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Interatomic potentials and the structural properties of silicon dioxide under pressure

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First-principles interatomic potentials based on *ab initio* Hartree-Fock self-consistent-field calculations have recently been proposed for silicon dioxide. These pairwise potentials yield accurate ambient-pressure internal-structure parameters and dynamically stable polymorphs for several known forms of silica. We use these potentials to analyze crystallographic data for α-quartz under pressure. We find the potentials do not describe the changes in the internal parameters of α-quartz under pressure. Specifically, the potentials do not give the correct trends for the O—Si—O angles or the c/a lattice-constant ratio. We have included bond-bending terms to modify the pairwise potentials. If the angles in question are fit to reproduce the experimental data, then the bulk modulus is in poor agreement with experiment. Our findings reinforce the need for a "covalent" term in the interatomic potential, which is not based on quadratic expansions of bond-bending and -stretching forces.

I. INTRODUCTION

Recently, Tsuneyuki, Tsukada, Aoki, and Matsui[1] (TTAM) proposed a new interatomic potential for silica. They used Hartree-Fock self-consistent-field calculations to examine clusters of SiO_2. From these calculations, they fitted *pairwise* interatomic potentials to the structural energies of large silicon oxide clusters. These potentials were in turn used to examine known polymorphs of silica: α-quartz α-cristobalite, coesite, and stishovite. Using molecular-dynamic simulations, TTAM found stable structures at normal pressures and temperatures. This was true despite large differences in the topologies and the densities of the structures considered. Moreover, they could reproduce the equilibrium structural parameters of the silica polymorphs. Earlier studies[2,3] of silicon dioxide clusters had suggested that interatomic potentials would describe qualitatively, and sometimes quantitatively, the Si—O bond in the solid state. Nonetheless, the TTAM work showed for the first time that dynamic stability in silica polymorphs could be achieved on the basis of simply pairwise potentials.

The use of accurate *pairwise* forces would greatly enhance our ability to use molecular-dynamics simulations to describe melting and glass formation of the silica polymorphs.[4,5] Moreover, there are some recent proposals for high-pressure forms of silica which could be examined by accurate pairwise forces.[6] However, SiO_2 has traditionally been viewed as a covalent material.[7] Tetrahedral units of SiO_4 dominate the structural properties for those structures containing fourfold coordinated silicon, e.g., α-quartz, α-cristobalite, and coesite. Therefore, the use of pairwise potentials would not be expected to reproduce angular forces present in SiO_2, especially the relatively open structures such as found in α-quartz and α-cristobalite. Indeed, other workers[2,3] have found it necessary to include three-body forces in their description of silicas to replicate the ground-state structural parameters. Unfortunately, the use of three-body forces can greatly complicate the simulations for melting or crystal stability. Hence, the creation of an accurate pairwise potential would be quite useful and would have widespread applications.

To explore this issue more thoroughly, we have extended the results of TTAM to the pressure behavior of α-quartz. Specifically, we use their interatomic potential to optimize the structure of α-quartz as a function of pressure and compare the results to recent experiments. Also, we examine possible modifications of their potential which include explicit three-body interactions.

II. INTERATOMIC POTENTIALS

An interatomic potential for silicon dioxide is often based on an ionic model. For such a model, the potential for two interacting species (ij) is given by

$$U_{ij}(R)=q_iq_j/R+g_0(b_i+b_j)\times\exp[(a_i+a_j-R)/(b_i+b_j)]-c_ic_j/R^6\ , \tag{1}$$

TABLE I. Equation of state and structural parameters for SiO_2 in the α-quartz structure. The theoretical values are from the interatomic potential of Tsuneyuki *et al.* (Ref. 1). The experimental values are from Levien *et al.* (Ref. 10) and Ginnemann *et al.* (Ref. 12). The crystal energy is the energy required to separate the crystal into the constituent charged ions as defined by Eq. (1).

Property	Theory	Experiment
	Equation of state	
Crystal energy (kcal/mole)	−1236.7	
Cell volume (Å^3)	121.38	113.59
Bulk modulus (Mbar)	0.37	0.38(3)
$(\partial B/\partial P)_{P=0}$	3.20	6(2)
	Structural parameters	
c (Å)	5.56	5.42
a (Å)	5.02	4.92
u	0.4602	0.4698
x	0.4259	0.4151
y	0.2771	0.2675
z	0.1213	0.1194

where R is the interatomic distance between species (ij) and q_i is the charge on the ith species. This is the form used by TTAM (and others). The parameters a_i, b_i, g_0, and c_i may be found in Ref. 1. Equation (1) assumes ionic forces dominate the interatomic interactions. Such a form necessitates the evaluation of Madelung sums, which can increase the computational complexity of the problem.

We will use (1) to examine recent experimental data for the α-quartz structure. For this structure, the crystal energy varies with six structural parameters. If we fix the unit cell volume, then we are left with five parameters to optimize the crystal energy. We chose to vary the parameters: a, u, x, y, and z, as defined by Wyckoff.[8] The c parameter is then fixed by the unit cell volume. We used a simplex program to vary the parameters and minimize the crystal energy.

Our results for the equation of state for α-quartz agree very well with TTAM. We consider a Murnaghan equation of state:[9]

$$E(V)-E(V_0)=\frac{B_0 V}{B_0'(B_0'-1)}\left[B_0'\left[1-\frac{V_0}{V}\right]-\left[\frac{V_0}{V}\right]^{B_0'}-1\right], \qquad (2)$$

where $E(V_0)$ is the crystal energy, B_0 is the bulk modulus, B_0' is the pressure derivative of the bulk modulus, and V_0 is the volume, all taken at equilibrium. In Table I, we compare our results to the previous work. Generally, the equation of state parameters agree quite well. The equilibrium volume is larger than experiment[10] by about 6%. The bulk modulus is nearly in exact agreement with experiment. The crystal energy is the energy to separate the crystal into the separate ions. (This presents some conceptual issues for O^{2-} which is unbound in free space.) We have considered a variety of initial conditions for our structural parameters and are confident that our structure is a global and not a local minimum.

We have also checked the TTAM potential results against two other structures: the calcium fluorite and the rutile structures. We find that α-quartz is lower in energy by about 50 kcal per mole than the calcium fluorite structure. This is a surprising result as one might have expected the calcium fluorite structure to be favored by pairwise forces. We suspect that the anion-anion repulsion term is so large as to favor the α-quartz structure over the fluorite structure. However, the total energy of the optimized rutile structure is within ~1 kcal of the α-quartz structure. Within computational uncertainity it is indistinguishable from quartz. Our results are in agreement with TTAM, who point out that their potential may not describe crystal energies between different polymorphs. We speculate that the differences may worsen as a function of pressure since the structural properties were fixed at ambient pressures.

III. α-QUARTZ UNDER PRESSURE

Pressure measurements can provide a stringent test for interatomic potentials. For example, charge transfer between Si and O may occur with pressure. Moreover, we expect changes in the bonding hybridization between Si and O. Such bonding changes are difficult to reproduce with a classical potential. For example, only recently has it been possible to reproduce accurately the pressure behavior of elemental silicon.[11] It was necessary for Si to include explicitly the coordination dependence of the silicon potential and to use an angular-dependent interaction term which is modeled on the "covalent-to-metallic" transition in silicon.

One advantage we have in this study is an accurate description of structural changes as a function of pressure. Previous pressure work on SiO_2 has been carried by Levien *et al.* and Hazen *et al.*[10] However, their results were limited in pressure range and accuracy. We compare with the recent work of Glinnemann *et al.*[12] 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 bond angles and distances are well determined.

IV. COMPARISON BETWEEN EXPERIMENT AND THEORY

Using the TTAM potential, we attempted to reproduce the Glinnemann *et al.* data. To illustrate the behavior of α-quartz under pressure, we have considered three fiducial structural features: the c/a ratios, the Si—O—Si bond angle, and the O—Si—O bond angles. There are four distinct O—Si—O angles near the tetrahedral angle of 109.5°. Intuitively, the O—Si—O angle is expected to be "stiff" compared to the Si—O—Si angle. This condition would account for most polytypes of silica being based on the tetrahedral unit of SiO_4.

We have examined the c/a ratio and find that the TTAM potentials predict quadratic variation with pressure whereas experiment supports a linear behavior. Thus one might expect the angular changes to be poorly reproduced. This is not the case for the Si—O—Si angle. The angle is too large at zero pressure compared to experiment, but the change with pressure is well replicated by the theory. This is shown in Fig. 1.

In Fig. 2, we display the O—Si—O bond angles as measured and predicted as a function of pressure. The pressure behavior of these angles will provide a strong challenge to any pairwise force. The spread from the largest to smallest angle is semiquantitatively reproduced by the TTAM potential, but the details are poorly reproduced. While it is true that the variation in angle is small, it is also true that subtle variations play a crucial role in differentating the various polytypes of silica.[13]

To examine this feature is more detail, we considered the inclusion of nonpairwise forces, i.e., bond-bending forces. These forces in their simplest form can be written as

$$E_{\text{bond-bending}} = \alpha \sum_{\text{Si—O—Si}} (\theta_{\text{Si—O—Si}} - \theta^0_{\text{Si—O—Si}})^2 + \beta \sum_{\text{O—Si—O}} (\theta_{\text{O—Si—O}} - \theta^0_{\text{O—Si—O}})^2 , \quad (3)$$

where $\theta_{\text{Si—O—Si}}$ and $\theta_{\text{O—Si—O}}$ correspond to the equilibrium Si—O—Si and O—Si—O bonds. We take the equilibrium angles for the constant angles in (3) as $\theta^0_{\text{Si—O—Si}} = 144°$ and $\theta^0_{\text{O—Si—O}} = 109.5°$. Lasaga and Gibbs[2] have used this type of bond-bending interaction where (α,β) are fit to quantum chemistry calculations. Since the TTAM potential is not identical to the Lasaga-Gibbs potential, we have adjusted (α,β) to fit the pressure data.

We find that it is possible to adjust the two parameters (α,β) to reproduce qualitatively the experimental results for the complex O—Si—O bonding angles. This is shown in Fig. 3, where we illustrate the O—Si—O angles as a function of *volume*. The values we find for (α,β) are larger than those suggested by Lasaga and Gibbs, i.e., $\alpha \approx 0.02$ Kcal/mole/deg^2 and $\beta \approx 0.08$ Kcal/mole/deg^2. This results in a "stiffer" lattice.

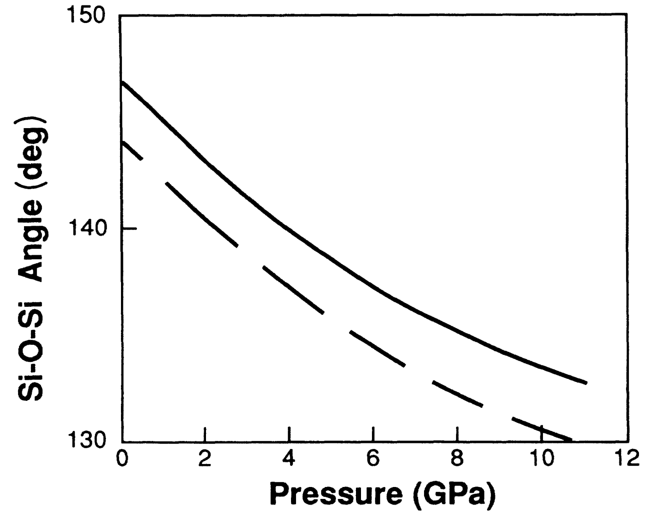

FIG. 1. The Si—O—Si angle in α-quartz as a function of pressure from experiment (Ref. 12) (dashed line) and as predicted by the interatomic potential of Tsuneyuki *et al.* (Ref. 1).

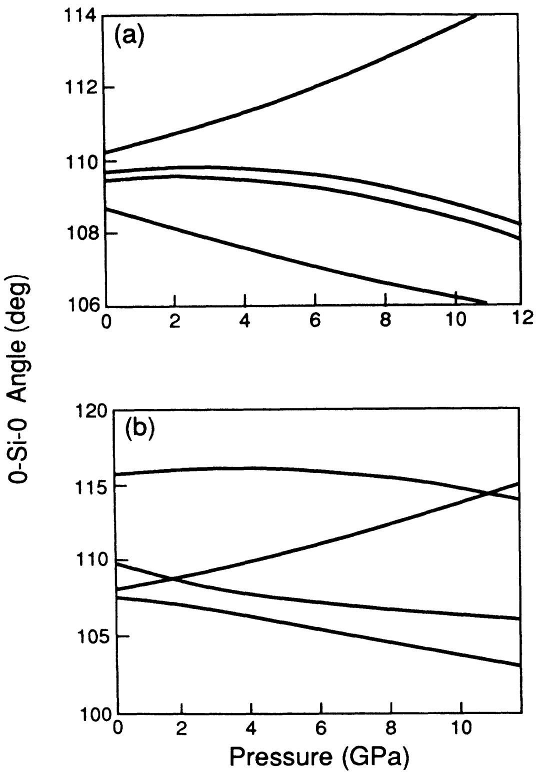

FIG. 2. (a) The O—Si—O angles in α-quartz as a function of pressure from experiment (Ref. 12). There are four distinct O—Si—O angles in α-quartz. An illustration of these angles may be found in Ref. 10. (b) The O—Si—O angles in α-quartz as a function of pressure as predicted by the interatomic potential of Tsuneyuki *et al.* (Ref. 1). The agreement with experiment is poor.

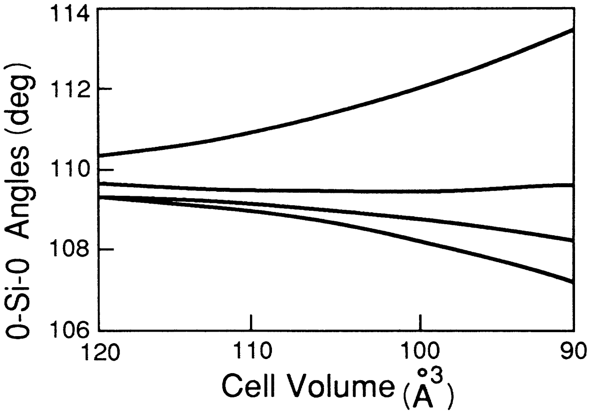

FIG. 3. The O—Si—O angles as a function of *volume* . The angles are from the interatomic potential of Tsuneyuki *et al.* (Ref. 1) as modified by the bond-binding forces as indicated in Eq. (3). While the behavior of the angles as a function of pressure is in qualitative agreement with experiment, the detailed behavior is not correct. The pressure vs volume curve for this potential yields a bulk modulus for α-quartz which is about 4–5 times larger than experiment.

We find that the first term in Eq. (3) will improve the agreement at the equilibrium volume. Specifically, the TTAM potential yields angles for the O—Si—O angles which deviate noticeably from the ideal tetrahedral angle. The first term in (3) reduces such deviations. The second term in (3) improves the angular dispersion with pressure. This suggests that the key term in controlling the pressure behavior is the "stiffness" of the Si—O—Si bond. However, this procedure has a serious flaw. Namely, the terms in (3) can only "stiffen" the crystal as they are positive definite terms. After adjusting (α,β) to reproduce the angular terms, we find that the bulk modulus is nearly 1.9 Mbar or about a factor 4 to 5 too large compared to experiment.

It is likely that the key issue here involves a subtle interplay involving the O-O repulsive interaction, i.e., the $q_i q_j/R$ term where (i,j) refer to the oxygen ion. This term is important in stabilizing the α-quartz structure versus the CaF_2 structure and in controlling the compressibility of silica. By reducing this term, the bulk modulus could be lowered. Conceivably, one could lower the charge on the Si and O ions to lower the bulk modulus and using (3) get an accurate angle dependence. However, in such a situation the relative stability of α-quartz structure versus the CaF_2 structure might suffer.

V. CONCLUSIONS

In summary, it is very significant that the TTAM potential results in dynamically stable structures for known polytypes of silica. As the authors note, the strong Si—O bond is no doubt responsible for this. However, as we have shown, pairwise interactions cannot fully reproduce the properities of silica. Specifically, the details of the internal structural parameters are not well reproduced. This result can be attributed to "covalent forces" which affect the angular interactions.

The TTAM potentials and similar ones have been used to describe structural features of silica polytypes. Given the results of our study it is unclear whether these potentials are accurate enough to provide detailed structural information, especially in comparing one polytype with another. From our work with angular forces, it might appear that one could achieve greater accuracy with the inclusion of the simple "bonding-bending" forces. At present, we feel this is not the best way to proceed. We feel potentials for silica should be made via the route for silicon interatomic potentials.[11] If we had detailed quantum-mechanical calculations for crystalline polymorphs of silicon dioxide, we could test whether a particular interatomic potential would yield the correct equation of state for a large number of structures.

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