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Structural properties of SiO₂ in the stishovite structure

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In addition to the familiar family of fourfold-coordinated polymorphs, silica exists in sixfold-coordinated structures, among which stishovite is the most important one. Here we predict the lattice parameters and structural properties of stishovite using two approaches: direct quantum-mechanical calculations and classical interatomic potentials. Our quantum-mechanical calculations are based on "soft" pseudopotentials constructed using the local-density approximation. For the interatomic potential calculations, we have used a recently developed two-body potential extracted from Hartree-Fock self-consistent calculations of the total energy of silica clusters. The results of these two types of calculations are compared and contrasted. Unlike similar comparisons for fourfold-coordinated polymorphs, we find that both approaches agree very well with experimental data. We attribute this difference to fewer internal degrees of freedom in stishovite. Angular, or many-body forces play a less significant role in this structure as contrasted to open structures such as quartz.

I. INTRODUCTION

Owing to its abundance in the Earth's crust and mantle, silica is one of the most important materials from a geophysicist's point of view. Moreover, it is one of the most useful materials in today's technology. Silica-based applications are widespread and range from glass to silicon-based microelectronic devices. The primary reasons for the use of silica in electronic devices are its passivation and encapsulation properties, which derive from the fact that the Si-SiO₂ interface is electrically inert. Because of these interesting electronic properties, silica becomes an attractive candidate for study by physicists and materials scientists. This explains why the literature in these areas of science abounds with experimental and theoretical studies of as many as 40 polymorphic forms of silica. Of all these forms, only α - and β -quartz, α -cristobalite, coesite, tridymite, stishovite, and a newly discovered phase in CaCl₂ structure have a temperature-density field of thermodynamic stability for chemically pure silica,^{1,2} i.e., in which no other element is needed for structural stability. If we are interested in understanding the chemical bonds in silica, these crystalline forms of SiO₂ form a fundamental intrinsic set.

In many polymorphs of silica, the silicon atoms are surrounded by an approximately tetrahedral array of oxygen atoms. The O-Si-O angle is close to the ideal tetrahedral bond angle of 109°28'. Each oxygen atom is

bonded to two silicon atoms and serves to link the tetrahedra. Examples of this kind of polymorphs are α - and β -quartz, α - and β -cristobalite, tridymite, and coesite. Stishovite, a high-pressure polymorph of silica, which occurs in the rutile structure, is a noteworthy exception. It is the first known form of silica in which each silicon atom is coordinated by six oxygen atoms in an octahedral configuration and each oxygen atom is bonded by three silicon atoms. It has distorted Si(O_{1/3})₆ octahedra sharing edges and corners. Garnet, hollandite and perovskite are a few more examples of high-pressure polyforms in which an octahedral configuration for a silicon cation is observed.³

Stishovite was first synthesized in the laboratory in 1961 by Stishov and Popova.⁴ They produced this high-density polymorph at 1200–1400 °C and at a pressure reported to be above 16 GPa. This pressure is equivalent to that at a depth of 400–500 km in the earth. Thus, finding stishovite on the surface of the earth was somewhat surprising. The presence of stishovite in Coconino Sandstone Meteor Crater must be attributed to the transient shock pressure accompanying the meteorite impact.^{5,6} When compared to other forms of silica, stishovite is 46% denser than coesite and 60% denser than α -quartz as expected for the rutile structure, which is not as open. Birch⁷ pointed out that the observed increase in seismic velocities with depth from 200 to 900 km, in the Earth can be accounted by phase transformations in

which silicates and oxides with open structures break down into close-packed polymorphs with an increase in the coordination number of silicon. An example is the transformation of quartz into stishovite.⁸ It has been demonstrated that the pressure-temperature conditions in Earth's mantle coincide with the stability fields of coesite and stishovite. Thus, knowledge of the structural properties of high-pressure substances like garnet, spinel, olivine, and stishovite is vitally important for the study of Earth's mantle. Such high-pressure phases are characterized by high densities, elastic ratios (i.e., the ratio of the bulk modulus to the density), seismic velocities, and by low compressibilities.^{9,10}

In order to understand some of these features, we need to be able to predict the structural properties of silica. Such predictions are quite difficult as forms of silica often have nearly identical total energies. Moreover, differences in the internal coordinates of such forms as quartz and coesite are often quite small. In general, the prediction of crystal structures and their properties is of prime importance in solid state physics. For this reason, a number of different approaches have been developed to predict structural energies. These approaches range from first-principles quantum-mechanical methods,¹¹⁻¹⁶ which require extensive computational resources, to empirical interatomic potentials.^{1,17-19}

Interatomic potentials are much easier to implement than quantum-mechanical methods. It is well known that monatomic systems with close-packed structures (e.g., simple metals and inert gases) can be reasonably described using two-body potentials. These two-body potentials have an attractive part that represents the cohesion of the condensed phase and a repulsive part that describes the scale of the atomic size. The repulsive part describes the fact that each ion resists overlap with the electron distributions of the neighboring ions. Although two-body potentials are very convenient to use, they fail to describe open structures. For example, the structure of elemental semiconductors that have the diamond structure are not reproduced, since this structure is not close-packed. One has to include three-body terms to take into account the covalent nature of interatomic interactions.¹⁷⁻¹⁹ The construction of such potentials is difficult, and accurate ones for silica are lacking.

Nonetheless, a few applications of interatomic potentials to silica have been attempted. For example, interatomic potentials have been used to understand the structure of amorphous SiO₂ and similar materials. Because of the simplicity of their use, pair potentials can greatly enhance our ability to use molecular dynamics and simulations to describe melting and glass formation in silica. Molecular-dynamics (MD) simulations for a glass (BeF₂) were performed by Rahman, Fowler, and Narten²⁰ and Woodcock, Angell, and Cheeseman²¹ carried out a MD simulation of amorphous SiO₂. The potentials used were purely ionic. The interactions consisted of a Born-Mayer-Huggins repulsion term and an attractive Coulomb interaction. Vashishta *et al.*,²² have recently proposed an interaction potential that can be used in molecular-dynamics studies of structural and dynamical correlations of crystalline, molten, and vitreous states of

silica under various conditions of densities and temperatures. The two-body contribution to this potential includes terms describing steric repulsion owing to atomic sizes, Coulomb interactions resulting from charge transfer, and charge-dipole interactions to include the effects of large electronic polarizability of anions. The three-body covalent terms include O-Si-O and Si-O-Si interactions, which are dependent on bond angles and Si-O bond length. They noted that the negative ions such as O²⁻, S²⁻, Se²⁻, and Te²⁻ are among the largest in the Periodic Table and thus highly polarizable. Thus, they postulated that the electronic polarizability of these ions is an important term in the interaction potential.

In this work, we have used two approaches. We consider a simple interatomic potential, which has recently been constructed from Hartree-Fock calculations on SiO₂ molecular species.¹ We also perform quantum-mechanical calculations. These calculations are based on recently developed *ab initio* pseudopotentials, which have been constructed within a local-density approximation.²³ Past studies²⁴ have indicated that interatomic potential with simple two-body terms fail to describe α -quartz. Moreover, since the two-body potential that we use was obtained by fitting its results to total-energy calculations for fourfold coordinated silica structures,¹ one might question whether such an approach will yield accurate results for stishovite. Earlier work¹ has suggested that such potentials may give an accurate description of silica in the higher coordinated form, but this effort did not compare to experiment in detail, nor did it consider the details of structural changes under pressure. Our objective here is to deal with such issues and predict the minimum energy equilibrium structure at different pressures, lattice parameters, and elastic constants such as the bulk modulus, the pressure derivative of the bulk modulus and the Poisson ratio using both approaches. We compare and contrast the results of the two theoretical approaches and make a detailed comparison with the available experimental data.

II. COMPUTATIONAL METHODS

First-principles quantum-mechanical approaches can be used for prediction of properties; however, they can be computationally intensive. One goal has been to determine whether it is necessary to do the computations for each form of silica independently. For example, if one wishes to look at several polymorphs of silica, one could seek a procedure in which a simple classical mechanical potential is fit to quantum-mechanical calculations for a specific structure. This potential could then be applied to describe and predict the properties of other structural forms. Such a procedure has been developed by Tsuneyuki *et al.*¹ They employed a Hartree-Fock self-consistent-field method, which is known to give very precise structures of molecules, to the total-energy calculation of SiO₄⁴⁻ clusters. By fitting the results of these calculations to a proposed form of two-body potential, they have fitted the adjustable parameters to an empirical form of interatomic potentials for silicon and oxygen. The functional form of their interatomic potential is as

follows:

$$U_{ij}(r) = \frac{Q_i Q_j}{r} + f_0(b_i + b_j) \exp \left[\frac{a_i + a_j - r}{b_i + b_j} \right] - \frac{c_i c_j}{r^6}, \quad (1)$$

where U_{ij} is the potential energy of interaction between the i th and j th atoms, r is the distance between them, $f_0 = 1 \text{ kcal } \text{Å}^{-1} \text{ mol}^{-1}$, and (a_i, b_i) are the effective radius and softness parameter for the i th atom. The potential parameters from Ref. 1 are given in Table I. Using the two-body potential mentioned above, the total energy of the crystal can be trivially calculated as

$$U = \frac{1}{2} \sum_{i,j} U_{ij}(r). \quad (2)$$

In Eq. (1), the first term is the long-range Coulomb interaction, the second term represents Born-Mayer type of energy, whereas the third term gives the Van der Waals component of energy. The Born-Mayer and Van der Waals terms decay quite rapidly. For this reason, the summations for Born-Mayer and Van der Waal energies are evaluated directly. The Madelung energy is computed via Ewald's method.

Owing to the simplicity by which the interatomic potentials can be evaluated, the total energy of the crystal can be easily computed. This is highly advantageous for complex crystals. For example, if the crystal has several internal parameters, the total energy as a function of these parameters must be optimized. This adds to the degree of complexity of the already difficult problem. In this situation, classical calculations might be preferred over full quantum-mechanical calculations, if they can give sufficiently accurate results. One of the objectives of this paper is to assess this issue for stishovite.

We have already outlined some of the difficulties that arise in predictions of properties of solids in general. In addition to the complex structures that silica forms, there are electronic interactions, which are difficult to describe in terms of quantum-mechanical interactions. For example, in the pseudopotential method, oxygen is difficult to work with, since it has no p states within the core. There exists no orthogonality condition for the p states, and the oxygen potential for this component is much stronger than that for the s state. The large nonlocality in the oxygen pseudopotential results in localized p states when contrasted to the s state. Silicon is more amenable to the pseudopotential treatment as the cancellation in both the s and p states are similar.

In situations where states can be highly localized, local orbital bases such as Gaussian are often employed.²⁵ These basis give rise to complicated matrix elements, al-

though the resulting diagonalization involves a smaller matrix than a plane-wave basis. We have not employed this approach. We have used newly developed pseudopotentials that are especially constructed for use with a plane-wave basis.²³ The matrix elements that arise in this case are much simpler than those that arise in case of the local bases. We have used special techniques to handle large matrix manipulations.²⁶

The details of our quantum-mechanical calculations have been presented in detail elsewhere.¹¹ Here we briefly review the essential features. Our pseudopotentials were generated self-consistently within the local-density approximation using the method of Troullier and Martins.²³ This method produces "soft" pseudopotentials, i.e., potentials that allow a rapid convergence in terms of a plane-wave basis. The oxygen potential was generated from the atomic $2s^2 2p^4$ ground-state configuration with a radial cutoff of 1.45 a.u. for both the s and p components of the potential. The oxygen d component was neglected owing to its high-energy relative to the atomic $2s$ and $2p$ valence states. For silicon, s , p , and d components of the potential were included. The radial cutoff for all three components was taken to be 1.80 a.u. As is commonly done, we take one component of the potential to be "local" and project out the remaining components. Here the local potential was the p component for silicon and for oxygen.

The one-electron Schrödinger equation was solved using a fast iterative diagonalization method.²⁶ One advantage of this method is that it does not require a calculation of the full Hamiltonian matrix. Rather only $H\psi$ is calculated. This procedure leads to a dramatic reduction in storage and a considerable reduction in computational time. Plane waves up to an energy cutoff of 64 Ry were included in the basis set. Typically, 2300 plane waves were used in the basis. Increasing the cutoff to 144 Ry altered the total energy by less than 0.1 eV/molecular unit. We used six special \mathbf{k} points to evaluate the total energy.

III. STRUCTURAL PARAMETERS OF STISHOVITE

Stishovite belongs to the tetragonal system; it has the point group $D_{4h}^{14} (P4_2/mnm)$. In Fig. 1, we illustrate a unit cell of stishovite. The structure of stishovite is completely defined by the lattice constants (c, a) and a single internal coordinate, u . The basis vectors for the tetragonal structure are $\mathbf{a} = a\hat{x}$; $\mathbf{b} = a\hat{y}$; $\mathbf{c} = c\hat{z}$.

The unit cell contains two molecules of SiO₂. The coordinates of the two silicon atoms and four oxygen atoms are given by

$$\begin{aligned} \mathbf{R}(\text{Si})_1 &= \mathbf{0}, \\ \mathbf{R}(\text{Si})_2 &= \frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b} + \frac{1}{2}\mathbf{c}, \\ \mathbf{R}(\text{O})_1 &= u\mathbf{a} + u\mathbf{b}, \\ \mathbf{R}(\text{O})_2 &= (1-u)\mathbf{a} + (1-u)\mathbf{b}, \\ \mathbf{R}(\text{O})_3 &= (\frac{1}{2}+u)\mathbf{a} + (\frac{1}{2}-u)\mathbf{b} + \frac{1}{2}\mathbf{c}, \\ \mathbf{R}(\text{O})_4 &= (\frac{1}{2}-u)\mathbf{a} + (\frac{1}{2}+u)\mathbf{b} + \frac{1}{2}\mathbf{c}. \end{aligned}$$

TABLE I. Parameters used in the classical two-body potential used in this study (Ref. 1).

	Q/e	a (Å)	b (Å)	c (kcal ^{1/2} Å ³ mole ^{1/2})
O	-1.200	2.0474	0.175 66	70.37
Si	+2.400	0.8688	0.032 85	23.18

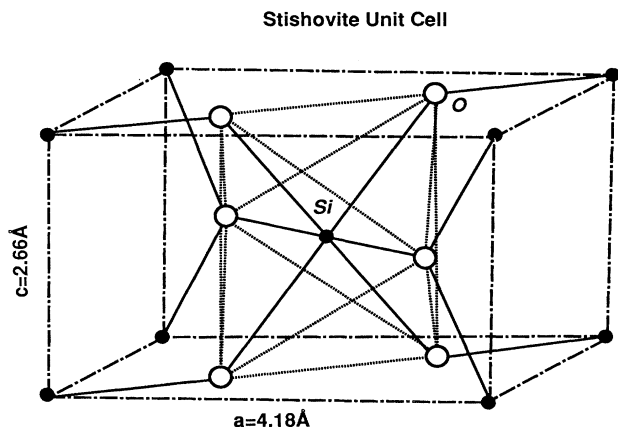


FIG. 1. Structure of the unit cell of stishovite. The value of c and a are given at ambient pressure. Also illustrated is the octahedral coordination of the silicon atom.

For a fixed volume of the unit cell, the total electronic energy is a function of two parameters: u and a (or u and c). Minimizing the energy with respect to these parameters is equivalent to putting the material under hydrostatic pressure. We examined several volumes and minimized the total energy using a method given by Davison.²⁷ A plot of equilibrium energy as a function of unit-cell volume is given in Fig. 2 for classical interaction potential and quantum-mechanical calculations. A Murnaghan equation of state was fit to these points to compute the equilibrium energy and volume, the zero pressure bulk modulus, and the pressure derivative of bulk modulus. A Birch-Murnaghan form of the equation of state gives essentially the same values. The results of the calculation of binding energy with the interatomic calculations are normalized with that of quantum-mechanical calculations by matching the equilibrium binding energy

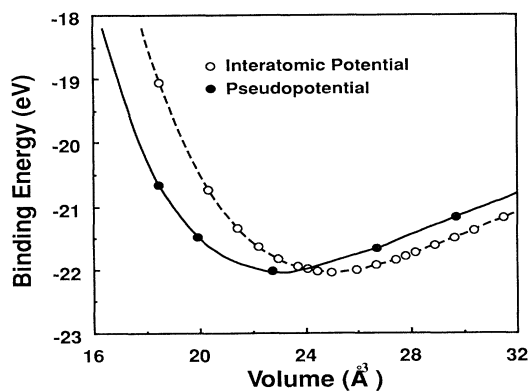


FIG. 2. Calculated binding energy per molecular unit of stishovite. Results of classical calculations are normalized using the equilibrium cohesive energy calculated quantum mechanically. The volume is per molecular unit.

gies of both. Binding energy is the energy per molecular unit of the crystals with respect to infinitely separated constituent atoms. In the case of the quantum-mechanical calculations, the atoms are "pseudoatoms," i.e., the total valence energy as determined for isolated silicon and oxygen atoms using the respective pseudopotentials. For silicon, the energy of the pseudoatom is -101.89 eV; for oxygen the energy is -426.60 eV. Per molecular unit, the energy of the isolated atoms is -955.09 eV. The total energy per molecular unit for stishovite is -977.29 eV, leading to a calculated binding energy of 22.2 eV/molecular unit. The experimental binding energy of silica in the quartz structure is about 19.2 eV/molecular unit, which is expected to be nearly equal to that of stishovite. Our over-estimate of the binding energy is a typical finding of local-density calculations.

The binding energy of stishovite as calculated from the interatomic potentials can only be determined if one is provided with the energy to "prepare" the ions from which the solid is formed. The appropriate ions for the interatomic potentials used here are $\text{Si}^{2.4+}$ and $\text{O}^{1.2-}$. While it is possible to consider fractional charge within the local density approximation, oxygen ions can present difficult conceptual issues. If we consider $\text{O}^{\delta-}$, then for $\delta \gtrsim 1$, oxygen does not form a stable ion. Purely ionic models with $\text{Si}^{2\delta+}$ and $\text{O}^{\delta-}$ with $\delta \gtrsim 1$ result in undefined reference energies for the isolated ions. Moreover, even if we were able to consider a local-density solution, no "error cancellation" would occur between the atom and the solid as we would be comparing a local-density calculation with a "classical" result. Here we avoid such issues by equating the classical binding energy to the quantum mechanical.

We note that in both the classical and quantum-mechanical calculations, α -quartz is only slightly lower in energy than stishovite. From the pseudopotential calculations, quartz is more stable by about ~ 0.1 eV/molecular unit. Similar results are observed for the interatomic work, although the energy difference is slightly less, i.e., ~ 0.05 eV/molecular unit. It is not surprising that quartz is more stable; however, it is surprising that two such different structures are so close in energy. We postulate that entropic differences might further enhance the stability of quartz at finite temperatures as its open structure might be expected to yield a larger phonon contribution to the entropy than the more close-packed structure of stishovite.

The best estimations of bulk modulus and its pressure derivative are 298.8 GPa and 6.69 for classical calculations and 292.0 GPa and 5.86 for quantum-mechanical calculations respectively. Several investigators have gathered data on the structural parameters using a diverse range of techniques. Here we review briefly some of the important works on the study of structural parameters. Chao *et al.*,⁵ identified stishovite in the coesite-bearing Coconino Sandstone of Meteor Crater, Arizona. They compared the x-ray-diffraction data on natural stishovite with that for synthetic stishovite prepared by Stishov and Popova⁴ and found that the agreement is excellent both in spacings and in intensity of reflections.

TABLE II. Structural parameters for stishovite as determined from experiment and theory.

	c (Å)	a (Å)	c/a	Unit-cell volume Å ³
Powder diffraction data				
Chao (Ref. 5)	2.6649	4.1790	0.6377	46.541
Ida, Syono, and Akimoto (Ref. 35)	2.665	4.178	0.6379	46.519
Bassett and Barnett (Ref. 28)	2.663	4.178	0.6374	46.484
Liu, Bassett, and Takahashi (Ref. 2)	2.666	4.180	0.6378	46.581
Single crystal data				
Sinclair and Ringwood (Ref. 29)	2.6651	4.1772	0.6380	46.503
Hill, Newton, and Gibbs (Ref. 3)	2.6655	4.1773	0.6381	46.513
Sugiyama, Endo, and Koto (Ref. 36)	2.6669	4.1797	0.6381	46.591
Ross (Ref. 30)	2.6678	4.1801	0.6382	46.615
Theory				
Pseudopotentials	2.67	4.14	0.645	45.64
Interatomic potentials	2.75	4.26	0.645	49.93

They reported $a=4.1790$ Å and $c=2.6649$ Å as the refined parameters. Bassett and Barnett²⁸ determined $a=4.178$ Å and $c=2.663$ Å from a Debye-Scherrer pattern.

The experimental values mentioned in the previous paragraph were obtained using powder diffraction data. Single-crystal data have been made available recently. Sinclair and Ringwood²⁹ synthesized single crystals of stishovite at a pressure of 9 GPa and a temperature of 700 °C. The refined values of lattice parameters were reported to be $a=4.1772$ Å and $c=2.6651$ Å. Ross *et al.*, obtained³⁰ $a=4.1801$ Å and $c=2.6678$ Å using x-ray-diffraction data on single crystals. These values compare very well with the values $a=4.26$ Å and $c=2.75$ Å estimated using the two-body potential and even better with the values $a=4.14$ Å and $c=2.67$ Å obtained by our pseudopotential calculations.

In Table II, we have listed optimized lattice parameters

at equilibrium along with experimental data gathered by several researchers. The agreement between our pseudopotential results and the experiment is within 1%. The interatomic potentials also yields a satisfactory agreement, i.e., the difference is still within about 4%.

In Table III, we summarize a brief survey of the compressibility data and also compare to the full-potential linear-augmented-plane-wave (FLAPW) calculation of Park, *et al.*¹ We may consider the single crystal values as most reliable. Our pseudopotential and pair potential calculations give $B_0=292.0$ GPa and $B'_0=298.8$ GPa, respectively. These values are in excellent agreement with isothermal bulk modulus obtained from the single-crystal data.

Figure 3 gives the equation of state of stishovite from experiment and theory. In Fig. 3 we have given the variation of V/V_0 as a function of pressure. Here V_0 and V are the volume per molecular unit at zero pressure and the volume at any arbitrary pressure, respectively. We notice that the theoretical calculations and experimental data of Liu, Bassett, and Takahashi² and of Bassett and Barnett²⁸ are within a few percent for the pressure range of about 0–25 GPa. At higher pressures (40–80 GPa), both the interatomic potentials and pseudopotentials are seen to underestimate the pressure as compared to the experimental work of Wackerle³¹ and Weidner *et al.*³² However, the experimental data exhibits a considerable scatter. The pressure derivative of bulk modulus estimated from the single-crystal experimental data is, however, lower than the values obtained from theory. We may note that pressure derivative of the bulk modulus is still a controversial quantity. Many pairs of values of B_0 and B'_0 can satisfy the same $P-V$ data.³³ As a consequence, if static compression data alone are used to determine both these quantities, a large error may enter the estimation. Weidner *et al.*,³² have suggested that since other rutile structure oxides have B'_0 of about 6, a low value for stishovite might be incorrect.

In Fig. 4, we have illustrated the lattice parameters as a function of pressure and compared it with single-crystal high-pressure study by Weidner *et al.*³² It should be noted that theory underestimates the ratio c/c_0 , while the agreement between the theoretical calculation of a/a_0 is

TABLE III. Bulk modulus data for stishovite.

	B_0 (GPa)	B'_0
Shock wave experiments		
McQueen, Fritz, and Marsh (Ref. 37)	435.0	
Anderson and Kanamori (Ref. 38)	462.2	2.66
Ahrens, Anderson, and Ringwood (Ref. 39)	362.7	3.04
Ahrens, Takahashi, and Davies (Ref. 40)	300.0	7.0
Static experiments		
Ida, Syono, and Akimoto (Ref. 35)	710.0	
Liu, Bassett, and Takahashi, (Ref. 2)	344.0	4.0
Bassett and Barnett (Ref. 28)	300.0	4.0
Ultrasonic experiments		
Mizutani, Hamano, and Akimoto (Ref. 34)	346.0	4
Single crystal data		
Weidner (Ref. 32)	306.0	
Sugiyama, Endo, and Koto (Ref. 36)	313.0	6.0
Ross (Ref. 30)	313.0	1.7
Theory		
Pseudopotentials	292.0	5.86
Interatomic potentials	298.8	6.69
FLAPW (Ref. 1)	288	3.14

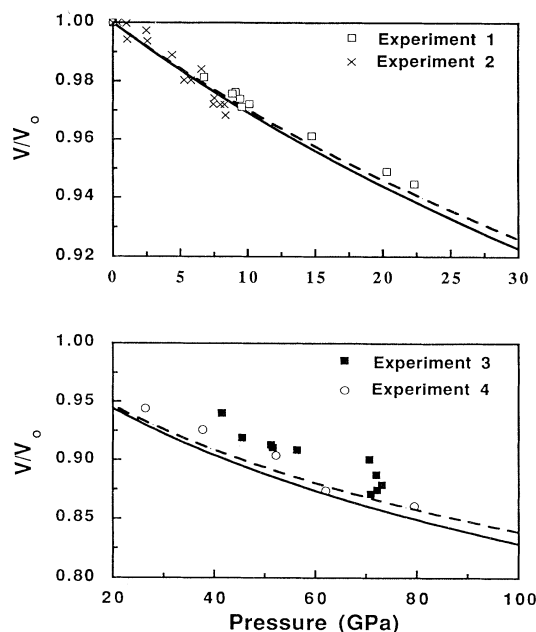


FIG. 3. Equation of state for stishovite. Experiments 1, 2, 3, and 4 are from Liu, Bassett, and Takahashi (Ref. 2), Bassett and Barnett (Ref. 28), Wakerle (Ref. 31), and Tsuchida and Yagi, (Ref. 1), respectively. The dashed and solid curve are the theoretical Murnaghan equation of state fit to energy calculations using interatomic potentials and pseudopotential calculations (as discussed in the text), respectively. Note the change in scale in the lower panel.

more satisfactory. The ratios a/a_0 and c/c_0 are seen to decrease monotonically in an almost linear way as a function of pressure. The c/a ratio, although not as sensitive to pressure as a/a_0 and c/c_0 , is seen to increase very gradually as a function of pressure. Given the small variation in c/a over the pressure range illustrated, it is not surprising that a considerable scatter occurs in the experimental measurements.

Like the c/a ratio, the variation of the internal coordinate u with pressure is very difficult to determine experimentally. Theoretically, it decreases monotonically in the pressure range 0–50 GPa. The results of calculations done using the interatomic potential agree with the pseudopotential calculations within about 1% and indicate that u decreases from about 0.305 at ambient pressures to 0.302 at 50 GPa. The value of the u parameter computed by theory agrees well with the experimental value of 0.3062 obtained by single-crystal x-ray-diffraction measurements.²⁹

We also compute the negative ratio of the transverse strain to the corresponding axial strain in a body subjected to uniaxial stress, i.e., the Poisson ratio. To determine this ratio we need to know the value of a , which minimizes the total energy for a given value of c . We proceed in a manner similar to that outlined for the calculation of the bulk modulus. We minimize the cohesive energy as a function of u and volume of the unit cell at several values of c . The Poisson ratio is defined as

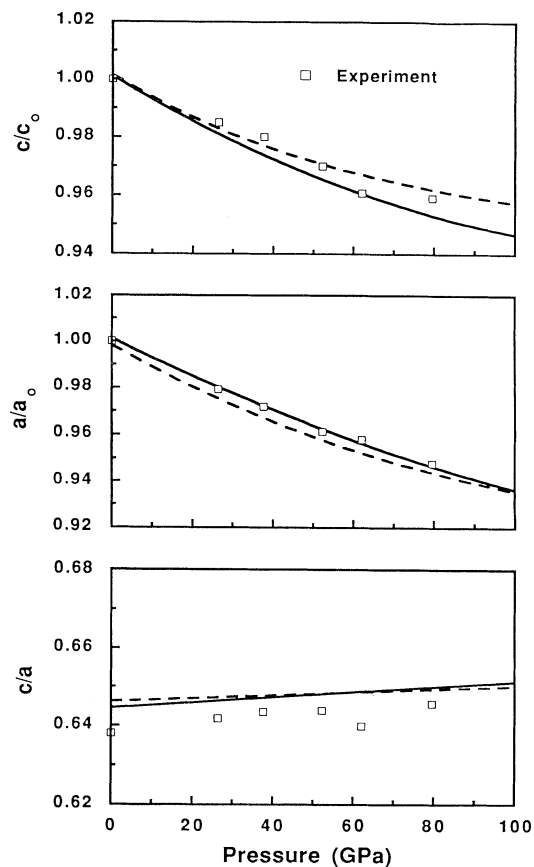


FIG. 4. Comparison of theoretical calculation of lattice parameters with experimental data from Tsuchida and Yagi.¹ The dashed and solid curve are the theoretical results, which have been fit to total energy calculations. Result using interatomic potentials (dashed line) and quantum-mechanical calculations (solid line) are illustrated.

$$\sigma = -\frac{\Delta a/a}{\Delta c/c} = -\frac{\Delta \ln(a)}{\Delta \ln(c)}. \quad (3)$$

We fit a straight line to the graph of $\ln(a)$ vs $\ln(c)$. The Poisson ratio, as defined in Eq. (3) is the negative slope of this line. The values are 0.314, obtained using the interatomic potential, and 0.290, obtained by pseudopotential calculations, as illustrated in Fig. 5. These values compare well with 0.333, which were obtained by Mizutani, Hamano and Akimoto³⁴ using data from ultrasonic experiments.

In previous work,^{11,24} we examined the structural properties of α -quartz under pressure. We found that the ambient pressure structure was well represented by interatomic pairwise potentials; however, pressure-induced changes in the structure were not reproduced even qualitatively. This is not the case for stishovite. Changes with pressure for the internal structural parameters, i.e., c , a and u are accurately reproduced when compared to experiment or pseudopotential calculations. Likewise Poisson's ratio and the compressibility of stishovite as calculated by either interatomic pairwise potentials or

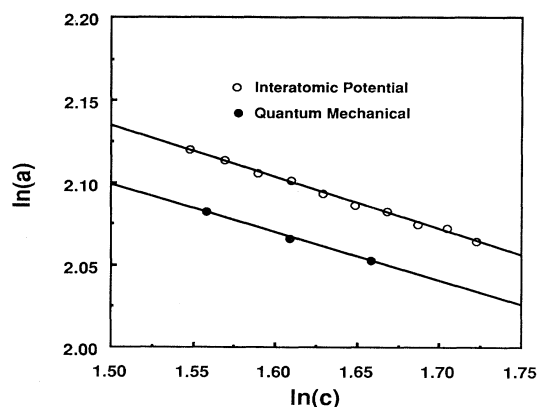


FIG. 5. Calculation of Poisson ratio of stishovite by fitting a straight line to the graph of $\ln(a)$ as a function of $\ln(c)$.

pseudopotential methods agree with each other and experiment. We attribute the success of pairwise forces in the case of stishovite to fewer internal degrees of freedom present as compared to the open structures, e.g., the quartz structure. From the measured behavior of the internal structural parameters with pressure, angular terms are not expected to be significant in stishovite. For example, in α -quartz, the Si-O-Si angle changes by 15° with a pressure increase of 10 GPa. Over a similar range, the Si-O-Si angles in stishovite change by less than 1°. Unless the bond bending energies in stishovite differ by an order of magnitude from those in quartz (which is not likely), changes in the bond angles in stishovite are too small to have a significant effect on the total energy.

It has been suggested¹ that once the silicon—oxygen bond length is fixed, and the symmetry of the structure specified, the internal coordinates at ambient pressure of many of the silica structures follow directly. This would account for the good agreement with experiment of the ambient pressure structures predicted by pairwise forces and the failure of such potentials to account for pressure induced changes in open structures.

IV. CONCLUSIONS

In this paper we have examined the structural properties of SiO₂ in the rutile structure, i.e., stishovite, as a

function of pressure. We considered two approaches. One approach is based on the interatomic pairwise potentials as proposed by Tsuneyuki, *et al.*¹ The other approach is based on pseudopotential calculations using the local-density approximation and *ab initio* pseudopotentials. Both approaches lead to an accurate description of the structural changes, which occur in stishovite under pressure. Specifically, we have examined the equation of state and the internal structural parameters as a function of pressure. The chief difference between the two approaches is that the interatomic potentials yield a value for the ambient pressure unit cell which is about 10% larger than experiment and the quantum-mechanical work.

This is in contrast to the case of silica in the α -quartz case where interatomic pairwise potentials do a poor job in describing the structural changes under pressure.²⁴ We attribute these differences to the importance of many-body, i.e., angular forces, which are present in open structures such as quartz. In quartz, the details of the pressure dependence of the Si-O-Si and O-Si-O angles are quite complex, e.g., there exist four unique O-Si-O angles, and these angles do not scale in a similar fashion with pressure. These angles control the orientation of the Si(O₄)_{1/2} tetrahedra and are crucial in determining the various silica polytypes. It would be surprising if a simple pairwise potential, with no explicit angular dependence, replicated the angular changes with pressure. (Even adding a simple bond-bending term does not significantly improve the changes of angles with pressure.²⁴) Conversely, in stishovite, where the number of internal degrees of freedom are fewer, it should not be surprising that a pairwise interatomic potentials yields accurate structural trends with pressure.

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