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Anomalous elastic behavior in crystalline silica

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A low-density polymorph of silica, α-cristobalite, has been observed to have a *negative* Poisson ratio, i.e., when subjected to a uniaxial compression, this crystal contracts in the transverse direction. This behavior is uncommon. Other low-density polymorphs of silica, which have a similar chemical environment, have been reported to have *positive* Poisson ratios. We have investigated the elastic behavior of several silica phases: α-quartz, β-quartz and α-cristobalite, with first-principles quantum-mechanical calculations, and with interatomic potentials. Our calculations confirm a negative Poisson ratio in α-cristobalite. We predict that α-quartz will have a negative Poisson ratio at high tensile strains, and that β-quartz will *never* assume a negative ratio. We compute the second-order elastic constants of α-quartz and α-cristobalite using interatomic potentials and apply them in discussing the anisotropy of Poisson ratios in these materials. We demonstrate that the rigidity of the SiO_4 tetrahedral units is intimately related to the occurrence of negative Poisson ratios in crystalline forms of silica.

I. INTRODUCTION

The response of a solid to a uniaxial stress is characterized by its Poisson ratio. It is determined by the coupling between the stretching force and accompanying shear deformation. It is defined as the negative quotient of the strain in the transverse direction to the strain applied in the longitudinal direction. Most solids contract laterally when subjected to a uniaxial tension; thereby giving a positive Poisson ratio. Few examples of materials with negative Poisson ratios are available in the literature. While certain isotropic polymer foams have been seen to have a negative Poisson ratio,[1] for crystalline solids it is a rarity. An example of cubic single-crystal pyrite with a Poisson ratio of $-\frac{1}{7}$ has been cited.[2] However, it was suggested that this case may have resulted from "twinning" of the crystals. In a study of anisotropy of elastic properties for hexagonal crystals,[3] it was shown that Poisson ratio for single-crystal cadmium is negative in certain directions.

Given this background, it was surprising to find a negative Poisson ratio in a common crystalline material. In a recent experimental study, Weidner *et al.*[4] found α-cristobalite to have a negative Poisson ratio. α-cristobalite is a low-density silica polymorph in which silicon atoms are tetrahedrally coordinated. Other polymorphs like α- and β-quartz have a similar bonding environment. However, they have been reported to have a positive Poisson ratio.[5]

In this paper, we have calculated the Poisson ratios of these crystalline solids for a loading along the c axis. For our computations, we have employed first-principles pseudopotentials developed in the Troullier-Martins scheme.[6] These reliable pseudopotentials have given a highly accurate picture of electronic and structural properties of silica.[7–10] We have also applied a two-body potential developed from Hartree-Fock calculations on SiO_4^{-4} clusters.[11] This interatomic potential has been tested thoroughly for crystalline silica. Surprisingly, it often gives an accurate description of structural and elastic properties of silica. We have confirmed our pair potential calculations with the fully quantum-mechanical calculations.

On the basis of our calculations, we find a negative Poisson ratio for α-cristobalite at ambient conditions.[12] We predict that α-quartz will also have a negative Poisson ratio at high tensile strains when subjected to a uniaxial loading along the c axis. We also explain why β-quartz can never exhibit this property for such a loading. We study how the atomic arrangements in these materials change with a uniaxial stress. We follow the motion of the $Si(O_{1/2})_4$ tetrahedra in α-cristobalite and demonstrate that the rigidity of these tetrahedral units is the cause of negative Poisson ratios in low-density crystalline silica.

We have computed the elastic constants of α-quartz and α-cristobalite in the pair potential framework. For this purpose, the method of long waves is used.[13] They

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agree with the experimental values[4,14] within a few percent. We have analyzed the anisotropy of the Poisson ratios in α-quartz and α-cristobalite using these calculations. This analysis shows that even at ambient conditions, both these materials exhibit anisotropy and have negative Poisson ratios for loading in certain directions. However, the anisotropy is markedly higher for α-cristobalite. This causes a negative isotropic aggregate Poisson ratio in this material.

II. POISSON RATIO OF CRYSTALLINE SILICA

A generalized definition for the Poisson ratio (σ_{ij}) in a material is the negative ratio of transverse strain in the i direction resulting from an applied strain in the j direction. For a crystalline material with a tetragonal or a hexagonal unit cell defined by the lattice parameters a and c, the Poisson ratio for a uniaxial loading along the c axis is given by

$$\sigma_{13} = -\frac{\triangle a/a}{\triangle c/c} = -\frac{\triangle \ln(a)}{\triangle \ln(c)} \ . \qquad (1)$$

Since a solid usually attempts to conserve volume, compression along an axis is expected to result in an expansion in the transverse direction. This gives a positive value of Poisson ratio; an empirical rule that is satisfied by most known materials. The requirement that the strain energy for an elastic isotropic solid be nonnegative only leads to the restriction $-1 \leq \sigma \leq \frac{1}{2}$: the lower and upper limits indicate conservation of shape and size, respectively. A negative value of Poisson ratio is not forbidden by thermodynamic considerations.

Weidner, Yeganeh-Haeri, and Parise[4] measured single-crystal elastic moduli of α-cristobalite. They reported a Poisson ratio (Voigt-Reuss-Hill average[5]) of -0.163 for α-cristobalite calculated using the following relationship:

$$\sigma_{\rm avg} = \frac{3B - 2G}{2(3B+G)} \qquad (2)$$

where B, G, and $\sigma_{\rm avg}$ stand for the bulk modulus, shear modulus, and the isotropic average Poisson ratio, respectively.

Considering the rarity of crystalline materials with a negative ratio, this result is surprising. Moreover, α-cristobalite has the same chemical environment as other low-density forms of crystalline silica such as α- and β-quartz. These latter crystals are reported to have a positive Poisson ratio at ambient pressure.[5] An experimental determination of a negative Poisson ratio is difficult and could be spurious.[15] A theoretical determination can provide a strong corroboration of the experimental observation; however, few such calculations have been performed. Since $\sigma_{\rm avg}$ is negative for α-cristobalite, the Poisson ratio *has* to be negative for loading in certain directions. By calculating σ_{13} as defined in Eq. 1, we can study the effect of loading along the c axis. To study complete anisotropy (loading in arbitrary directions) of elastic properties, the second-order elastic constants have to be computed.

III. COMPUTATION OF ELASTIC PROPERTIES

We have carried out a detailed analysis of the elastic behavior of crystalline silica using two theoretical approaches. One approach is based on *ab initio* pseudopotentials and is fully quantum mechanical. We have applied "soft" pseudopotentials constructed within the local density approximation (LDA). These pseudopotentials have been shown to have a wide range of applicability and transferability.[6] These calculations are highly accurate in terms of structural properties, but they are computationally intensive.

The details of our quantum-mechanical calculations have been presented in detail elsewhere.[7] The essential features are as follows. Our pseudopotentials were generated self-consistently within the LDA using the method of Troullier and Martins.[6] This method produces "soft" pseudopotentials, i.e., potentials which 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 both silicon and oxygen.

The one-electron Schrödinger equation was solved using a fast iterative diagonalization method.[16] 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, a few thousand (5000–10 000) plane waves were used in the basis. In our calculations, we used one special **k**-point to evaluate the total energy.

Our other approach is based on classical interatomic potentials. The pair potential that we have used in this study was developed using Hartree-Fock self-consistent calculations on SiO_4^{-4} clusters.[11] Earlier studies have indicated that this interatomic potential works well for structural and elastic properties of silica structures.[10,11] However, one might not expect this approach to work for details of the elastic properties of silica, especially for open structures where angular forces might be important.

A. Uniaxial loading along the c axis

Determining the Poisson ratio of these polymorphs is complicated by their large unit cells and the number of degrees of freedom that the atoms have. For example, α-cristobalite has a tetragonal unit cell which is completely defined by the lattice constants a and c, and by the internal coordinates u, x, y, and z.[17] We used the following methodology based on Eq. (1). For a fixed value of c, we let the lattice parameter a and internal coordinates relax to find a minimum energy structure. We then changed the values of c and let the a parameter and the internal coordinates relax to find the minimum energy structure for the new value of c. This gives us $\ln(a)$ as a function of $\ln(c)$.

Owing to computational intensity of this calculation, we optimized geometries using pseudopotential calculations at four values of c for each polymorph. For these calculations, we employed a minimization routine based on a method given by Davidon *et al.*[18] Figure 1(a) illustrates the optimization of the structure for a given c. The variation of $\ln(a)$ with $\ln(c)$ is shown in Fig. 1(b).

In our pair potential calculations, we examined about 50 values of lattice parameter c. Here we optimized the geometries using the routine AMOEBA, the details of which can be found in Ref. 19. We plotted $\ln(a)$ as a function of $\ln(c)$ for this uniaxial compression. Over the large range of c that we examined (corresponding to -10 to $+5\%$ strain), the variation is no longer linear. We fit a third order polynomial to the data. The negative of the slope of this curve gives us the Poisson ratio at the corresponding value of c.

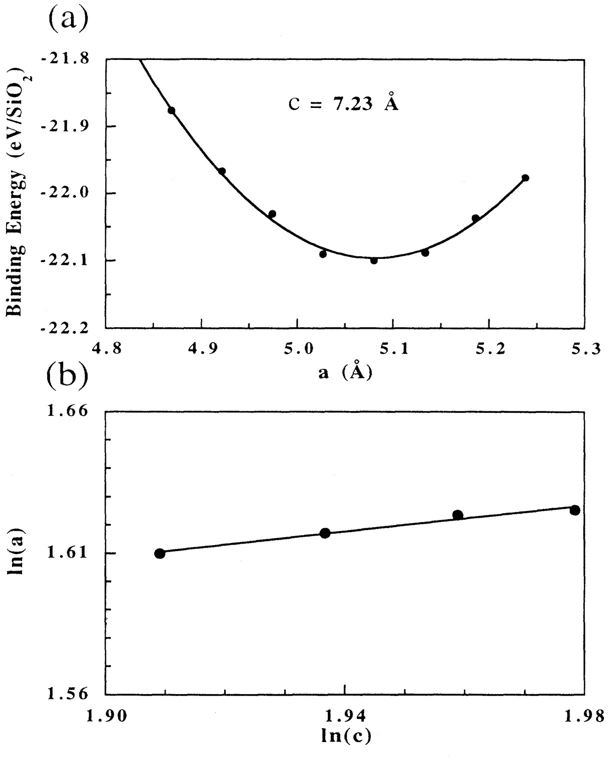

FIG. 1. Computing the Poisson ratio for a loading along the c axis: (a) The variation of the total energy of α-cristobalite as a function of the lattice parameter a at $c = 7.23$ Å. This gives the minimum energy structure at the given value of c for a uniaxial loading. (b) The variation of the lattice parameter a as a function of c on a logarithmic scale. The slope of the best fitting straight line is the Poisson ratio of α-cristobalite at zero pressure.

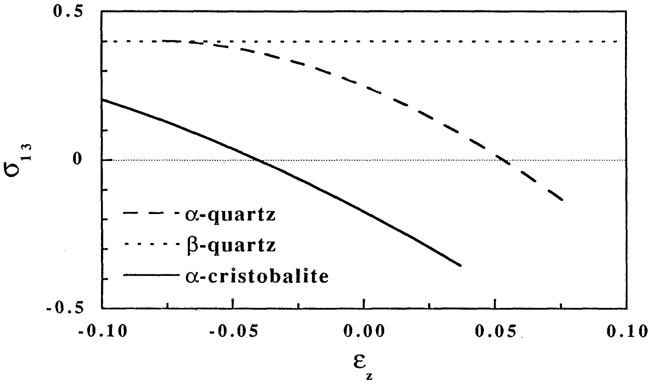

FIG. 2. The variation of the Poisson ratios of α-quartz and α-cristobalite as a function of the uniaxial strain along the c axis. This figure is based on our pair potential calculations. Note that a *positive* strain occurs for a material under *tension.*

In Fig. 2, we have shown the variation of the Poisson ratio as a function of the engineering strain along the c axis defined as $\epsilon_z = (c - c_0)/c_0$. It is interesting to see that if α-cristobalite is compressed beyond $\epsilon_z = -0.04$ (which corresponds to a compressive stress of about 2.5 GPa) the Poisson ratio assumes positive values. As the material is compressed along the c axis, the Poisson ratio becomes more and more positive. We predict at high compressive strains the ratio to saturate near a value of 0.3 as compared to the value of 0.5 for an incompressible solid. Our pair potential and pseudopotential calculations give values -0.17 and -0.2, respectively, for the Poisson ratio (σ_{13}) at the unstrained geometry. The isotropic average value (σ_{avg}) reported from recent experiments[4] is -0.163.

For α-quartz at ambient pressure, the pair potentials and pseudopotentials give Poisson ratio (σ_{13}) of 0.2 and 0.1, respectively. The reported isotropic average value[5] (σ_{avg}) is 0.08. The variation of the Poisson ratio for α-quartz as a function of strain shows similar trends as α-cristobalite (Fig. 2). The Poisson ratio decreases and for large tensile strain exhibits a negative ratio. The major difference between α-quartz and α-cristobalite is that the ratio becomes negative for α-cristobalite at ambient pressure whereas for α-quartz the ratio remains positive. On the basis of this work, we *predict* that the Poisson ratio for α-quartz will be *negative* at high tensile strains as it is for α-cristobalite at ambient pressure.

For β-quartz, we applied the pair potential over a wide range of strain, $-0.15 < \epsilon_z < 0.15$. Unlike α-quartz and α-cristobalite, β-quartz is found to have a constant Poisson ratio (σ_{13}) of 0.4. Our pseudopotential calculations for ambient pressure give a Poisson ratio of 0.4, confirming our pair potential calculations. It is surprising to see that despite the similarities between the low-density silica polymorphs, β-quartz shows a significantly different elastic behavior when compared to the other two polymorphs.

B. Second-order elastic constants

As seen above, the computation of the Poisson ratio σ_{13} is relatively straightforward. To get a complete pic-

TABLE I. Single-crystal elastic constants (in GPa) of α-quartz and α-cristobalite.

	α-quartz		α-cristobalite	
	Experiment[a]	Theory	Experiment[b]	Theory
C_{11}	87.103	71.5	59.4	51.5
C_{33}	108.552	99.1	42.4	35.3
C_{44}	59.215	42.4	67.2	59.0
C_{66}	38.339	30.9	25.7	17.5
C_{12}	10.425	9.7	3.8	6.0
C_{13}	12.894	15.5	-4.4	-3.1
C_{14}	-17.206	-13.1	–	–

[a] Reference 14.

[b] Reference 4.

ture of the elastic properties of a material, it is necessary to compute its second-order elastic constants. Here we apply the pair potential approach for this purpose. (It is possible to compute the second-order elastic constants of a solid from *ab initio* pseudopotentials. However, owing to the required accuracy, these calculations are very intensive.)

For the pair potential approach, we applied the method of long waves[13] to compute the elastic constants of α-quartz and α-cristobalite. This method is based on the following principle: when lattice vibrations with wavelengths much larger than the interatomic spacings interact with matter, its microscopic nature (other than the symmetry properties) may be neglected. Since a phonon wave vector $\mathbf{q}$ is associated with lattice vibrations of wavelength $\lambda = 2\pi/|\ q\ |$, the vibrational modes of the crystal for $\mathbf{q} \to \mathbf{0}$ must be associated with its continuum properties (e.g., elastic constants). To apply this principle, we compute the dynamical matrix, and its first and second derivatives for $\mathbf{q}=\mathbf{0}$, and use them in determining the elastic stiffness matrix (C). For the non-Coulombic part of the potential, this does not pose a problem. However, the Coulomb part of the interatomic potential has a very long range and we applied the Ewald method for computing lattice sums.

The advantage of this technique is that given an optimized structure at any pressure, we can compute all the second-order elastic constants in one run. The results of our computations are in good agreement with the experimental values[4,14] of the single-crystal elastic moduli (Table I). The compliance matrix (S) may be computed as the inverse of the stiffness (C) matrix.

IV. ANISOTROPY OF POISSON RATIO

In the previous section, we discussed the Poisson ratio of low-density silica polymorphs for a uniaxial loading along the c axis. The problem is much more complicated if the elastic response for loading in an arbitrary direction is to be studied. Towards this end, the second-order elastic compliances (S_{ij}) have to be used. Kittinger, Tichý, and Bertagnolli[20] have shown that α-quartz has an "effective" negative Poisson ratio in certain directions. Here, we will discuss α-cristobalite along similar lines and compare it with α-quartz. For this purpose, we will use the elastic compliances from our pair potential calculations.

If the orientation of the crystal is changed, the compliances (S_{ij}) transform to (S'_{ij}). References 21 and 22 describe the coordinate transformations of the elastic properties of crystals in depth. In particular, we consider S'_{13}, S'_{23}, and S'_{33} when the crystals of α-quartz and α-cristobalite are rotated about their x axes by angle ξ (Fig. 3). The new axes are denoted by primes as well $(x' = x, y', z')$. These compliances transform as follows:

$$\begin{aligned} S'_{13} &= s^2 S_{12} + c^2 S_{13} - scS_{14}\ , \\ S'_{23} &= (s^4 + c^4)S_{13} + c^2 s^2 (S_{11} + S_{33} - S_{44}) \\ &\quad + sc(c^2 - s^2)S_{14}\ , \\ S'_{33} &= s^4 S_{11} + c^4 S_{33} + c^2 s^2 (2S_{13} + S_{44}) + 2csS_{14}\ , \end{aligned} \tag{3}$$

where $s = \sin\xi$ and $c = \cos\xi$. (In α-cristobalite, $S_{14} = 0$ and the equations simplify.)

For a loading along the j axis, the generalized Poisson ratio is given by

$$\sigma'_{ij} = -\frac{S'_{ij}}{S'_{jj}} \quad (i,j = 1,2,3)\ , \tag{4}$$

where i is a transverse direction under consideration.

We consider a loading along the z' axis. Let the Poisson ratio in a transverse direction (in the $x'y'$ plane) making an azimuthal angle ϕ with the $x' = x$ axis be denoted by $\sigma'_3(\xi,\phi)$. In particular, $\sigma'(\xi,0) = \sigma'_{13}(\xi)$ and $\sigma'(\xi,\frac{\pi}{2}) = \sigma'_{23}(\xi)$. Kittinger, Tichý, and Bertagnolli[20] define an "effective Poisson ratio" $\overline{\sigma_3}(\xi)$ as

$$\overline{\sigma'_3}(\xi) = \frac{1}{2\pi}\int_0^{2\pi} \sigma'_3(\xi,\phi)d\phi\ . \tag{5}$$

They further give a simpler expression for α-quartz, which also holds for α-cristobalite:

$$\overline{\sigma'_3}(\xi) = \frac{\sigma'_{13}(\xi) + \sigma'_{23}(\xi)}{2}\ . \tag{6}$$

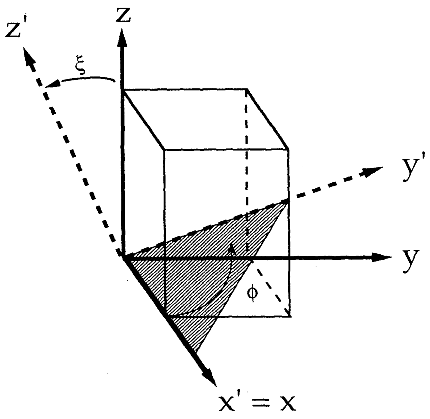

FIG. 3. Rotation of the crystal about the x axis by an angle ξ. ϕ denotes an angle made by a transverse direction in the $x'y'$ plane with the $x' = x$ axis.

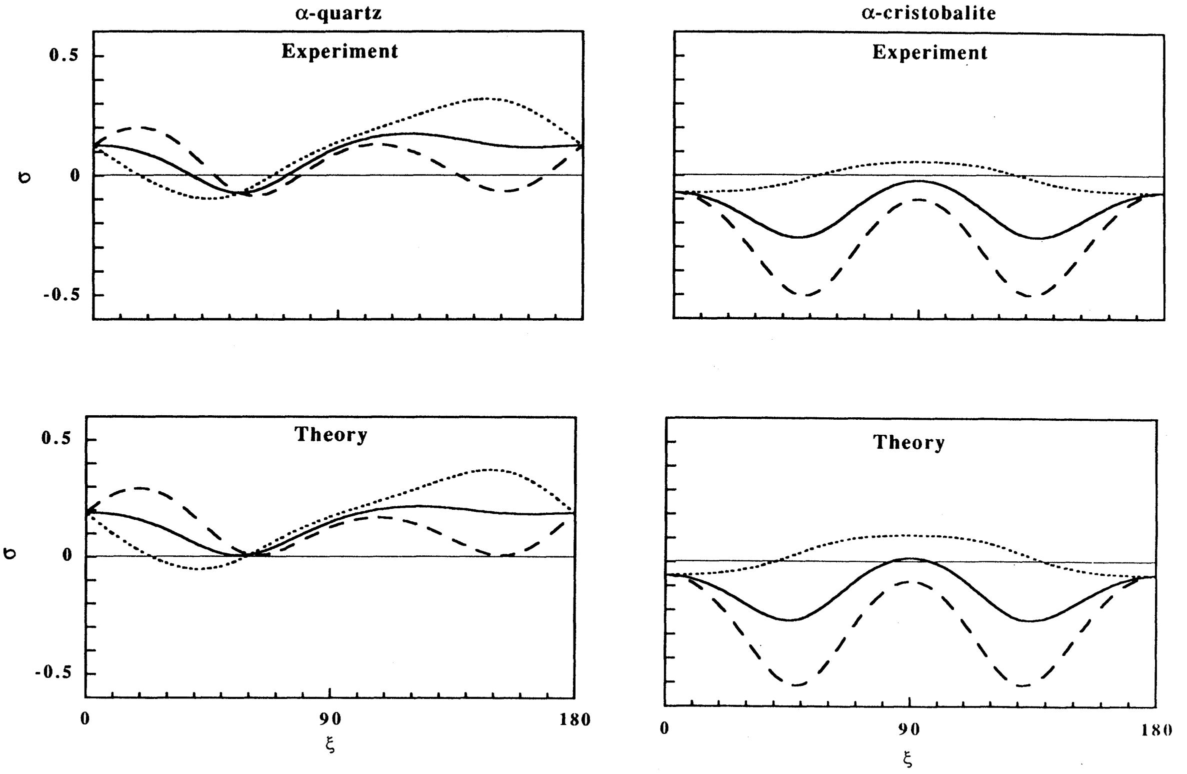

FIG. 4. The variation of uniaxial and biaxial Poisson ratios for a uniaxial loading along the c axis as the crystals are rotated about the x axis by an angle ξ. In defining σ'_{13} (dotted) and σ'_{23} (dashed), $x' = x$ and y' are the transverse directions. $\overline{\sigma'_3}$ (solid) is an "effective" Poisson ratio (Ref. 20) for the transverse $x'y'$ plane. The theoretical plots are based on the results of our pair potential calculations. For the experimental curves, the data from Refs. 4 and 14 were used. To be consistent with Ref. 20 we have adjusted the sign of S_{14} for α-quartz.

In Fig. 4, we have shown the variation of σ'_{13}, σ'_{23}, and $\overline{\sigma'_3}$ with the polar angle ξ between the y and y' axes. For this figure, we have used the elastic compliances from our pair potential calculations and from experiments.[4,14] The theoretical variation is in good agreement with the experimental one. It is interesting that even α-quartz has negative biaxial[20] and uniaxial Poisson ratios for loading along certain directions. Elastic anisotropy is even stronger in the case of α-cristobalite. Although the uniaxial value σ'_{13} takes small positive values over a certain range of ξ, σ'_{23} and the biaxial ratio $\overline{\sigma'_3}$ remain mostly negative. From Eq. (4) it is clear that this is caused by the anomalous sign of S_{13}. Since the uniaxial and biaxial Poisson ratios are predominantly negative in case of α-cristobalite, this material has a negative isotropic aggregate value of Poisson ratio. However, this does not happen in the case of α-quartz.

V. DISCUSSION AND RESULTS

The microscopic origin of the negative Poisson ratio is subtle. An unanticipated conclusion is that angular forces *per se* are not required for reproducing the negative Poisson ratio behavior in silica. Pairwise forces alone, as determined from classical interatomic potentials, can reproduce the Poisson ratio in these materials. Given this situation, we examined the nearest-neighbor interatomic distances between Si-O and O-O. (We expect on physical grounds that the Si-Si distance should not be relevant.) We found no significant differences, or trends for the Si-O bonds for these polymorphs. The Si-O bond lengths vary by no more than 0.02 Å over a wide range of stresses. However, the O-O distances show an interesting trend (Fig. 5). For uniaxial tension, the four unique O-O distances in α-quartz[12] and α-cristobalite both tend to saturate to constant values. However, this is not the case with β-quartz.[12] Constant Si-O and O-O distances are synonymous with *rigid* SiO_4 tetrahedra as this fixes the O-Si-O angles. This relationship between the Si-O and O-O distances and the tetrahedral angles may account for the surprising accuracy of pair potentials for silica.

To verify that the rigidity of the tetrahedral SiO_4 units plays a crucial role in the occurrence of negative Poisson ratio in α-quartz and α-cristobalite, we adopted the following approach. In both these materials, there are four distinct O-O distances. We found expressions for these distances in terms of the four internal coordinates and the lattice parameters a and c.

For α-cristobalite,

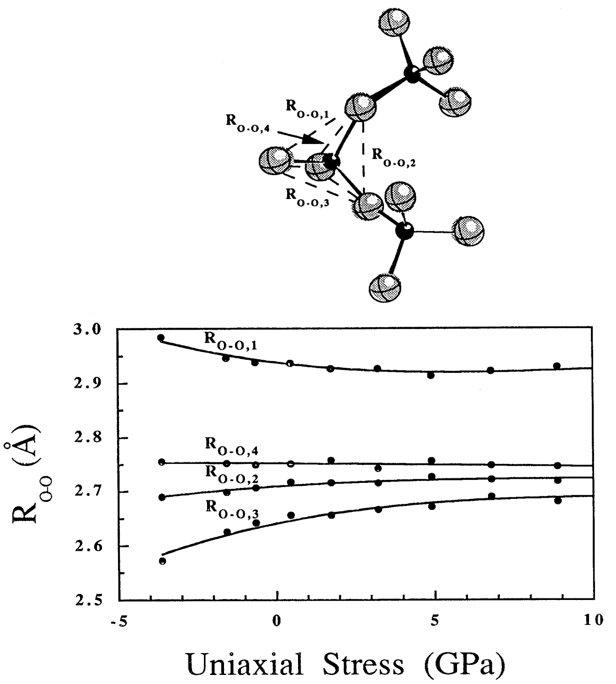

FIG. 5. The variation of the nearest-neighbor O-O distances in α-cristobalite as a function of the uniaxial stress. We have shown only a few illustrative data points from our pair potential calculations. A silica fragment is shown here to illustrate the connection between the O-Si-O angles and the Si-O and O-O distances. The dark and light circles are silicon and oxygen atoms, respectively.

$$
\begin{aligned}
R^2_{\text{Si-O}} &= a^2\left[(u-x)^2+(u-y)^2\right]+c^2z^2 ,\\
R^2_{\text{O-O},1} &= a^2\left[\frac{1}{4}+\left(\frac{1}{2}-x\right)^2\right]+c^2\left(\frac{1}{4}-2z\right)^2 ,\\
R^2_{\text{O-O},2} &= a^2\left[\left(\frac{1}{2}-x-y\right)^2+\left(\frac{1}{2}-x+y\right)^2\right]+\frac{c^2}{16} ,\\
R^2_{\text{O-O},3} &= 2a^2(x-y)^2+4c^2z^2 ,\\
R^2_{\text{O-O},4} &= 2a^2(x+y)^2+c^2\left(\frac{1}{2}-2z\right)^2 . \qquad (7)
\end{aligned}
$$

For α-quartz,

$$
\begin{aligned}
R^2_{\text{Si-O},1} &= \frac{a^2}{4}\left[(u-x-y)^2+3(u-x+y)^2\right]+c^2z^2 ,\\
R^2_{\text{Si-O},2} &= \frac{a^2}{4}\left[(u-x+2y-1)^2+3(u+x-y)^2\right]\\
&\quad +c^2\left(\frac{1}{3}-z\right)^2 ,\\
R^2_{\text{O-O},1} &= 3a^2(x-y)^2+4c^2\left(\frac{1}{3}-z\right)^2 ,\\
R^2_{\text{O-O},2} &= a^2\left[\frac{1}{4}+3\left(\frac{1}{2}-x\right)^2\right]+4c^2\left(\frac{1}{6}-z\right)^2 ,\\
R^2_{\text{O-O},3} &= \frac{a^2}{4}\left[(1-3y)^2+3(1-2x+y)^2\right]+\frac{c^2}{9} ,\\
R^2_{\text{O-O},4} &= 3a^2y^2+4c^2z^2 . \qquad (8)
\end{aligned}
$$

The values of the Si-O and O-O distances in naturally occurring crystals of these polymorphs are listed in Table II. We fixed the O-O distances and the unique Si-O distance in α-cristobalite to those in its naturally occurring crystal. For α-quartz, we fixed the four O-O distances and $R_{\text{Si-O},1}$. At different values of the c parameter, we solved for u, x, y, z, and a with the above constraint. For this purpose, we used the Newton-Raphson method. (In the case of α-quartz, we found that $R_{\text{Si-O},2}$ remains constant when the other Si-O distance and the O-O distances are constrained.)

This model calculation is equivalent to compressing these materials along the c axis while maintaining the rigidity of the tetrahedra. We plotted $\ln(a)$ as a function of $\ln(c)$, and computed the Poisson ratios. We found that in these artificially constrained structures of rigid tetrahedra, the Poisson ratios of both α-quartz and α-cristobalite are -0.6 and -0.5, respectively. This confirms the role of rigid tetrahedra in imparting negative Poisson ratios to these polymorphs

In the case of β-quartz, we have a unique Si-O distance and three distinct O-O distances as follows:

$$
\begin{aligned}
R^2_{\text{Si-O}} &= \frac{a^2}{4}\left[\left(\frac{1}{2}-3y\right)^2+3\left(\frac{1}{2}-y\right)^2\right]+\frac{c^2}{36} ,\\
R^2_{\text{O-O},1} &= 3a^2y^2+\frac{c^2}{9} ,\\
R^2_{\text{O-O},2} &= a^2\left[\frac{1}{4}+3\left(\frac{1}{2}-2y\right)^2\right] ,\\
R^2_{\text{O-O},3} &= a^2(1-3y)^2+\frac{c^2}{9} . \qquad (9)
\end{aligned}
$$

If we impose the constraints of constant Si-O and O-O distances in β-quartz at various values of c, this system of equations becomes overdetermined. This means that it is not possible to maintain the rigidity of SiO_4 units in β-quartz while maintaining its symmetry. As a result, β-quartz will *never* exhibit a negative Poisson ratio when a uniaxial stress is applied along the c axis.

The motion of the tetrahedra in α-cristobalite is illustrated explicitly in Fig. 6. (A discussion of all these polymorphs is given elsewhere.[12]) In this figure, we have indicated the motions of atoms, as determined from our pair potential calculations, in the unit cells of this polymorph as it is subjected to a uniaxial tension. As the c axis is extended the SiO_4 units in α-cristobalite rotate "outward" by increasing the Si-O-Si bridging angle. From our quantum-mechanical calculations as well as from other computations,[23] this angle between the units is known to be soft. The rotation of the tetrahedral SiO_4 units allows the a lattice parameter to increase

TABLE II. Si-O and O-O distances in the naturally occurring crystals of low-density silica polymorphs.

	Si-O (Å)	O-O (Å)
α-quartz	1.611, 1.608	2.607, 2.610, 2.643, 2.653
β-quartz	1.616	2.499, 2.669, 2.743
α-cristobalite	1.592	2.582, 2.590, 2.630, 2.640

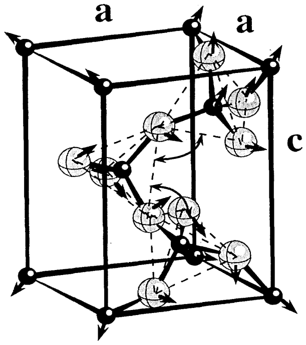

FIG. 6. The motion of atoms in as it is subjected to a uniaxial tension. Note that the displayed geometry is the one at ambient pressure and the motions of the atoms are relative to the center of the corresponding unit cells. We have also shown the variation of the intertetrahedral angles. The dark and light circles are silicon and oxygen atoms, respectively. The lattice parameters a and c are labeled here.

along with the volume of the unit cell, and a negative Poisson ratio occurs. This behavior does not follow for high *compressive strains* as the SiO_4 unit eventually distorts as indicated by the variation in the O-O distances in Fig. 5. α-cristobalite and α-quartz under tension are similar in that the O-O distances in both these materials saturate to constant values. If sufficient distance occurs between the tetrahedral units, then the strain can be accommodated by a reduction in the intertetrahedral distances while preserving the SiO_4 units. This situation is necessary for a negative Poisson ratio.

VI. CONCLUSION

In this paper, we have investigated the response of three polymorphs of silica under a uniaxial stress along the c axis of these crystals. This response is characterized by their Poisson ratios. In α-quartz and α-cristobalite, we find that the Poisson ratio σ_{13} varies as a function of the applied stress. In particular, it exhibits a negative value at ambient pressure for α-cristobalite, a result consistent with recent experimental finding.[4] We also predict that at high values of tensile stress, α-quartz will exhibit a negative Poisson ratio for a loading along the c axis. In the case of β-quartz, the Poisson ratio σ_{13} is seen to have a constant value over a wide range of strain. On geometrical grounds, we conclude that for a loading along the c axis, it is not possible to maintain the symmetry of β-quartz and the rigidity of the SiO_4 tetrahedra simultaneously. This is the reason why this polymorph *never* exhibits a negative Poisson ratio for a loading along the c axis. We conclude that the sign of the Poisson ratio in these low-density polymorphs of silica is a result of the rigidity of the SiO_4 units that are the building blocks of these materials.

We have applied the elastic constants from our pair potential calculations to study the directional dependence of Poisson ratios in these crystals. Even at ambient conditions, α-quartz shows a negative Poisson ratio for loading in certain directions. This is even more apparent in case of α-cristobalite. Thus in both these materials, the Poisson ratio shows a strong anisotropic behavior. However, the isotropic average value is positive for the former, whereas it is negative for the latter.

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