PHYSICAL REVIEW B VOLUME 44, NUMBER 2 1 JULY 1991-II

Pressure dependence of the structural properties of α-quartz near the amorphous transition

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(Received 12 December 1990)

Silicon dioxide exists in a number of structures. The lowest-energy structure is that of α-quartz. We predict the structural properties of α-quartz as a function of pressure via total-energy calculations. The calculations are based on recently developed pseudopotentials constructed within the local-density approximation. In addition, we examine the structural properties of α-quartz near an order-disorder transition. Quartz undergoes a gradual transition with pressure from a crystalline to an amorphous state. The driving mechanism for this pressure-induced transition is not well understood. We suggest that highly unfavorable interpolyhedral oxygen-oxygen distances, which occur in α-quartz at the transition pressure, play a key role in driving the transition.

I. INTRODUCTION

SiO_2 is one of the most difficult materials to describe theoretically. SiO_2 occurs in a wide variety of forms[1] with only small energy differences between the phases. The multitude of structures and the small energy differences between structures demand that theoretical methods possess high accuracy for structural predictions. Most SiO_2 polytypes have a tetrahedral unit of $Si(O_4)_{1/2}$. Each Si atom is surrounded by four O atoms with the O—Si—O bond angles being very close to the ideal tetrahedral bond angle of 109.5°. The tetrahedral units are joined by bridging O atoms. Small variations in the Si—O—Si angles tend to dominate the structural differences between polytypes, e.g., coesite and α-quartz. In term of total-energy differences, these differences can be on the order of 0.01 eV/atom or less.

Adding to the problem of structural determinations, the Si—O bond combines strong ionic and covalent bonding, and lone-pair oxygen orbitals are present. It is difficult to treat such systems quantum mechanically as correlation energies are large. Care must be used in choosing a basis and obtaining a self-consistent potential. Rather than treat the problem by a direct quantum-mechanical approach, many workers have chosen to construct more empirical approaches to the structure of silicates. For example, one might envision constructing empirical interatomic potentials to model structural energies of SiO_2. Unfortunately, simple interatomic potentials for SiO_2 are difficult to construct. The covalent component of the Si—O bond does not avail itself to simple ionic models. Covalent contributions are known to play an important role in determining the bond angles: Simple pairwise forces do not reproduce the O—Si—O bond angles even qualitatively.[2] Another problem with this model centers on the fact that O^{2-} does not exist as a free species. Models which treat SiO_2 as $Si^{4+}O^{2-}{}_2$ have ill-defined reference points with respect to isolated species.

We note that not only is SiO_2 of theoretical interest, it is one of the most technologically useful materials. Widespread applications of SiO_2 range from glass to silicon-based microelectronic devices. One of the primary reasons for the use of silicon in electronic devices is the passivation properties of SiO_2. SiO_2 is electronically inert, and its encapsulation properties make it the material of choice. GaAs possesses some electronic properties which are more desirable than Si, e.g., higher mobilities. However, GaAs cannot be oxidized to produce similar passivation properties.

Given the complexity of the Si—O bond, it may not be too surprising that SiO_2 exhibits an unusual order-to-disorder transition under pressure. Hemley *et al.*[3] report that α-quartz undergoes a gradual transition from a crystalline to an amorphous form at approximately ~30 GPa. More recent work by Hazen *et al.*[4] has suggested that there is evidence for the onset of this transition at even lower pressures. From their study on single crystals, as opposed to powdered samples, they noted at 15.3 GPa that peak broadening occurred to the extent that weak peaks were difficult to measure. The peaks remained broad on release of pressure even though the "crystal was neither crushed nor otherwise mechanically damaged."[4] They interpreted this irreversible crystal degradation in a quasihydrostatic medium as evidence for the onset of amorphization. The powder measurements show no such trends until ~20 GPa. Such amorphization transitions occur in other oxides, e.g., in ice[5] and $AIPO_4$.[6] In $AIPO_4$ the problem is compounded by a glass "memory" phenomena. Upon the release of pressure, the glassy $AIPO_4$ reverts to the previous crystallographic orientation of the crystal from which it forms.[6]

Here we concentrate on SiO_2 in the α-quartz structure. A common interpretation for the structure of many forms of SiO_2 is that the key structural unit consists of $Si(O_4)_{1/2}$ tetrahedra. These tetrahedra are preserved as a function of moderate pressure. However, the orientation of the tetrahedra and their role in the order-disorder transition are not well understood. Several structural studies[4,7–13] of α-quartz exist as a function of pressure, but experimental uncertainties become very large near the order-disorder transition. While theoretical methods[14–20] have been applied to the structural properties of SiO_2 as a function of pressure, these methods have often concentrated on molecular analogs as opposed to the crystalline state.[15–17] Even if these models include many-body forces, they have not been able to describe the pressure dependence of the bond angles and lengths in α-quartz. A few solid-state calculations exist,[14,18,20] but these have been limited to examining the electronic properties or ambient pressure structures.

We employ recently developed pseudopotential methods to describe subtle changes in the structure of α-quartz as a function of pressure. The only input into our calculations is the atomic number of the species present and the crystal symmetry. Our procedure, while computationally intensive, has the advantage of including the many-body forces and hybridization changes as a function of pressure directly via quantum-mechanical calculations. We find that we are able to predict the subtle angular and bond-length changes with pressure in α-quartz which are consistent with the best experimental measurements to date. In addition, we predict the structure of the crystalline material at pressures considerably above the order-disorder transition. For example, it has been proposed that under pressure α-quartz experiences bond-angle changes to highly strained geometries. To relieve such strains, the crystal transforms to a glassy state. However, such angle changes cannot be directly observed from experiment and one must rely on extrapolation or other indirect probes. Theoretical methods can describe accurately the structural parameters of hypothetical or metastable high-pressure phases with the same accuracy as ambient pressure structures. Thus the theoretical structural properties of the α-quartz structure can be probed directly in states which cannot be obtained experimentally.

II. COMPUTATIONAL METHODS

A key difficulty in describing the structural properties for α-quartz is that the unit cell is large for *ab initio* calculations. It contains three molecular units of SiO_2 and requires the specification of several internal coordinates. Theoretical determinations of the structural parameters involves minimizing a multiparameter total-energy function. This is a primary reason why interatomic potentials based on molecular-orbital methods are often employed instead of computing the quantum-mechanical forces for the solid state. Numerous evaluations of the forces must be made to ensure that a global minimum of the total energy has been obtained as a function of the structural parameters. In previous work the quantum-mechanical forces have been too complex to evaluate quickly enough for an accurate search within the parameter manifold.[15]

In addition to the complex structure, SiO_2 is difficult to describe in terms of the electronic interactions present. The oxygen potential cannot be constructed as a weak pseudopotential as oxygen has no p states within the ion core. No orthogonality condition exists for the p states, and the oxygen potential for this component is much stronger than the corresponding s states. Silicon does not present such difficulties as the cancellations for both s and p states are similar. The large nonlocality in the oxygen potential results in localized p states. In such situations local bases such as Gaussians are often employed.[21] These bases usually result in rather complicated matrix elements, which can be computationally cumbersome. Here we use newly developed pseudopotentials which allow the use of a plane-wave basis. The matrix which must be handled via plane waves is larger than the matrix originating from a local basis, but special techniques can be used to handle large matrix manipulations.

Our pseudopotentials were generated self-consistently within the local-density approximation using the method of Troullier and Martins.[22] This method produces "soft" pseudopotentials that allow the description of "localized" states such as the oxygen $2p$ states with a plane-wave basis. The oxygen pseudopotential was generated from the atomic $2s^2 2p^4$ ground-state configuration with radial cutoffs of 1.45 a.u. for both the s and p components of the potential; i.e., within this radial cutoff the "pseudo" wave function may deviate from the all-electron wave function for the atom. 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. The two pseudopotentials were transformed using the Kleinman and Bylander separation procedure.[23] As is commonly done, we take one potential component to be "local" and project out the remaining components. For example, with the oxygen potential, the p component was taken as the local potential and the difference between the s and p components is treated as a correction to the local potential. The higher angular components are handled as if they all experienced the same potential as the p component. Usually, the local component is chosen on the basis of increasing the transferability of the pseudopotential.

In the case of a Kleinman and Bylander pseudopotential, we must make sure no "ghost" states exist for either the s or p component of the potential.[24] We have verified this using the theorem of Gonze, Käckell, and Scheffler[24] and by calculating explicitly the logarithmic derivatives of the wave functions in the energy range of the valence and lower conduction bands of α-quartz. The logarithmic derivatives also showed that using the p component as the local potential more closely mimics the missing d component in oxygen than does the s component. We took the p component as the local potential in silicon. No "ghost" states are produced with this potential, independent of the local component choice. However, the choice of the p component as the local potential improves the overall transferability of the pseudopotential. In Fig. 1 we illustrate the ionic pseudopotentials for both silicon

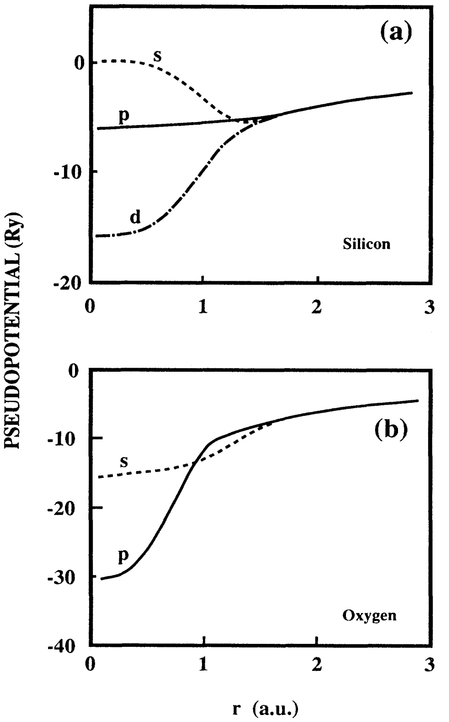

FIG. 1. Ionic pseudopotentials for (a) silicon and (b) oxygen. The potentials were determined using the method of Troullier and Martins (Ref. 22). Distance is in atomic units (a.u.).

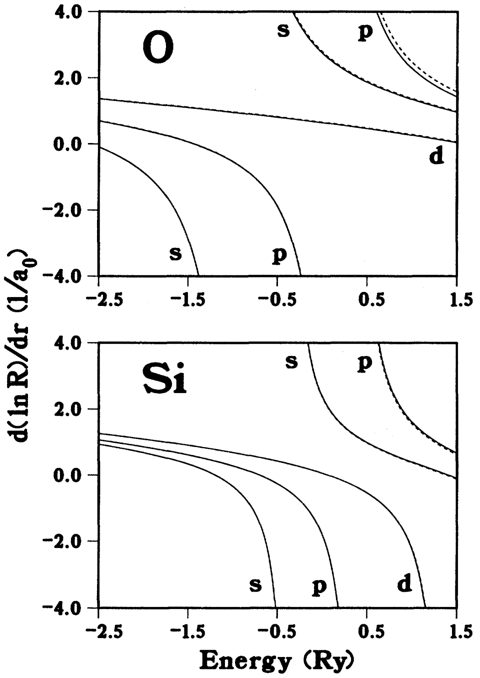

FIG. 2. Logarithmic derivatives for the Kleinman-Bylander separated pseudopotential (dashed line) and the all-electron potential (solid line) for the *s*, *p*, and *d* radial wave functions. The values were obtained at a radius of 1.8 a.u. for O and 3.0 for Si.

and oxygen. In Fig. 2 the logarithmic derivatives for both the silicon and oxygen Kleinman-Bylander pseudopotentials are presented.

The one-electron Schrödinger equation was solved using a fast iterative diagonalization technique.[25] One of the major advantages 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 with an energy up to a cutoff of 64 Ry were included in the basis set. Typically, 6700 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. The structural parameters converge more rapidly than the "absolute" energy. We used one special **k** point to evaluate the total electronic energy.[26] The energy change from one special point versus three **k** points was less than 0.01 eV/atom. This is not surprising given the large unit cell of α-quartz and the large band gap for this material. As one increases the unit-cell dimensions of a given crystal, zone-folding maps point back into the Brillouin zone. Although the three units of SiO_2 in the unit cell are not identical, they possess similar environments. Thus the mapping process results effectively in a "larger" number of sampling points than what might be expected. Since α-quartz is an insulator, one is not concerned about careful sampling near a Fermi level. To evaluate the total energy, a reciprocal-space method was used.[21]

As indicated above, determining the theoretical structural properties of SiO_2 in the α-quartz structure is complicated by the number of structural parameters. However, our pseudopotential-plane-wave method allows the rapid computation of forces. These forces were incorporated in a method by Davidon to minimize the total energy.[27] This algorithm avoids the one-dimensional line minimizations of the traditional conjugate gradient method. It should be more efficient when the computational effort required to calculate the forces is a fraction of the effort required to calculate the total energy. This is the case in our calculations. Several starting configurations were used to verify that the optimal structural parameters correspond to a global rather than a local minimum.

III. EQUATION OF STATE FOR α-QUARTZ

The α-quartz structure has hexagonal D_3^4 ($P3_121$) space-group symmetry.[1,28] In Fig. 3 we illustrate an α-quartz fragment and indicate the bond angles for Si—O—Si and O—Si—O. There exists only one distinct Si—O—Si angle, but four distinct O—Si—O angles. However, at ambient pressure the angles for O—Si—O are within a few degrees of the ideal tetrahedral angle. A primary challenge for interatomic potentials is to reproduce the observed changes in these angles with pressure. Several interatomic potentials have been developed which attempt to include bond-angle force for Si—O—Si and O—Si—O, but these potentials have not provided the

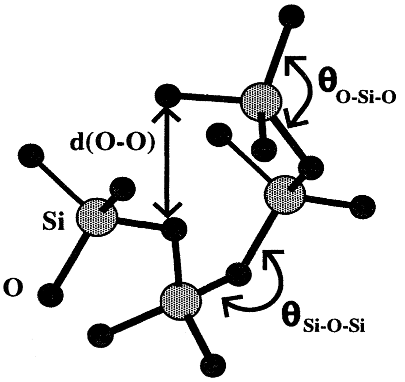

FIG. 3. Fragment of α-quartz illustrating the interpolyhedral O-O distance, the Si—O—Si bond angle, and the O—Si—O bond angle.

same accuracy available as fully quantum-mechanical calculations.[2,15–17]

To define the α-quartz structure, the lattice constants (c,a) and four internal parameters (u,x,y,z) must be specified.[28] If we fix a unit-cell volume, then the total electronic energy of the solid is a function of five parameters, e.g., $c/a,u,x,y,z$. In terms of the basis vectors, we have

$$\begin{aligned} \mathbf{a}&=(a/2)(\hat{\mathbf{x}}-\sqrt{3}\hat{\mathbf{y}}) , \\ \mathbf{b}&=(a/2)(\hat{\mathbf{x}}+\sqrt{3}\hat{\mathbf{y}}) , \qquad (1)\\ \mathbf{c}&=c\hat{\mathbf{z}} . \end{aligned}$$

The coordinates for the three silicon atoms are given by

$$\begin{aligned} \mathbf{R}(\mathrm{Si}_{(1)})&=-u(\mathbf{a}+\mathbf{b})+\tfrac{1}{3}\mathbf{c} , \\ \mathbf{R}(\mathrm{Si}_{(2)})&=u\mathbf{a} , \qquad (2)\\ \mathbf{R}(\mathrm{Si}_{(3)})&=u\mathbf{b}+\frac{2}{3}\mathbf{c} , \end{aligned}$$

and the coordinates for the six oxygen atoms are given by

$$\begin{aligned} \mathbf{R}(\mathrm{O}_{(1)})&=x\mathbf{a}+y\mathbf{b}+z\mathbf{c} , \\ \mathbf{R}(\mathrm{O}_{(2)})&=(y-x)\mathbf{a}-x\mathbf{b}+(z+\tfrac{1}{3})\mathbf{c} , \\ \mathbf{R}(\mathrm{O}_{(3)})&=-y\mathbf{a}+(x-y)\mathbf{b}+(z+\tfrac{2}{3})\mathbf{c} , \qquad (3)\\ \mathbf{R}(\mathrm{O}_{(4)})&=(x-y)\mathbf{a}-y\mathbf{b}-z\mathbf{c} , \\ \mathbf{R}(\mathrm{O}_{(5)})&=y\mathbf{a}+x\mathbf{b}+(\tfrac{2}{3}-z)\mathbf{c} , \\ \mathbf{R}(\mathrm{O}_{(6)})&=-x\mathbf{a}+(y-x)\mathbf{b}+(\tfrac{1}{3}-z)\mathbf{c} . \end{aligned}$$

We examined eight volumes and determined the optimal internal structure for each case; i.e., we optimized $c/a,u,x,y,z$ for each volume. In Fig. 4(a) we illustrate the calculated energy versus volume. A Murnaghan equation of state was fit to these points and used to determine the equilibrium energy and volume, the compressibility, and the derivative of the compressibility with pressure. These values are compared to experiment in Table I. A Birch-Murnaghan form[29] yielded essentially the same equation of state.

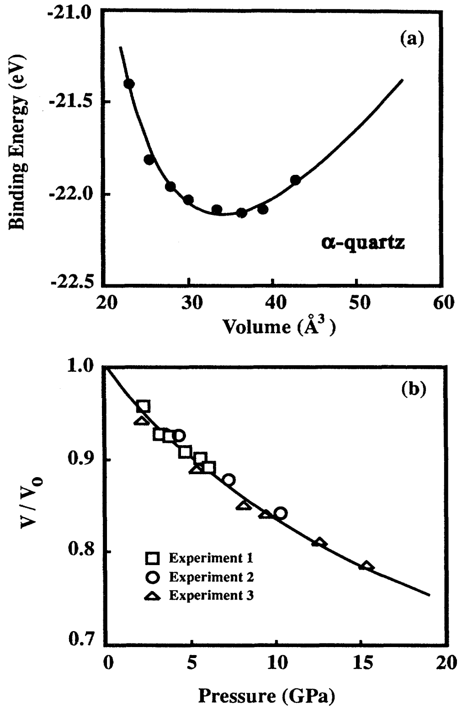

FIG. 4. (a) Calculated binding energy per molecular unit for α-quartz. The energy is referenced to the free atoms. The volume is per molecular unit. The curve is a Murnaghan fit to the calculated points. (b) Equation of state for α-quartz. The volume is normalized to the ambient experimental volume. Experiment 1 is from Levien, Prewitt, and Weidner (Ref. 8). Experiment 2 is from Glinnemann *et al.* (Ref. 7). Experiment 3 is from Hazen *et al.* (Ref. 4). The solid curve is the theoretical Murnaghan equation of state from the fit in (a).

As expected, our cohesive energy exceeds experiment by ~10%, as is normally the case for calculations using the local-density approximation. In general, the cohesive energy is a good test of the basis. If the cohesive energy is less than indicated by experiment, the basis is most likely poorly converged. We have included spin-polarization corrections in the cohesive-energy calculation.[30] For silicon the energy of the pseudoatom is −101.89 eV, including a correction of −0.65 eV for spin polarization. For oxygen the energy is −426.60 eV, including a correction of −1.51 eV for spin polarization. To arrive at the binding energy in Table I, we used a heat

TABLE I. Equation-of-state parameters for α-quartz. The experimental value of the cohesive energy is from Ref. 31; the structural parameters are from Refs. 4, 7, and 8. The volume and energy are per molecular unit of SiO_2.

	Equilibrium volume (Å^3)	Cohesive energy (eV)	Bulk modulus (GPa)	Pressure derivative of bulk modulus
Theory	35.8	22.2	38.1	3.9
Experiment	37.9	19.2	~34–37	~5–6

for formation of α-quartz of -217.7 kcal/mol, a cohesive energy for silicon of -106.5 kcal/mol, and a dissociation energy for O_2 of 119.2 kcal/mol.[31] We have not adjusted the experimental values for zero temperature (and zero-point motion), as would be appropriate in comparing experiment to our theoretical results. The inherent errors in the local-density theory probably exceeds any errors present in ignoring the role of temperature. This may not be true for the structural properties; however, we are not in a position at this stage to include changes in structure as a function of temperature.

The structural properties determined by local-density theory are expected to be more accurate than the cohesive energy as the cancellation of errors is expected to be more complete. We find this to be the case as the equilibrium volume is within ~5% of experiment and the bulk modulus within a few percent. The derivative of the bulk modulus merits special note. This quantity is very sensitive to the pressure-range fit and the weighting factors used. Such problems associated with determining the pressure derivative of the bulk modulus have been discussed by Bass *et al.*[32] Specifically, they note that the best estimates from the data of Levien, Prewitt, and Weidner[8] are 40.4±3.3 GPa for the bulk modulus and 4.5±1.8 for the derivative of the bulk modulus. This is consistent with the theoretical values of 38.1 GPa and 3.9, respectively. However, other experiments are not entirely consistent with the Levien data. For example, ultrasonic data, which is considered more reliable, yields values of 37.1±0.2 GPA and 6.3±0.3, respectively. We note that similar differences exist between experiment and theory for rutile.[33,34] The rutile calculation yields a smaller value for the derivative of the bulk modulus than measured by ultrasonic methods. We also note that the theoretical work is in accord with values of the derivative of the bulk modulus for other solids, i.e., values which typically range from ~3–5, whereas the values for oxides tend be larger, i.e., ~7–8. At present we have no clear explanation for these differences. Despite the differences for the derivative of the bulk modulus, the agreement between experiment and theory for the volume-versus-pressure curve is quite good [Fig. 4(b)].

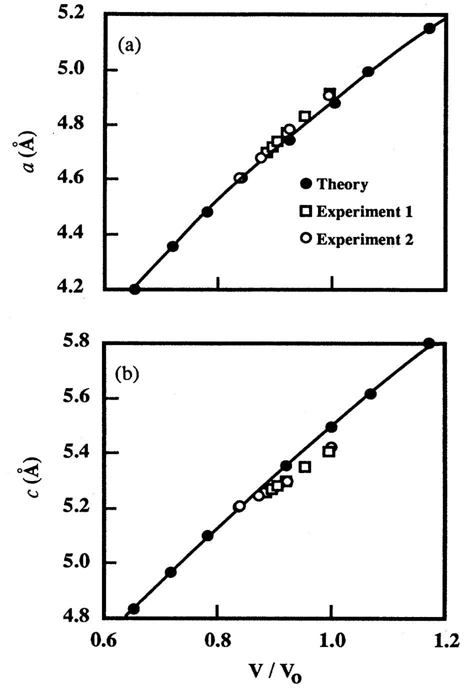

FIG. 5. Theoretical structural parameters for (a,c) vs the molecular volume for α-quartz and comparison to experiment. The volume has been normalized to the experimental volume. Experiments 1 and 2 are as in Fig. 4.

IV. STRUCTURAL PROPERTIES AS A FUNCTION OF PRESSURE

In Table II we give the optimized structural parameters for each volume we have investigated. In Fig. 5 we illustrate the (c,a) parameters as a function of volume and compare them to experiment.[4,7,8] The behavior of (c,a) is primarily linear as a function of volume within ~10% of the equilibrium. Experimentally, this ratio changes by ~2% from 1.101 at ambient pressure to 1.131 at 10.2 GPa (or $V/V_0=0.841$).[7] Theoretically, the change is less than 1% with the c/a ratio being about

TABLE II. Structural parameters for α-quartz as for a given molecular unit volume. The parameters have been determined on the basis of a self-consistent pseudopotential calculation using the local-density approximation.

Volume (Å^3)	V/V_0	a (Å)	c (Å)	u	x	y	z
44.460	1.174	5.1539	5.7981	0.4850	0.4359	0.2476	0.1455
40.508	1.070	4.9983	5.6171	0.4808	0.4265	0.2551	0.1339
37.862	1.000	4.8861	5.4944	0.4688	0.4176	0.2740	0.1184
34.914	0.922	4.7520	5.3558	0.4620	0.4100	0.2832	0.1063
31.860	0.842	4.6040	5.2067	0.4438	0.3951	0.3081	0.0901
29.640	0.783	4.4929	5.1044	0.4270	0.3842	0.3245	0.0836
27.169	0.718	4.3516	4.9704	0.4157	0.3717	0.3366	0.0765
24.701	0.652	4.2066	4.8347	0.4059	0.3497	0.3388	0.0769

1.125 at ambient pressure and about 1.131 at $V/V_0=0.842$. Since the structural parameters (c,a) can only be predicted to within a few percent, the c/a ratio cannot be expected to reproduce precisely the small experimental changes. The primary difference between experiment and theory is for the c parameter as indicated in Fig. 5. At ambient pressure the experimental value is 5.416 Å, and at $V/V_0=0.841$ the value is 5.207 Å. The corresponding theoretical values are 5.494 and 5.207 Å. The error in c is about 1.4% at ambient pressure and negligible at the higher pressure.

In Figs. 6 and 7 we present the variation of the internal parameters (u,x,y,z) with volume. Theory, unlike experiment, can determine the variation of these parameters for expanded systems, i.e., negative pressures, and for pressures higher than the transformation pressures. Unlike the (c,a) parameters, the internal parameters exhibit a more complex behavior; e.g., the u parameter tends to saturate quickly at large expanded volumes. Considering the inherent difficulties in our calculations and experiment, the agreement between theory and experiment is very good.

Although these internal parameters define the structure, the bond angles and lengths are of more physical interest. Experimentally accessible pressures indicate that the Si—O bond length is hardly altered with pressure. At ambient pressure this bond length is approximately 1.61 Å.[4,7,8] Within 0.01 Å the experimental x-ray work indicates that the bond length remains unchanged, or sightly shortens, with pressure up to 10 GPa. Our calculations agree with these results in that we find little change in the bond length. However, the theoretical bond length does not contract, but expands slightly between ambient pressure and 10 GPa. This counterintuitive finding is suggested from other experiments. For example, Hemley[35] has suggested on the basis of his Raman work that at modest pressures the Si—O bond may lengthen with pressure.

In Fig. 8 the bond angles for the Si—O—Si and O—Si—O angles are given and compared to experiment as a function of pressure (see Fig. 3 for an illustration of the geometry). In order to establish a common pressure scale, we have taken the equation-of-state parameters from Levien, Prewitt, and Weidner[8] and taken the equilibrium volume from experiment. This assures us that the unit-cell volumes for theory and experiment are identical when comparing the bond lengths and angles.

Our theoretical calculations are consistent with the experimental picture of α-quartz under pressure. Namely, with increasing pressure the tetrahedral O—Si—O angles show little variation until about 8 GPa. Above this pressure the tetrahedral angles show considerable distortion from the ideal value of 109.5°. For example, the predicted values for the largest and smallest angles at 20 GPa are about 116° and 104°, respectively. The bridging oxygen atom between the tetrahedral units forms very pliant bonds. The variation of the Si—O—Si angle dominates the differences between the various SiO_2 polytypes and among silicate structures. This angle shows considerable variation with pressure, which is consistent with experiment. Previous theoretical work[2] has not been able to

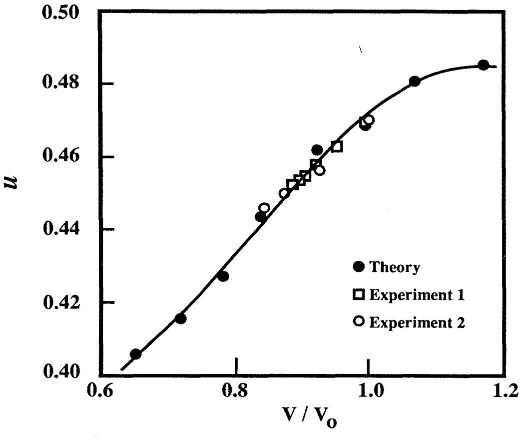

FIG. 6. Theoretical silicon structural parameter u vs the molecular volume for α-quartz and comparison to experiment. The volume has been normalized to the experimental volume. Experiments 1 and 2 are as in Fig. 4.

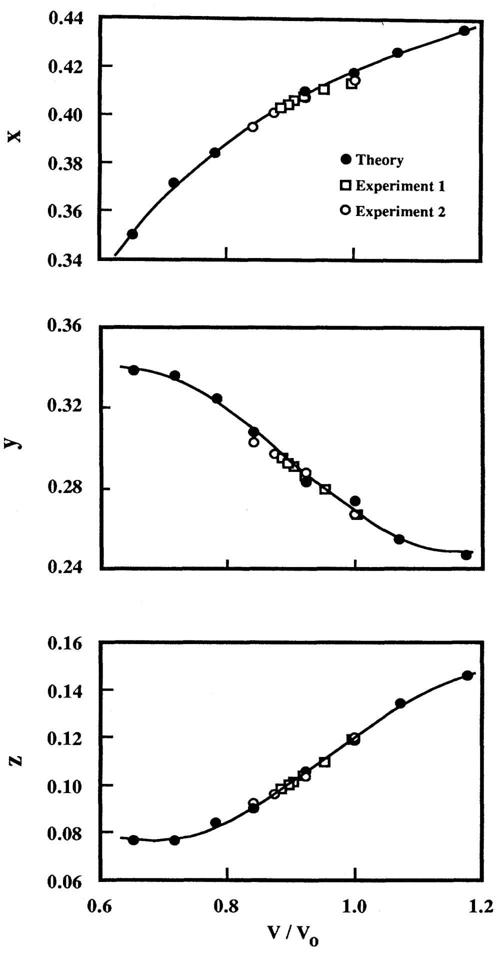

FIG. 7. Theoretical oxygen structural parameters x,y,z vs the molecular volume for α-quartz and comparison to experiment. The volume has been normalized to the experimental volume. Experiments 1 and 2 are as in Fig. 4.

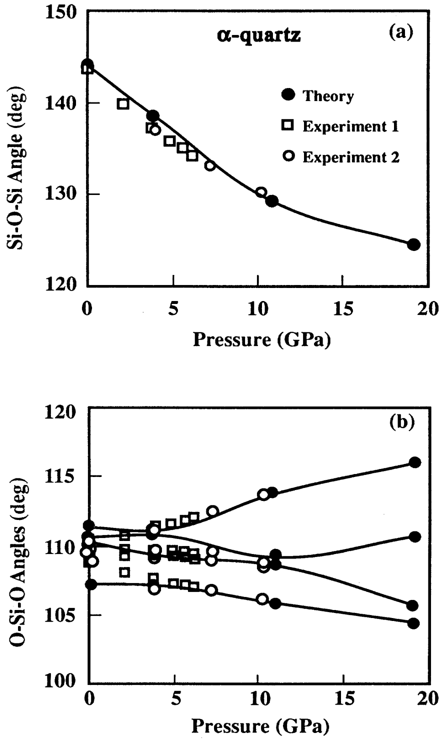

FIG. 8. Theoretical bond angles in α-quartz vs the molecular volume and comparison to experiment. The volume has been normalized to the experimental volume. Experiments 1 and 2 area as in Fig. 4. The bond angles are illustrated in Fig. 3.

yield such an accurate description of these bond-angle changes under pressure. Pairwise interatomic potentials have been developed to describe the ambient phases of SiO_2. These potentials predict the Si—O—Si angle deviation under pressure, but fail to account even qualitatively for changes in the O—Si—O bond angles. These latter angles are known to be strongly dependent on many-body, i.e., covalent, forces. The reason that the interatomic potentials work as well as they do for ambient pressure has been attributed to the strong Si—O bond and the incompressibility of this bond. Specifically, it appears that by constraining the Si—O bond length to be approximately 1.6 Å and preserving the symmetry for a given crystal structure, many of the structural parameters follow directly.

V. STRUCTURAL PROPERTIES NEAR THE ORDER-DISORDER TRANSITION

A primary problem in understanding the order-disorder transition of α-quartz is that experimental measurements become increasingly difficult near the transition. Moreover, surface effects can alter the nature of the transition.[3,4] For example, Hazen *et al.*[4] find evidence for incipient amorphization at a lower pressure than Hemley *et al.*[3] They suggest that this difference arises from their use of a single crystal as opposed to a polycrystalline sample. Our theoretical methods do not suffer from such problems. By preserving the crystalline symmetry, we can examine α-quartz in a perfect crystalline form at, and far above, the transition. The accuracy of the structural parameters for hypothetical high-pressure forms is expected to be similar to accuracy obtained for the ambient pressure case. Therefore, we can determine accurate bond angles and lengths for pressure regimes not accessible to experiment.

As α-quartz is subjected to pressure, we expect that strain fields will be created which are at variance with the bonding found in ambient pressure α-quartz. Eventually, the strain will be large enough to drive the crystal into another form of SiO_2. While we are not in a position to address the precise nature of the disordered form of SiO_2, we can ask whether the order-disorder transition pressure can be related to changes in bond angles or lengths. Hazen *et al.*[4] have attempted to correlate strains in the Si—O—Si angle with this transition. They used their data to extrapolate a value for this angle above ~15 GPa. The extrapolated angle is 120° or smaller. Moreover, they noted that molecular-orbital calculations[16] suggest a sharp increase of the strain energy with Si—O—Si angles below 120°. Thus they suggest that quartz approaches an energetically unfavorable configuration at 15 GPa. The chief driving force for disorder is the small Si—O—Si angle. We can test this suggestion with our theoretical work and the previous measurements of α-quartz under pressure. In Fig. 8 we plot the theoretical Si—O—Si angle out to approximately 20 GPa. At 20 GPa this angle is approximately 125°. We predict that this angle does not fall below 120° until a pressure of above ~40 GPa, a pressure well above the order-disorder transition. Our prediction is somewhat at variance with the Hazen *et al.*[4] suggestion, but it is consistent with other data.[7,8]

While the bond-angle behavior may be in question, there is no similar issue for the O-O interpolyhedral distance. A very useful approach to understanding the behavior of α-quartz is to envision the structure consisting of polyhedral units. Such an approach has led to qualitative predictions of the thermal expansion and bulk modulus.[36] Within this model the volume of empty voids in the framework is reduced under pressure and the compressibility of the crystal structure is much larger than that of a single tetrahedral unit.[37] It is common to use the O-O interpolyhedral distance as a fiducial measure of the empty voids between the tetrahedral units in α-quartz. As α-quartz is subjected to pressure, the volume between the tetrahedra rapidly decreases. This is reflected in the O-O interpolyhedral distance, which is the most rapidly varying structure parameter. Other O-O distances may be shorter and reflect stronger anion-anion interactions, but they correspond to oxygens bonded via a Si atom.

In Fig. 9 we illustrate the predicted separation distance as a function of pressure and compare it to experiment. Specifically, the minimum O-O separation between oxygens associated with different tetrahedral units is displayed. This O-O distance changes from 3.4 Å at ambient pressure to about 2.8 Å at 10 GPa. One can contrast this large change in distance with the Si—O bond

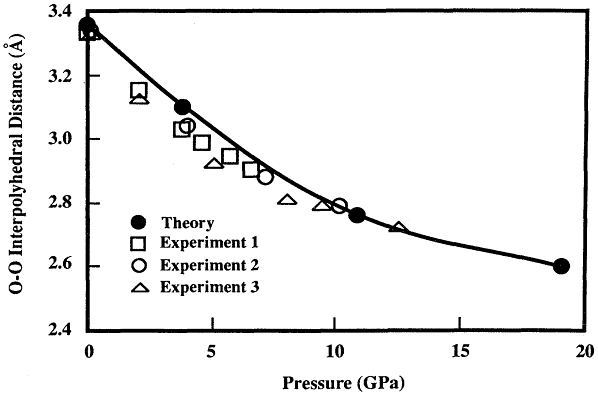

FIG. 9. Minimum O-O interpolyhedral distance vs pressure as predicted and measured for α-quartz. Experiments 1–3 are as in Fig. 4.

which changes less than 0.01 Å over a similar pressure range. The experimental and theoretical data in Fig. 9 both suggest that the distance is less than 2.75 Å above ~15 GPa. This value of 2.75 Å is significant according to Zemann.[38] Through an exhaustive search of the crystallographic literature, Zemann has concluded that the *shortest* known interpolyhedral distance in silicate materials is 2.75 Å and occurs in Be_2SiO_4. We note that at pressures which exceed ~15 GPa, the interpolyhedral distance in α-quartz falls below the shortest known distance occurring in nature. We suggest that the primary driving force for the order-disorder transition is not the bond-angle deviation in α-quartz, but the unphysically short interpolyhedral distance which occurs above 15 GPa. Our suggestion is consistent with the Hazen *et al.*[4] finding of incipient amorphization occurring at pressures near 15 GPa.

We also note that Sowa[37] has shown recently that a geometric consequence of extending the trends observed for the compression of α-quartz is a transition to a body-centered-cubic arrangement of the oxygen anions. Sowa predicts that the structural parameters for this ideal structure should be $c/a=\sqrt{3}/\sqrt{2}=1.225$ with the oxygen parameters given by $x=\frac{1}{3}$, $y=\frac{1}{3}$, and $z=\frac{1}{2}$. At the smallest volume we examined, ($V/V_0=0.652$) or at a pressure of ~80 GPa, we find $c/a=1.149$, and for the oxygen parameters, $x=0.350$, $y=0.339$, and $z=0.077$. Our oxygen parameters at high pressure agree very well with Sowa's suggestion, but the c/a ratio is significantly smaller than what one might expect for the ideal case. The pressure to achieve this hypothetical structure is far above the amorphization pressure for α-quartz. Nonetheless, it is interesting to speculate that such a structure might be conducive to forming an amorphous state. In the ideal cubic-body-centered arrangement of the oxygen anions, two types of tetrahedral structures occur: both of similar structure, but one with a silicon cation and one without. If the energy to switch silicons from a "filled" tetrahedral structure to an "empty" tetrahedral structure is small, then the barrier for a randomly arranged tetrahedron with and without a silicon cation might be small. It might be possible even in the nonideal form of this structure to have a low barrier to place randomly silicon atoms in the tetrahedral units and produce an amorphous phase.

VI. CONCLUSIONS

We note that this is an *ab initio* theoretical examination of α-quartz under pressure. Only recently have theoretical methods developed to the point of providing the accuracy and speed necessary for this type of calculation. Because we can maintain the symmetry of the crystal in our theoretical work, we can investigate α-quartz above the amorphous transition. Unlike experiment, which may exhibit large scatter in the structural parameters near the order-disorder transition, we lose no accuracy in our theoretical parameters near, or even far above, the transition pressure. Moreover, we can also predict the structural properties of α-quartz under large negative pressures.

With respect to the order-disorder transition, we suggest that the O-O interpolyhedral distance, which shows large variations with pressure, is a key mechanism in the transition. The shortest known O-O interpolyhedral distance is about 2.75 Å, which occurs for Be_2SiO_4. Our calculations predict that above ~15 GPa, this interpolyhedral distance approaches the shortest known value. Thus we might expect the α-quartz structure to become increasingly less stable when compared to other structures. The work of Hazen *et al.*,[4] which suggests incipient amorphization at a pressure as low as 15 GPa, is consistent with our suggestion.

ACKNOWLEDGMENTS

One of us (J.R.C.) would like to acknowledge support for this work by the U.S. Department of Energy of the Office of Basic Energy Sciences (Division of Materials Research) under Grant No. DE-FG02-89ER45391. We would also like to acknowledge computational support from Cray Research, Inc. and the Minnesota Supercomputer Institute.

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[1] A. F. Wells, *Structural Inorganic Chemistry,* 5th ed. (Oxford University Press, New York, 1984).

[2] J. R. Chelikowsky, H. E. King, Jr., and J. Glinnemann, Phys. Rev. B **41**, 10 866 (1990).

[3] R. J. Hemley, A. P. Jepcoat, H. K. Mao, L. C. Ming, and M. H. Manghnani, Nature **334**, 52 (1988).

[4] R. M. Hazen, L. W. Finger, R. J. Hemley, and H. K. Mao, Solid State Commun. **72**, 507 (1989).

[5] O. Mishima, L. D. Calvert, and E. Whalley, Nature **310**, 393 (1984).

[6] M. B. Kruger and R. Jeanloz, Science **249**, 647 (1990).

[7] J. Glinnemann, H. E. King, Jr., H. Schultz, Th. Hahn, S. J. LaPlaca, and F. Dacol, Z. Kristall. (to be published).

[8] L. Levien, C. T. Prewitt, and D. J. Weidner, Am. Mineral. **65**, 920 (1980).

[9] H. d'Amour, W. Denner, and H. Schultz, Acta Crystallogr. B **35**, 550 (1979).

[10] J. D. Jorgensen, J. Appl. Phys. **49**, 5473 (1978).

[11] D. B. McWhan, J. Appl. Phys. **38**, 347 (1967).

[12] B. Olinger and P. M. Halleck, J. Geophys. Res. **81**, 5711 (1976).

[13] S. N. Vaidya, S. Bailey, T. Paternack, and G. C. Kennedy, J. Geophys. Res. **78**, 6893 (1973).

[14] D. C. Allan and M. P. Teter, Phys. Rev. Lett. **59**, 1136 (1987).

[15] A. C. Lasaga and G. V. Gibbs, Phys. Chem. Miner. **14**, 107 (1987), and references cited therein.

[16] K. L. Geisinger, G. V. Gibbs, and A. Navrotsky, Phys. Chem. Miner. **11**, 266 (1985).

[17] S. Tsuneyuki, M. Tsukada, H. Aoki, and Y. Matsui, Phys. Rev. Lett. **61**, 869 (1988).

[18] J. R. Chelikowsky and M. Schlüter, Phys. Rev. B **15**, 4020 (1977).

[19] J. A. Tossel, D. J. Vaughan, and K. H. Johson, Chem. Phys. Lett. **20**, 329 (1973).

[20] K. L. Yup and W. B. Fowler, Phys. Rev. B **10**, 1400 (1974).

[21] For example, J. R. Chelikowsky and S. G. Louie, Phys. Rev. B **29**, 3470 (1984).

[22] N. Troullier and J. L. Martins, Solid State Commun. **74**, 613 (1990); Phys. Rev. B **43**, 1993, 8861 (1991).

[23] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1983).

[24] X. Gonze, P. Käckell, and M. Scheffler, Phys. Rev. B **41**, 12264 (1990).

[25] J. L. Martins and M. L. Cohen, Phys. Rev. B **37**, 6134 (1988).

[26] D. J. Chadi and M. L. Cohen, Phys. Rev. B **8**, 5747 (1973).

[27] See, e.g., W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes* (Cambridge University Press, Cambridge, England, 1988).

[28] W. G. Wyckoff, *Crytal Structures,* 4th ed. (Interscience, New York, 1974); Refs. 6–8.

[29] K. Y. Kim and A. L. Ruoff, J. Appl. Phys. **52**, 245 (1981).

[30] O. Gunnarsson, B. I. Lundqvist, and J. W. Wilkins, Phys. Rev. B **10**, 1319 (1974).

[31] *CRC Handbook of Chemistry and Physics,* 64th ed. (CRC, Boca Raton, Florida, 1983).

[32] J. D. Bass, R. C. Liebermann, D. J. Weidner, and S. J. Finch, Phys. Earth Planet. Inter. **25**, 140 (1981).

[33] H. J. McSkimin, P. Andreactch, Jr., and R. N. Thurston, J. Appl. Phys. **36**, 1624 (1965).

[34] K. M. Glassford, N. Troullier, J. L. Martins, and J. R. Chelikowsky, Solid State Comun. **76**, 635 (1990).

[35] R. J. Hemley, in *High Pressure Research in Mineral Physics,* edited by M. H. Manghnani and Y. Syono (Terra Scientific, American Geophysical Union, Washington, D.C., 1987), p. 347.

[36] R. M. Hazen and L. W. Finger, *Comparative Crystal Chemistry* (Wiley, New York, 1982).

[37] H. Sowa, Z. Kritstallogr. **184**, 257 (1988).

[38] J. Zemann, Z. Kritstallogr. **175**, 299 (1986).