmm structure to at least 120 GPa [Andraut et al., 1998]. Such transitions are predicted to involve a volume discontinuity and thus destabilize the silicate perovskite. Whether or not these transitions occur and can serve as a diagnostic of silica within D" (e.g., in ultralow velocity zones) remains to be determined.

Notation

- a, b, c lattice parameters of the orthorhombic phase when used in strain equations.
- a, b Landau coefficients when used in Landau expansions.
- a₀, c₀ lattice parameters of the tetragonal phase extrapolated into the stability field of the orthorhombic phase.
- b* renormalized fourth-order Landau coefficient.
- Cᵦ elastic constants, as modified by the phase transition.
- Cᵦ² bare elastic constants, excluding the influence of the phase transition.
- χ⁻¹ inverse susceptibility.
- e₁, e₂ spontaneous strains, in Voigt notation.
- G excess free energy when used in Landau expansion.
- K shear modulus.
- bulk modulus.
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References


Nagel, L., and M. O’Keefe, Pressure and stress induced polymorphism.


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