Pressure-induced phase transition in cristobalite: An X-ray powder diffraction study to 4.4 GPa

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ABSTRACT

The structural behavior of cristobalite, SiO₂, has been studied under hydrostatic conditions in a diamond-anvil cell to 4.4 GPa, using high-resolution synchrotron X-ray powder diffraction. On increasing pressure, we observed a phase transition at $P_c \sim 1.5$ GPa, characterized by the onset of twinning and the splitting of powder diffraction lines. This transition is reversible and first-order in character. The high-pressure phase, referred to here as cristobalite II, can be indexed according to a monoclinic unit cell with $a = 9.124(5)$, $b = 4.625(3)$, $c = 8.394(5)$ Å, $\beta = 124.91(5)^\circ$, and $V = 290.5(2)$ Å³ at $P = 3.1$ GPa. The transition from tetragonal α cristobalite to monoclinic cristobalite II involves a doubling of the unit-cell size and must therefore be induced by a zone-boundary instability. The resulting components of the spontaneous strain tensor are analyzed in terms of the change in point group symmetry from 422 to 2 and of coupling with the macroscopic order parameter. There is a significant non-symmetry-breaking (volume) strain. The actual symmetry-breaking process is a shear parallel to [011] in the tetragonal (101) planes, corresponding to slip on the {111} tetrahedral sheets of the high-$T$ cubic $\beta$-cristobalite phase.

INTRODUCTION

The phase transition behavior of framework silicate minerals has been the subject of major interest in recent years. The concomitant development of mean-field theories of phase transition behavior, microscopic computer modeling, and new experimental techniques probing a range of length scales and dynamical phenomena has facilitated a profound reevaluation of structural behavior in complex silicates. Many common rock-forming aluminosilicates exhibit diverse structural behavior with changing temperature (and presumably also with changing pressure), such as cation order-disorder processes (e.g., Al-Si), and elastic instabilities that lead to displacive phase transitions. The coupling between individual order parameters, often by means of a common lattice strain, can make the overall behavior very complex.

One way in which the resulting behavior can be rationalized is by comparison with well-characterized model systems, which exemplify particular aspects of structural behavior. Many phase transitions involve distortions of the aluminosilicate framework. Attention has therefore been focused on similar distortions observed in the tetrahedral framework structures of pure SiO₂ polymorphs in the absence of cation ordering effects, cation mobility, etc. The expectation is that these phases are most likely to epitomize the intrinsic behavior of SiO₂ linkages.

Cristobalite is a high-temperature polymorph of SiO₂, generally associated with the late stages of crystallization in volcanic rocks. In common with tridymite (with which it is often associated in nature), cristobalite is metastable under standard conditions, the expected reconstructive transformation to the equilibrium polymorph, quartz, being kinetically hindered. The crystal structure of cristobalite comprises a three-dimensional network of corner-sharing SiO₄ tetrahedra. Each O atom is a bridging O atom, and so the structure is a fully polymerized tetrahedral framework. The SiO₄ tetrahedra are arrayed in six-membered rings, within close-packed layers, stacked parallel to [111], with three-layer, ABCABC... repeat. (This idealized cubic structure is analogous to that of diamond, with the C-C bond replaced by Si-O-Si.)

At high temperatures cristobalite shows macroscopic cubic symmetry, and an aristotype structure of space group $Fd\bar{3}m$ is inferred, although the microscopic nature of this phase is the subject of some debate (Wright and Leadbetter, 1975; Hatch and Ghose, 1991; Schmahl et al., 1992; Swainson, 1992). On decreasing temperature there is a first-order displacive phase transition to a tetragonal form with space group $P4_2_2_2$. This phase transition involves a large spontaneous strain ($\sim 4\%$), which can cause some single crystals to fracture (Schmahl et al., 1992). Recent theoretical analysis (Swainson, 1992; Dove et al., 1992; Giddy et al., 1993) suggests that this phase transition is due to the condensation of a low-lying rigid-unit mode.

Early evidence for an additional structural phase transition, occurring at high pressures, came from unpub-
lished Raman spectroscopy experiments (Russell Hem-
ley, personal communication), which showed the splitting of
certain modes above \( P \sim 2.0 \) GPa. These findings were
confirmed by later, more detailed Raman spectroscopy
experiments (Palmer et al., 1991). The first direct evidence
for a structural phase transition was reported by
Yeganeh-Haeri et al. (1990), who used energy-dispersive
X-ray diffraction on a powdered sample in a large-vol-
ume press. They observed the splitting of certain diffraction
lines at \( P \sim 1.0 \) GPa, which suggested a phase transi-
tion to a new phase with lower symmetry. The authors
noted that the phase transition appeared to be second-
order and nonquenchable but were unable to index the
high-pressure phase. This low-pressure phase transition
was not detected in another diffraction study on cristo-
balite (Tsuchida and Yagi, 1990), which nevertheless
managed to uncover two other phase transitions at the
higher pressures of 10 and 30–40 GPa. Again, the nature
of the high-pressure phases remained a mystery.

Our own study is part of a long-term investigation con-
cerned with the pressure dependence of structural behavior
in tectosilicates. We focus on the low-pressure phase
transition in cristobalite to illuminate possible framework
distortions that may occur in other, commonly oc-
curring tectosilicates at moderate pressures.

**Experimental**

The sample used for this work is cristobalite from the
Ellora Caves, near Hyderabad, India (Harvard Mineral-
ological Museum, no. 97849), and is described by Van Val-
kenburg and Buie (1945) and Wolfe (1945). The crystals
formed in a hydrothermal vein, nucleating on fibers of
the zeolite mordenite. Most of the cristobalite crystals are
gem-quality octahedra, about 0.5 mm in diameter, some
with interpenetrant growth twins. In addition, the crystals
are very heavily twinned on a microscopic scale, presum-
ably as a result of the cubic-tetragonal phase transition at
\( T_c \sim 220 \) °C. The same sample has been used in a num-
er of other studies (Dollase, 1965; Peacock, 1973; Yeganeh-
Haeri et al., 1992; Downs and Palmer, 1994).

For these experiments, a single cristobalite octahedron
was crushed to a fine powder, and transferred to Merrill-
Bassett-type diamond-anvil cell. We used an Inconel al-
loy gasket, between opposing diamond crystals with 600-
µm culets. A 4:1 methanol to ethanol mixture was the
hydrostatic pressure medium. Pressure calibration was
achieved by measuring the laser-induced fluorescence of
tiny ruby chips scattered throughout the sample chamber
and correlating it with the ruby pressure scale of Mao et
al. (1978). Because of the relatively low pressures in this
study, we put great emphasis on trying to ensure a con-
sistent and relatively accurate pressure calibration. Ruby
fluorescence spectra were fitted using least-squares profile
refinement, with Lorentzian functions for the R1 and R2
peaks. Absolute calibration was achieved with reference
to a ruby 1-atm standard, measured in an identical man-
ner to the sample at pressure. In these experiments, pres-
sure gradients were all less than the experimental preci-
sion of \( \pm 0.5 \) kbar.

Synchrotron X-ray diffraction experiments were car-
ried out at beam line X7A of the National Synchrotron
Light Source, Brookhaven National Laboratory, New
York. Monochromatic X-radiation of wavelength \( \lambda \sim 0.7 \)
Å was selected with a curved, asymmetrically cut Si(111)
or Ge(111) monochromator crystal. The diamond-anvil cell
was mounted with its axis parallel to the incident
X-rays, and this orientation was maintained throughout
the experiment. The scattered X-rays were measured by
scanning a detector through 2\( \theta \). Two types of detectors
were used during this work: a conventional, single-chan-
nel Kevex detector and a linear position-sensitive detect-
or. The position-sensitive detector allowed simultaneous
data collection within a diffraction window of 2° 2\( \theta \),
with the detector moved in 2° steps between successive scans.
This allowed for relatively fast data collection, at high
resolution: \( \Delta d/d = 0.001 \), an order of magnitude better
than the best resolution possible from energy-dispersive
detectors. Further details about this design may be found
in Jephcoat et al. (1992).

Wavelength and 2\( \theta \) calibrations were determined by
measuring a CeO\(_2\) reference specimen mounted in the
same position as the diamond-anvil cell. The positions
of diffraction peaks were determined by least-squares
profile refinement, employing a pseudo-Voigt function and
an asymmetry correction.

**Lattice parameters**

X-ray diffraction patterns were collected at five pres-
sures in the diamond-anvil cell, with an additional pat-
tern measured at 1 atm using a laboratory-based Scintag
powder diffractometer. At \( P \sim 0.7 \) GPa the cristobalite
remained tetragonal, but, on increasing the pressure to \( P \)
= 1.5 GPa, a dramatic difference was observed in the
diffraction patterns. Formerly single tetragonal reflections
had split into a cluster of weaker peaks, as illustrated in
Figure 1. With a further increase in pressure, the spli-
tings became better resolved, and the diffraction peaks
moved to higher angles.

The distinct and sudden splitting of diffraction lines
denotes a structural phase transition, as reported by Ye-
specifically, the similarity between clusters of peaks in the
high-\( P \) phase and individual peaks in the low-\( P \) phase
suggests a definite crystallographic relationship (e.g.,
subgroup-supergroup) between the two phases. In our own
single-crystal study of the tetragonal phase (Downs and
Palmer, 1994), we had noticed a transition at \( P \sim 1.2 \)
GPa; slow, \( \omega \) and 0/20 scans across selected diffrac-
tion peaks revealed splittings characteristic of lamellar
twinning.

In order to distinguish the various phases of cristobal-
ite at high pressures, we recommend an alternative to the
traditional \( \alpha, \beta \) nomenclature. We opt for a numbered
system, reflecting the number of symmetry reductions that
the high-temperature aristotype structure might undergo. Other workers, e.g., Tóledano and Tóledano (1987), have already advocated a numbered system, based as it is on a symmetry classification. The phase with highest possible symmetry, i.e., the aristotype, is denoted phase 0, then its subgroups are numbered in succession, with decreasing symmetry. The high-temperature, cubic aristotype structure (Fd3m) therefore becomes cristobalite 0, the tetragonal \( \alpha \) phase (P4\( _{2} \)2) is cristobalite 1, and this new, high-pressure phase is henceforth referred to as cristobalite II.

**Indexing the high-pressure unit cell**

Although we were able to resolve the separation of tetragonal peaks into a number of components, it was not immediately obvious how the diffraction peaks of the high-\( P \) phase could be indexed. The suddenness of the phase transition and the identical profiles displayed by all diffraction peaks at and above this pressure indicated that we were dealing with one specific phase, and not a mixture of two or more phases. This was confirmed in Raman spectroscopy experiments (Palmer et al., in preparation), which show an abrupt discontinuity in the frequencies of certain modes on moving from one phase to the other. These measurements also indicate that for samples repeatedly cycled through the phase transition, it is possible to observe the coexistence of both low-\( P \) and high-\( P \) phases within the well-defined hysteresis interval (\( P_{c} \approx 0.2 \); \( P_{h} \approx 1.2 \) GPa), characteristic of a first-order displacive transition.

Using the TREOR90 computer program (Werner et al., 1985) we were able to index the high-\( P \) powder diffraction data automatically on the basis of a monoclinic unit cell. Since the phase transition is a reversible one, apparently displacive, we would expect a simple relationship between the unit cells of low- and high-\( P \) phases. In order to compare these unit cells directly, the tetragonal cell must be extrapolated to the corresponding pressure within the stability field of the monoclinic phase. The unit-cell data of Downs and Palmer (1994) for the same (tetragonal) cristobalite sample are used for comparison. A least-squares fit of the third-order Birch-Murnaghan equation of state, with \( V_{0} = 171.1 \) \( \text{Å}^{3} \), gives values of 11(1) GPa for the isothermal bulk modulus, \( K_{0T} \), and 12(4) for the pressure derivative, \( K' \). By replacing the term \( V_{0} \) by the axial ratio \( a_{0}/a \) or \( c_{0}/c \), we can extrapolate the cell parameters \( a \) and \( c \) to high pressures. The resulting moduli are \( K_{0T} = 39(5) \), \( K' = 40(20) \), and \( K_{0T} = 30 \pm 10 \), \( K_{0T} = 26(3) \) GPa for the \( a \) and \( c \) axes, respectively.

At \( P = 3.1 \) GPa, the high-\( P \) monoclinic cell is approximately double the volume of the extrapolated tetragonal cell (Table 1). Furthermore, the \( b \) cell length is close (within 3%) to the extrapolated \( a \) (or \( b \)) parameter for the tetragonal cell. In order to facilitate the comparison of the two structures, it is useful to describe the high-pressure cell in terms of a pseudotetragonal cell, with its axes approximately parallel to the axes of the low-\( P \) tetragonal cell. This nonconventional cell is double the volume of the standard cell and is \( B \)-face centered. The orientation relation may therefore be expressed as

\[
\begin{pmatrix}
\mathbf{a} \\
\mathbf{b} \\
\mathbf{c}
\end{pmatrix}
= 
\begin{pmatrix}
1 & 0 & 1 \\
0 & 1 & 0 \\
-1 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\mathbf{a} \\
\mathbf{b} \\
\mathbf{c}
\end{pmatrix}_{\text{m}}.
\]

In the absence of single-crystal diffraction data for the cristobalite II phase, we cannot be absolutely certain of the relative orientations of the cristobalite I and II lattices. However, it is possible to infer the orientation relation by observing how the tetragonal powder diffraction lines split into their monoclinic counterparts (Fig. 1) and noting relationships between the unit-cell parameters. Our proposed relationship between the extrapolated tetragonal unit cell and the monoclinic \( P \) (conventional) and \( B \) (nonconventional) unit cells is illustrated in Figure 2. The monoclinic \( B \) cell is interpreted as a supercell comprising four unit cells of the low-pressure tetragonal cell. The orientational relationship between cristobalite I (tetragonal \( P \)) and cristobalite II (monoclinic \( B \)) can then be approximated by

\[
\begin{pmatrix}
\mathbf{a} \\
\mathbf{b} \\
\mathbf{c}
\end{pmatrix}
= 
\begin{pmatrix}
2 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 2
\end{pmatrix}
\begin{pmatrix}
\mathbf{a} \\
\mathbf{b} \\
\mathbf{c}
\end{pmatrix}_{\text{m}}.
\]
The inferred space group of the monoclinic phase is $P2_1$, which is a subgroup of $P4_12_12$; for this case the unit-cell volume doubles at the phase transition, with the driving order parameter relating to an R-point zone-boundary instability (Stokes and Hatch, 1988). The crystal structure has been solved from a combination of DLS and Rietveld techniques and will be presented elsewhere (Palmer and Finger, in preparation). The new structure has a displacive relationship with the low-$P$ form, consistent with the relations presented here.

Pressure-dependence of the lattice parameters

Using the orientation relation between the tetragonal and monoclinic structures, we may directly compare the lattice parameters for $\alpha$ cristobalite (single-crystal data from the same crystals. Downs and Palmer, 1994) and cristobalite II (this study). Figure 3 reveals the abrupt nature of the structural phase transition at $P \sim 1.6$ GPa. The unit cell collapses parallel to $a$ and $b$, and the $\beta$ angle increases dramatically from 90 to 91.6° at the phase transition. Rather intriguingly, the $c$ axis, which is the most compressible axis in the tetragonal phase, shows a remarkable increase, or rebound, at $P_s$, almost as if a compressed structural spring had been released. The cell parameters then follow a curved path of decreasing slope, with continued compression, which must reflect a high compressibility and pressure derivative for cristobalite II.

![Comparison of the low- and high-$P$ phases of cristobalite (designated cristobalite I and II, respectively), projected onto (010). The low-$P$ cell (shaded and with a dashed outline) is based on the extrapolation of tetragonal parameters to 3.1 GPa. Two settings of the monoclinic cell are shown.](image)

**Table 1. Lattice parameters for cristobalite I and cristobalite II**

<table>
<thead>
<tr>
<th>$P$ (GPa)</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\beta$ (°)</th>
<th>$V$ (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001</td>
<td>$1/2 \times 9.950(2)$</td>
<td>4.975(1)</td>
<td>$1/2 \times 13.848(6)$</td>
<td>90</td>
<td>$1/4 \times 658.5(3)$</td>
</tr>
<tr>
<td>1.61(1)</td>
<td>9.401(9)</td>
<td>4.743(3)</td>
<td>13.890(9)</td>
<td>91.63(4)</td>
<td>618.6(5)</td>
</tr>
<tr>
<td>2.04(3)</td>
<td>9.312(9)</td>
<td>4.706(3)</td>
<td>13.83(1)</td>
<td>91.80(5)</td>
<td>605.8(5)</td>
</tr>
<tr>
<td>2.61(7)</td>
<td>9.146(66)</td>
<td>4.639(4)</td>
<td>13.792(12)</td>
<td>92.08(5)</td>
<td>584.7(5)</td>
</tr>
<tr>
<td>3.05(6)</td>
<td>9.123(5)</td>
<td>4.625(3)</td>
<td>13.775(6)</td>
<td>92.02(4)</td>
<td>580.9(4)</td>
</tr>
<tr>
<td>4.37(4)</td>
<td>8.951(2)</td>
<td>4.561(1)</td>
<td>13.743(3)</td>
<td>92.43(1)</td>
<td>560.9(1)</td>
</tr>
</tbody>
</table>

*Note:* lattice parameters for the tetragonal cell extrapolated to $P = 3.05$ GPa are $a = 1/2 \times 9.554$, $b = 4.777$, $c = 1/2 \times 13.046$ Å, $V = 1/4 \times 597.6$ Å³. A monoclinic $B$ cell is used for cristobalite II.

**Spontaneous strain**

For a displacive phase transition involving a supergroup to subgroup relation, the order parameter, $Q$, may couple to the lattice strain. The resulting excess lattice distortion is characteristic of the phase transition and is usually expressed as the spontaneous strain, $\epsilon$ (Carpenter, 1992). Because one can never measure $Q$ directly, measurements of macroscopic properties, such as the spontaneous strain, are essential for the thermodynamic description of phase transition behavior. The zone-boundary nature of the cristobalite I $\rightarrow$ II phase transition (accepting the change in space group from $P4_12_12$ to $P2_1$) leads us to expect quadratic coupling, $\epsilon \propto Q^2$ (in lowest order), to the spontaneous strain.

The symmetry of the spontaneous strain tensor is determined by point-group relations. The subgroups of 422 and the nonzero components of their spontaneous strain tensors are listed in Table 2. For the phase transition 422 $\rightarrow$ 2, the active representation is of type $E$ (Janovec et al., 1975; Salje, 1990), comprising an orthogonal pair of basis functions. The $xz (e_{xz})$ basis function describes a shear parallel to $a$, such that the angle $\beta$ departs from 90° (Fig. 4a). The tetragonal condition $a = b$ is relaxed in the monoclinic system, and so an additional improper strain is allowed, involving extensions or contractions parallel to these two axes (i.e., nonzero $e_{11}$, $e_{22}$). This strain is subject to the constraint that there shall be no net volume change, and therefore we have the condition that $e_{11} = -e_{22}$.

The alternative basis function $yz - xz (e_x = -e_y)$ is a shear parallel to [110] in the (110) plane of the tetragonal cell, leaving a unique (diad) axis perpendicular to the (110) shear plane (Fig. 4b). There is no longer any constraint that $\gamma = 90°$, and so an additional improper strain, $e_{13}$, is allowed. The resulting unit cell has $\alpha = \beta \neq 90°$ (because of $e_{13}$ and $e_{11}$, respectively) and $\gamma \neq 90°$. This is better described by a conventional, monoclinic unit cell, with $b$ perpendicular to the (110) shear plane of the tetragonal phase and with $a$ and $c$ lying within this plane.

The two distortion schemes and the unit-cell relationships are summarized in Figure 4. By comparing this figure with the actual monoclinic unit cell (and its pseudotetragonal relation) displayed in Figure 2, it is clear that deformation can be described by the $xz$ basis function but not by the $yz - xz$ basis function.

We have described the spontaneous strain that violates
the symmetry of the supergroup 422. In addition to this symmetry-breaking strain \(e_{ab}\), extra, non-symmetry-breaking strains \((e^{nb})\) are allowed, which couple to the \(A\) representation of 422. These strains do not affect the off-diagonal (shear) terms of the strain tensor but may modify the on-diagonal terms, and hence, the unit-cell volume. From Table 2, we expect symmetry-breaking strains parallel to \(a\) and \(b\), but not \(c\); we may therefore express the axial strains as

\[
e_{11} = e_{11}^{ab} + e_{11}^{nb}\]

\[
e_{22} = e_{22}^{ab} + e_{22}^{nb}\]

\[
e_{33} = e_{33}^{nb}.\]

The non-symmetry-breaking strains must conform to the high-symmetry point group 422, and therefore we have the condition that

\[
e_{11}^{ab} = e_{22}^{ab} \neq e_{33}^{ab}.\]

Also, we already have a relation between two symmetry-breaking strain components (i.e., for no volume change) that

\[
e_{11}^{nb} = -e_{22}^{nb}.\]

From these conditions, we arrive at the relations

\[
e_{11}^{nb} = \frac{1}{2}(e_{11} + e_{22})\]

\[
e_{33}^{nb} = \frac{1}{2}(e_{11} - e_{22}).\]

The phase transition involves a shear plus a volume

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Fig. 3  Pressure dependence of the unit-cell parameters for cristobalite. The subscript 0 refers to the tetragonal phase and \(m\) refers to the pseudotetragonal setting of the monoclinic, cristobalite II phase. The solid symbols denote measurements from this study, using X-ray powder diffraction; the open symbols denote single-crystal X-ray diffraction measurements on the same sample, from Downs and Palmer (1994) (symbol size exceeds the experimental estimated standard deviations). The dashed lines through the tetragonal cell parameters \(a_0\), \(c_0\), and \(V_0\) represent the best-fit Birch-Murnaghan-type functions and are used to extrapolate the tetragonal base lines into the stability region of the monoclinic phase.
change. The measured strain tensor, \( S \), can therefore be separated into symmetry-breaking and non-symmetry-breaking tensors:

\[
S = \begin{pmatrix}
e_{11} & 0 & e_{13} \\
e_{22} & 0 & 0 \\
e_{33} & 0 & 0
\end{pmatrix} = \begin{pmatrix}
e_{11}^{sb} & 0 & 0 \\
e_{22}^{sb} & 0 & 0 \\
e_{33}^{sb} & 0 & 0
\end{pmatrix} + \begin{pmatrix}
e_{11}^{nsb} & 0 & 0 \\
e_{22}^{nsb} & 0 & 0 \\
e_{33}^{nsb} & 0 & 0
\end{pmatrix}.
\]

(10)

The symmetry-breaking strain tensor may be diagonalized to reveal the orientation (i.e., the shear plane) and magnitude of the corresponding strain ellipsoid.

The individual components of the spontaneous strain tensor may be calculated from the unit-cell parameters of cristobalite II, and those of cristobalite I extrapolated to the same pressure, using the general equations of Schlenker et al. (1978), summarized in Carpenter (1988). The spontaneous strain components are plotted in Figure 5. Note the very large non-symmetry-breaking strains \( e_{11}^{nsb} \), \( e_{22}^{nsb} \), and \( e_{33}^{nsb} \), in contrast to the rather smaller symmetry-breaking strains \( e_{11}^{sb} \) and \( e_{22}^{sb} \) and the shear strain, \( e_{13} \).

### DISCUSSION

One of the crucial questions facing anyone trying to extend the Landau description of phase transitions to conditions of high pressure is the behavior of the excess volume. It transforms according to the identity representation \( A_1 \), which is proportional to \( Q^2 \) in lowest order, but there may be higher order dependencies on \( Q \). For high-temperature phase transitions where the volume changes tend to be relatively small, the volume strain is observed, apparently without exception (Carpenter, 1992), to be proportional to the square of the order parameter. By contrast, at high pressures the volume changes are significantly larger, and one might expect to observe deviations from the ideal case \( V_s \propto Q^2 \).

One can test for nonideality by directly comparing the pressure dependence of symmetry-breaking and non-symmetry-breaking (volume) strains. Because of the zone-boundary nature of the phase transition cristobalite I \( \rightarrow \) II, both the symmetry-breaking strain \( (E \text{ representation}) \) and the non-symmetry-breaking strain \( (A_1 \text{ representation, volume}) \) are proportional to \( Q^2 \) in lowest order. In the absence of higher order terms, we would therefore expect linear scaling between the different strain components. However, if higher order coupling to the order parameter is significant, there is no longer any reason to believe that the various strain components will continue to scale linearly. (It is highly unlikely that individual strain components would have identical coupling constants.) Figure 6 demonstrates that \( e_{13} \propto e_{13}^{nsb} \), indicating that rather these components have identical higher order couplings to the order parameter (which would be exceedingly fortuitous), or, as seems more likely, there are no significant higher order coupling terms at all—in which case, the volume-changing strain remains proportional to the square of the order parameter. That is despite the fact that cristobalite is an example of a system with much
larger spontaneous strains (~6–10% for $e_{\text{sm}}$ and 2–4% for $e^0$) than is typical for proper ferroelastics (~2%) and improper ferroelastics (<1%).

Because the strain components are observed to be all proportional to each other, the overall spontaneous strain ellipsoid must change in size, but not orientation, with changing $P$ and $T$. For the total strain (including symmetry-breaking and non-symmetry-breaking components), the principal axis of the tensor is found to remain at about $\theta_{\text{tot}} = 10^\circ$ to the $x$ axis, while the ellipsoid of the symmetry-breaking strain remains oriented at approximately $\theta^0 = 40^\circ$ to the $x$ axis for all pressures. For ferroelastic phase transitions we consider the strain-order parameter coupling only, leading to renormalized elastic constants, reflecting the inverse susceptibility. Because the orientation of our strain ellipsoids is invariant with pressure, we can confidently state that the strain-order parameter coupling is invariant over this pressure range. This high-pressure phase transition can therefore be treated in the same Landau manner as many high-temperature structural phase transitions.

Because of the constant $\epsilon Q$ coupling, it is valid to calculate a total, scalar spontaneous strain from the different strain components. There are various definitions for such a strain, but perhaps the most commonly used one (e.g., Redfern and Salje, 1987; Carpenter, 1988; Salje, 1990) is

\[ e_{\text{tot}} = \sqrt{\sum_{i=1}^{n} e_i^2} \]  

(11)

where $e_i$ are the components of the spontaneous strain tensor derived above. The total strain, proportional to $Q^2$, is plotted in Figure 7 and shows good agreement with this first-order Landau model. The size of the step in $\epsilon$ at the phase transition is particularly important: it is proportional to the ratio of the $Q^2$ and $Q^4$ coefficients in the Landau potential. By combining this information with further measurements of other macroscopic properties, it will be possible to construct the effective Landau potential, and hence obtain the thermodynamic implications of the phase transition cristobalite I $\rightarrow$ II.

The orientation of the symmetry-breaking strain ellipsoid is intriguing. The extensional axis ($e_1$) is parallel to [\{01\}] in the [\{10\}] plane of the tetragonal phase: a plane of distorted six-membered tetrahedral rings, which in the high-temperature cubic phase, becomes the pseudo-close-packed [\{111\}] plane. This direction is equivalent to [\{112\}], precisely the slip direction one would expect for the smallest possible shear of the \{111\} layers. The cristobalite I $\rightarrow$ cristobalite II phase transition can therefore be viewed as a shear of the crystal structure, involving the sliding of adjacent close-packed sheets against each other, much as in the martensitic-type transformations of close-packed metals. Such transitions give rise to a defect microstructure, and one might predict the formation of stacking faults, and even glide twinning. In our single-crystal diffraction work on the high-pressure phase of cristobalite (Palmer and Downs, 1991), we observed split single-crystal diffraction peaks, as measured in $\omega$ and $\theta$ scans, indicative of such twinning. In addition, repeated cycling of the crystal through the phase transition, followed by quenching to ambient pressure, yielded a twinned, tetragonal crystal, whereas the original tetragonal crystal, before pressure treatment, had been untwinned. These deformation twins must be distinct from the tetragonal to monoclinic transformation twins, as the
latter cannot exist in the tetragonal phase. Further evidence for a strain-related, deformation microstructure is the coexistence of both high- and low-pressure phases within the hysteresis region, observed in the single-crystal X-ray experiments (Downs and Palmer, 1994) and Raman spectroscopy experiments (Palmer et al., 1991). The underlying microstructure should be revealed by transmission electron microscopy, and a systematic study of cristobalite before and after phase transition cycling would be very rewarding.

ACKNOWLEDGMENTS

We would like to thank the Harvard Mineralogical Museum for its loan of the sample. David Cox and Andrew Jephcoat provided invaluable assistance during the synchrotron X-ray experiments. Michael Carpenter, Ekhard Salje, and Charles Prewitt are to be thanked for their helpful comments. The manuscript was greatly improved by reviews from Ross Angel, Andrew Christy, and an anonymous reviewer. The National Synchrotron Light Source (Brookhaven National Laboratory) is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences (DOE grant DE-AC2-76CH00016). This research was funded by the National Science Foundation (NSF grants EAR-22-34530 to L.W.F., and EAR-91-17434 to C.T. Prewitt and D.C.P.) and by the Carnegie Institution of Washington.

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MANUSCRIPT RECEIVED APRIL 13, 1993
MANUSCRIPT ACCEPTED AUGUST 26, 1993