

Structural Properties of α -Quartz near the Amorphous Transition

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Quartz undergoes a gradual transition with pressure from a crystalline to an amorphous state. The mechanism for this pressure-induced transition is not well understood. By combining new experimental pressure data and recently developed theoretical methods, we have determined the structural properties of α -quartz near and above this transition. We suggest that highly unfavorable interpolyhedral anion-anion distances, which occur at the transition pressure, play a key role in driving the transition.

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One of the most difficult materials to describe theoretically is SiO_2 . The bonding in this material is complex. The Si-O bond combines strong ionic and covalent bonding, and lone-pair oxygen orbitals are present. Moreover, SiO_2 occurs in a wide variety of forms with only small energy differences between the forms. Thus, it may not be too surprising that SiO_2 also exhibits an unusual order-to-disorder transition under pressure.¹ At ~ 30 GPa, α -quartz undergoes a gradual transition from a crystalline to an amorphous form. Hazen *et al.*² have interpreted their pressure measurements on α -quartz as providing evidence for the onset of amorphization at ~ 15 GPa. Such transitions also occur in other oxides, e.g., in water³ and AlPO_4 .⁴ In AlPO_4 the problem is compounded by a glass "memory" phenomenon. Upon the release of pressure, the glass form of AlPO_4 reverts to the previous crystallographic orientation of the crystal from which it forms.⁴

Here we concentrate on SiO_2 in the α -quartz structure. This structure is dominated by tetrahedral units of silicon surrounded by four oxygen atoms. A common interpretation is that these tetrahedra are loosely preserved as a function of pressure; however, the orientation of the tetrahedra and their role in the order-disorder transition are not well understood. Several structural studies^{2,5-11} of α -quartz exist as a function of pressure, but these studies become increasingly unreliable near the transition. Moreover, while theoretical methods¹²⁻¹⁹ 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.¹³⁻¹⁶ A few solid-state calculations exist,^{12,17-19} but these have been limited to examining the electronic properties, or ambient-pressure structures.

In this work, we employ recently developed pseudopotential methods to describe the subtle changes in the structure of α -quartz as a function of pressure. The only input into our calculations are the atomic number of the species present and the crystal symmetry. This 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 can describe the structure of a hypothetical crystalline material at pressures considerably above the order-disorder transition. The theoretical structural properties for α -quartz above the transition can provide us with insights which cannot be obtained experimentally.

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 . Also, the oxygen potential is difficult to describe with a weak pseudopotential as oxygen has no p states with the ion core. No orthogonality condition exists for the p states and the oxygen potential for this component is much stronger than for the corresponding s states. In such situations, local bases such as Gaussians are often employed. These bases usually result in rather complicated matrix elements and are computationally cumbersome. Here we use newly developed pseudopotentials which allow the use of a plane-wave basis. Our pseudopotentials were generated self-consistently within the local-density approximation using the method of Troullier and Martins.²⁰ This method produces a "soft" pseudopotential. The Troullier-Martins pseudopotential allows 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. We also incorporate a Kleinman-Bylander separation²¹ in evaluating the required matrix elements.

The one-electron Schrödinger equation was solved using a fast iterative diagonalization technique.²² 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, leading to a dramatic reduction in storage and a considerable reduction in computational time. Plane waves with an energy 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. 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.

With respect to the experimental determination of structure, previous work has been carried out by Levien, Prewitt, and Weidner⁶ and Hazen *et al.*² However, their work was limited in pressure range and accuracy. We concentrate on the recent work of Glinnemann *et al.*⁵ who made measurements to 10.2 GPa. The measurements of Glinnemann *et al.* were made on a small single-crystal sample enclosed in a diamond-anvil cell. The cell design and equi-inclination x-ray-scattering geometry allowed higher pressures while maintaining high precision. The conventional crystallographic quality factors (R 's) obtained from the least-squares structural refinements were approximately 2.5%. Consequently, the lattice and internal structural parameters are well determined.

Determining the theoretical structural properties of SiO_2 in the α -quartz structure is complicated by the number of structural parameters. The α -quartz structure has hexagonal D_3^4 symmetry and contains three molecular units of SiO_2 . Each SiO_4 tetrahedral unit is bridged via Si-O-Si bonds to neighboring tetrahedra. To define this structure, the lattice constants (c, a) and four internal parameters (u, x, y, z) must be specified.²³ If we fix a unit-cell volume, then the total electronic energy of the solid is a function of five parameters, e.g., $c/a, u, x, y, z$. Determining the structural parameters involves minimizing a multiparameter total-energy function. This is a primary reason for using interatomic potentials based on molecular-orbital methods instead of computing the quantum-mechanical forces for the solid state. Numerous evaluations of the forces must be made to insure 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. However, our pseudopotential-plane-wave method allows the rapid

computation of forces. These forces were incorporated in a method by Davidson to minimize the total energy.²⁴ Several starting configurations were used to verify that the optimal structural parameters correspond to a global rather than a local minimum. This method is very efficient; however, the energy convergence required to determine the final set of parameters is quite high.

In Fig. 1, we compare our calculated pressure-volume relationship to experiment. We examined eight volumes and determined the optimal internal structure for each case. A Murnaghan equation of state was used to determine the equilibrium energy and volume, the compressibility, and the derivative of the compressibility with pressure. A Birch-Murnaghan form²⁵ yielded essentially the same equation of state. The calculated cohesive energy is 22.2 eV per molecular unit as contrasted to the experimental value²⁶ of 19.2 eV. Local-density calculations generally overestimate the binding energy of a solid by about 10% so an error of about 2 eV is not unexpected for this system. We have included spin-polarized corrections in the total-energy calculation, but not temperature. The inherent errors in local-density theory probably exceed any errors present in ignoring the role of temperature. The structural properties determined by

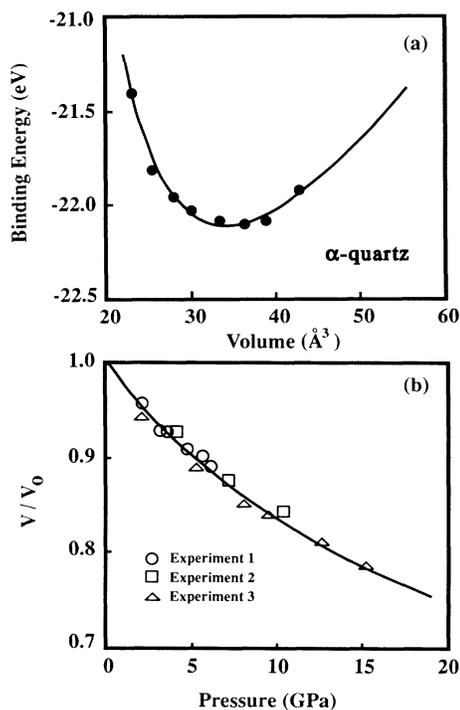


FIG. 1. (a) Calculated binding energy per molecular unit for α -quartz. The energy is referenced to the free atoms. The volume is per molecular unit. The curve is a Murnaghan fit to the calculated points. (b) Equation of state for α -quartz. The volume is normalized to the ambient experimental volume. Experiment 1 is from Levien, Prewitt, and Weidner (Ref. 6). Experiment 2 is from Glinnemann *et al.* (Ref. 5). Experiment 3 is from Hazen *et al.* (Ref. 2). The solid curve is the theoretical Murnaghan equation of state from the fit in (a).

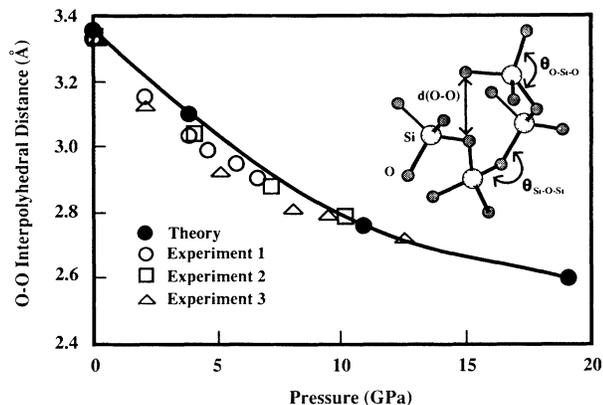


FIG. 2. The minimum O-O interpolyhedral distance vs pressure as predicted and measured for α -quartz. Experiments 1, 2, and 3 are as in Fig. 1(b). Inset: The O-O interpolyhedral distance along with the Si-O-Si and O-Si-O bond angles. The solid curve has been fitted to the calculated points.

local-density theory tend to be more accurate than the cohesive energy as the cancellation of errors is expected to be more complete. The equilibrium volume was computed to be 35.8 \AA^3 per molecular unit. The experimental value^{2,5,6} is 37.9 \AA^3 . The experimental value^{2,5,6} for the bulk modulus is about 34–37 GPa as compared to our theoretical value of 38.1 GPa.

The equation of state for α -quartz is consistent from one experiment to another and with theory; however, the internal structural parameters have been more contentious. Some general features are well accepted. Under pressure, the tetrahedral units initially remain unaltered while the separation of these units decreases. In Fig. 2, we show the predicted separation distance as a function of pressure and compare to experiment. Illustrated is the minimum O-O separation between oxygen atoms associated with different tetrahedral units. This O-O distance changes from 3.4 \AA at ambient pressure to about 2.8 \AA at 10 GPa. For comparison, the Si-O bond length is hardly altered. At ambient pressure this bond length is approximately 1.61 \AA . However, within 0.01 \AA the bond length remains unchanged² at pressures less than 10 GPa. The theoretical bond length may even lengthen a bit between ambient pressure and 10 GPa; the change in length is less than 0.01 \AA . However, recent experimental work by Hemley²⁷ does tend to confirm this prediction of a lengthened Si-O bond at modest pressures.

In Fig. 3, the bond angles for the Si-O-Si and O-Si-O angles are given and compared to experiment (see Fig. 2 for an illustration of the geometry). The 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 be-

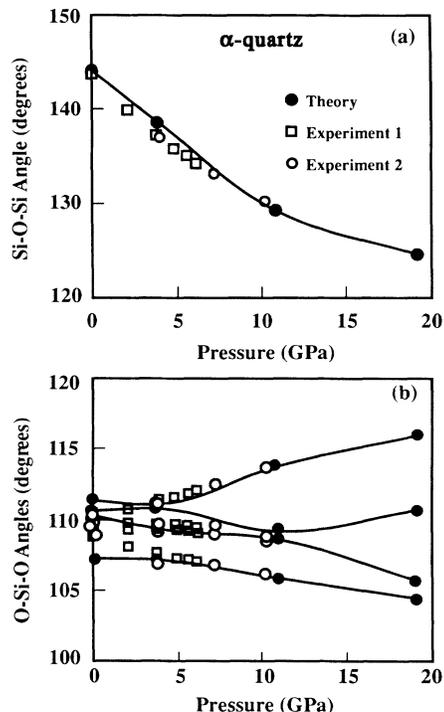


FIG. 3. (a) The Si-O-Si bond angle as a function of pressure as predicted and as measured. The solid curve is a guide to the eye; the calculated points are indicated by the solid circles. (b) The O-Si-O bond angles as a function of pressure as predicted and as measured. Four distinct angles exist for the α -quartz structure. The solid curve has been fitted to the calculated points. Experiments 1 and 2 are as in Fig. 1(b).

tween 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 in general. This angle shows considerable variation with pressure which is consistent with experiment and the decreasing O-O interpolyhedral distance. Previous theoretical work¹⁶ has not been able to 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.

A natural question to ask is whether the order-disorder transition pressure can be related to changes in bond angles or lengths. Hazen *et al.*² have attempted to correlate strains in the Si-O-Si angle with this transition. They use their data to extrapolate a value for this angle at 15 GPa. The extrapolated angle is 120° or smaller. Moreover, they note that molecular-orbital calculations¹⁴ indicate a sharp increase of the strain energy with Si-O-Si angles below 120° . Coupled with their measurements, they believe this calculation suggests that quartz approaches an energetically unfavorable configuration

above 15 GPa. The chief driving force 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. 3, 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 at least ~ 40 GPa, a pressure well above the order-disorder transition. Thus, our prediction is somewhat at variance with the Hazen *et al.*² suggestion.

While the bond-angle behavior may be in question, there is no similar issue for the O-O interpolyhedral distance. It is common to use this distance as a fiducial measure of the volume between the tetrahedral units. One can use this distance as a guide to the "openness" of the structure. Other O-O distances may be shorter, but they correspond to oxygen atoms bonded via a Si atom. Moreover, this distance is the most rapidly varying structural parameter as α -quartz is subjected to pressure. The experimental and theoretical data in Fig. 2 both suggest that the distance is less than 2.75 Å above ~ 15 GPa. This value of 2.75 Å is significant according to Zemmann.²⁸ Through an exhaustive search of the crystallographic literature, Zemmann 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. Thus, we suggest that the primary driving force for the order-disorder transition may not be the bond-angle deviation in α -quartz, but the unphysically short interpolyhedral distance which occurs above ~ 15 GPa. We also note that Sowa²⁹ 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. While our calculations confirm such a trend, the high-pressure phase remains significantly distorted from a true cubic structure.

In summary, we note that this is the first *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. We hope that the detailed structural information of this work will provide deeper insights into the chemical bond as a function of pressure, e.g., the role of the interpolyhedral O-O distance. Moreover, our work can serve as a standard by which more approximate methods can be tested.

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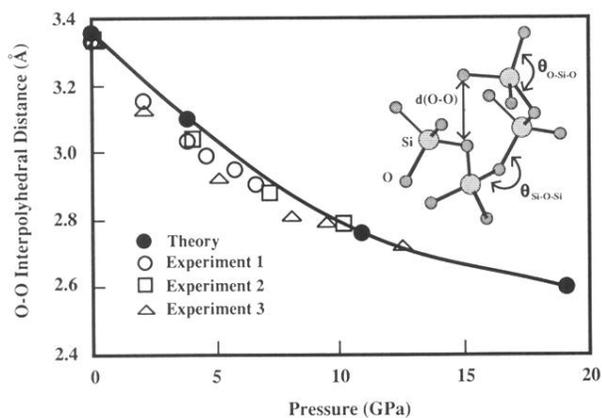


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