Lattice-dynamical study of the structure and elasticity of dodecasil-3C at elevated temperatures

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Using free-energy minimizations and three interatomic potentials, we calculated the structure of dodecasil-3C without guest molecules at several temperatures. For this structure, the interatomic potentials predict substantially different free energies relative to α-quartz. We find that dodecasil-3C without guest molecules is triclinic for temperatures between 0 and 1200 K. The positions of the O atoms in the experimental structure of calcined dodecasil-3C may not be well resolved. Furthermore, we present predictions for the elastic constants C_{11}, C_{12}, and C_{44} that are in reasonable agreement with experiment on material with guest molecules. As we find that the symmetry of dodecasil-3C is lower than cubic which was reported at the time of the elasticity measurements, it might be interesting to perform additional measurements on this compound to compare them with our predictions. [S0163-1829(96)00121-X]

I. INTRODUCTION

In 1982 Gies, Liebau, and Gerke[1] introduced a class of all-silica structures, the so-called clathrasils, which are isostructural to clathrate gas hydrates. Those frameworks have been extensively studied since then.[2–7] In all these structures, corner-connected tetrahedra form cages, large enough to occlude organic molecules during synthesis. One of these compounds is dodecasil-3C. This clathrasil is characterized by two types of cages: a dodecahedron built from 12 five-rings ([5^{12}]) and a larger one, consisting of 12 five-rings and four six-rings ([5^{12} 6^4]). A simplified picture of dodecasil-3C, showing only straight lines between adjacent Si atoms, is given in Fig. 1. The [5^{12}] cage can contain smaller molecules such as N_2, CH_4 or CO_2.[2–7] The larger [$5^{12}6^4$] cage, can occlude molecules such as pyridine, adamtylamine or trimethylamine.[2–7] Many different phases, dependent on temperature and the trapped guest molecules, have been reported for dodecasil-3C.[7] The relative stability of those phases and their transition temperatures are strongly dependent on the guest molecules enclathrated.[7] The structure of as-synthesized dodecasil-3C at low temperatures has not been resolved completely.[7] The x-ray powder-diffraction experiments of Gunawardane[8] indicate that the symmetry of dodecasil-3C, with guest molecules enclathrated, is maintained when the sample is calcinated, i.e., when the guest molecules are removed by heating the sample. According to the ^{29}Si NMR measurements of Groenen *et al.*,[9] the structure of dodecasil-3C changes slightly on calcination. This is understandable because dodecasil-3C is stable up to 1200 K, far beyond the temperature that causes breakdown of the guest molecules.[8] Recently, Könnecke, Miche, and Fuess[10] reported that the structure of calcined dodecasil-3C at $T \approx 523$ K has space group $Fd\bar{3}m$. These authors concluded that $Fd\bar{3}m$ was merely the space group for the averaged structure, which they attributed to static disorder of the O atoms in the lattice. The lower local symmetry of calcined

dodecasil-3C could not be determined because distance least squares simulations in subgroups of $Fd\bar{3}m$ failed, or could not explain the observed disorder.[10] The x-ray-diffraction and ^{29}Si NMR results of Tse *et al.*,[11] indicate that calcined dodecasil-3C remains a single phase between 80 and 400 K. Könnecke *et al.* reported, that this compound undergoes a small displacive phase transition at $T = 451$ K, which was detected using differential scanning calorimetry. We are not aware of other authors that report phase transitions of calcined dodecasil-3C. Furthermore, ^{29}Si NMR spectra that were reported[9,12] for dodecasil-3C after calcination at various temperatures above 400 K are similar, indicating that the empty structure changes only slightly with temperature.

Therefore, we have done a theoretical study, using free-energy minimizations, to determine the local symmetry of dodecasil-3C without guest molecules at variable temperatures and to investigate temperature-induced phase transitions of this material. This work extends a previous study on dodecasil-3C that was based on calculations at $T = 0$ K.[13] Our free-energy calculations require the use of interatomic potentials. Calculations are done with two shell-model po-
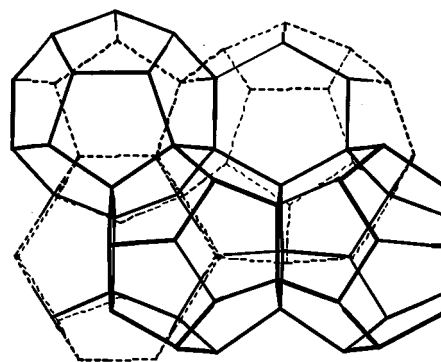

FIG. 1. Simplified picture of dodecasil-3C, showing only straight lines between adjacent Si atoms.

tentials and a rigid-ion model potential. According to the shell-model predictions, dodecasil-3C without guest molecules is triclinic for temperatures ranging from 0 to 1200 K. The rigid-ion model predictions, indicating a different structure, will be shown to be less reliable than the shell model. Our calculations also indicate that the experimentally determined positions of the O atoms in calcined dodecasil-3C may be not well resolved. Furthermore, we will compare predicted elastic constants of empty dodecasil-3C with experiment. One of the shell-model potentials used predicts values for C_{11}, C_{12} and C_{44} that are in reasonable agreement with experiment. Experimental values for other elastic constants were not determined because when those experiments were performed, dodecasil-3C was reported to be cubic.[15] As our calculations indicate that the symmetry of calcined dodecasil-3C is lower than cubic, we conclude that it might be interesting to perform additional elasticity measurements on this material, in comparison with our predictions.

II. METHOD AND COMPUTATIONAL DETAILS

Free-energy minimizations have been done with the code PARAPOCS,[16] which can be used to calculate physical properties of solids at variable temperatures and pressures. To calculate thermodynamical properties, the vibrational frequencies of the solid have to be computed. The calculations assume that vibrational motions in the solid are described by independent quantized harmonic oscillators the frequency of which varies with cell volume.[17] Minimization of the Gibbs free energy can be achieved by varying the cell volume and the positions of the ions until the configuration satisfies the following equilibrium conditions for a given temperature and pressure:

$$\frac{\partial A}{\partial V} = P_{\mathrm{app}}, \qquad (1)$$

$$\frac{\partial U_{\mathrm{stat}}}{\partial \mathbf{r}} = 0. \qquad (2)$$

In Eq. (1) A denotes the Helmholz free energy, V the cell volume and P_{app} the applied pressure. In Eq. (2) U_{stat} denotes the static energy due to the interatomic interactions and $\mathbf{r}$ denotes the atomic coordinates. Equation (1) states that the pressure exerted by the system (internal pressure) must equal the applied pressure. [Equation (1) is only valid for cubic crystals. For more general cases the derivatives of the Gibbs free energy with respect to the strain must be computed. Details can be found in Ref. 18.] Equation (2) states that the net force on each atom must vanish. After the Gibbs free energy is minimized, thermodynamical properties, elastic constants, dielectric constants and the structure of the solid can be computed. Calculation of the Helmholz free energy and other thermodynamical properties requires computation of the vibrational frequencies for all wave vectors in the Brillouin zone. This is done by computation of the frequencies on a three-dimensional grid within the Brillouin zone. In our calculations we used the grid of Pavesi[19] with each of the three coordinates having values

$$k_n = \frac{3(2^{n-1}) - 2}{4(2^N - 1)}.$$

In this formula N denotes the number of grid points in the reciprocal lattice and $n = 1, 2, \ldots N$. In our calculations we used the above grid with eight $\mathbf{k}$ points. This yields Gibbs free energies with an accuracy of 10^{-3} eV. The stability of the structures with minimal Gibbs free energy was tested by checking if all phonon frequencies were real on a grid in $\mathbf{k}$ space of 125 grid points. Furthermore, the calculations have been done on the structures without guest molecules. In our calculations we have employed the rigid-ion model potential derived by Kramer et al.[20] denoted as the Kramer-Farragher-van Beest-van Santen (KFBS) potential. We have used the shell-model potential of Jackson and Catlow[21] and the ab initio shell-model potential of de Boer, Jansen, and van Santen,[22] referred to as the JC and BJS potentials, respectively. Cutoffs applied in calculations using the KFBS and JC potential are 10 Å.[23] The covalent O-O interactions of the BJS potential are applied with a cutoff of 3.5 Å, because for larger distances all covalent potential terms are effectively zero. The covalent SiO interaction of this potential is applied with a cutoff of 2.5 Å (i.e., in between the nearest and next-nearest Si and O neighbors) to simulate a real Si-O bond. The electrostatic interactions are calculated using the Ewald summation.

III. RESULTS

We will first discuss predictions for the relative stabilities of the dodecasil-3C structures. Subsequently, we will compare predicted elastic constants of the most stable structures with experiment. Finally, we will discuss the comparison between predicted structures and experiment.

A. Free energies of dodecasil-3C at variable temperatures

Several experimental structures are used as starting structures in the minimizations. We used the cubic $Fd\bar{3}$ structure that was proposed by Gies[2] for dodecasil-3C at room temperature with Kr, Xe, and $N(CH_3)_3$ as guest molecules. This structure will further on be denoted as $D3C_c$. We employed the tetragonal $I\bar{4}2d$ structure reported[24] at ambient conditions for dodecasil-3C which contains pyridine as guest molecule. This structure will be denoted as $D3C_t$. Finally, we used the orthorhombic structure with space group $Fddd$ that was proposed[25] for dodecasil-3C at low temperatures. This structure will further on be referred to as $D3C_o$. We first performed $T = 0$ K minimizations on the above structures. For each potential used both the $D3C_o$ and $D3C_c$ structure relaxed to essentially the same cubic structure with space group $Fd\bar{3}$. The cubic structures are saddle-point structures as some of the frequencies, close to the Γ point, are imaginary. When the tetragonal $D3C_t$ structure is minimized at $T = 0$ K both the BJS and JC potential predict that this structure is a saddle-point structure with space group $I\bar{4}2d$. Minimization at $T = 0$ K of the $D3C_t$ structure with the KFBS potential gives a tetragonal structure without change of symmetry. The latter structure corresponds to a true minimum structure, because there are no imaginary frequencies. The saddle-point structures, obtained from the $T = 0$ K calcula-

TABLE I. Predicted energies of the local minima structures at variable T. Free energy, denoted as $G(T)$, with T in K, is in eV. Internal energy, denoted as U is also in eV.

Symmetry	$U(0)$	$G(200)$	$G(300)$	$G(400)$	$G(500)$
BJS					
$C2$	-2304.974	-2296.523	-2298.000	-2300.050	
$P1$	-2304.989	-2296.538	-2298.013	-2300.054	-2302.591
$P\bar{1}$	-2305.138	-2296.654	-2298.127	-2300.157	-2302.681
KFBS					
$I4_1/a$	-1970.382	-1959.702	-1960.832	-1962.442	-1964.493
$I\bar{4}2d$	-1970.465	-1959.738	-1960.866	-1962.476	-1964.530
JC					
$P1$	-4372.280	-4363.322	-4364.703	-4366.633	
$P\bar{1}$	-4372.353	-4363.345	-4364.703	-4366.606	-4368.994

tions, are used to calculate local minima structures, according to a well-known procedure.[13,14] Although many starting structures were used in this procedure, only a few local minima structures at $T=0$ K were obtained. Those structures are listed in Table I.

To investigate whether those local minima might correspond to different phases of dodecasil-$3C$ at elevated temperatures, we calculated the Gibbs free energy of those structures at several temperatures up to 1200 K. Dodecasil-$3C$ is thermally stable below 1200 K.[8] Differences of the Gibbs free energies between the local minima structures are very small. Table I lists those energies in the temperature range for which phase transitions of as-synthesized dodecasil-$3C$ have been reported.[7] The BJS potential predicts that the most stable phase of dodecasil-$3C$ is triclinic with space group $P\bar{1}$ in the temperature range 0 to 1200 K. Although the calculated Gibbs free energies of the local minima structures differ only slightly, the BJS potential predicts no phase transitions in the studied temperature range.

The JC potential predicts for temperatures below 300 K that a triclinic structure with space group $P\bar{1}$ is the most stable. Above $T=300$ K the triclinic $P1$ structure becomes more stable, indicating a phase transition at 300 K (see Table I). This prediction might correspond to the small displacive phase transition at $T=451$ K, reported by Könnecke, Miehe, and Fuess.[10] As the structural changes associated with this transition have not been reported, we cannot verify the JC prediction in more detail. For the $P1$ structure the JC potential predicts at $T=410$ K imaginary frequencies at several points in the Brillouin zone, that are not close to the Γ point. This indicates that the $P1$ structure becomes thermally unstable at $T=410$ K. We emphasize that, although the JC-predicted $P\bar{1}$ structure is thermally stable for temperatures above 410 K, it is *metastable* with respect to the $P1$ structure for temperatures above 300 K (see Table I). The JC-predicted $P1$ structure becomes thermally unstable at $T=410$ K. Thus, the JC potential essentially predicts that the structure of dodecasil-$3C$ is triclinic with space group $P1$ and that this structure becomes thermally unstable at $T=410$ K. This temperature is too low when compared to the experimental value of 1200 K. The KFBS potential predicts that the tetragonal $I\bar{4}2d$ structure is the most stable in the range 0 to 1200 K. No phase transition is predicted. Thus, the KFBS-predicted structure differs substantially from that as predicted by both other potentials. Predictions for the geometry of the most stable structures at 300 K are listed in Table II.

To investigate which predictions are the most reliable, we calculated the Gibbs free energies of the most stable structures, at variable temperatures, relative to the value predicted for α-quartz. The results are illustrated in Fig. 2. The relative Gibbs free energy will further on be denoted as ΔG_{trans}. The BJS and KFBS potentials predict correctly[26] that dodecasil-$3C$ is metastable with respect to α-quartz for temperatures ranging from 0 to 800 K. The JC-predicted structure, that is thermally stable up to 400 K, is predicted to be metastable with respect to α-quartz for temperature ranging from 0 to 400 K. At temperatures between 848 and 1200 K dodecasil-$3C$ must be metastable with respect to β-quartz.[27] At 1200 K, dodecasil-$3C$ must be less stable than β-cristobalite.[27] The relative Gibbs energy with respect to those β phases could not be calculated because, according to all three potentials, both phases are no true minima structures at any temperature.

The JC and BJS potential predict similar values for the ΔG_{trans} of dodecasil-$3C$, whereas the KFBS predicted values

TABLE II. Predicted geometries of dodecasil-$3C$ at $T=300$ K. Distances are in Å and angles in degrees. As the JC potential predicts the $P\bar{1}$ and $P1$ structures with ΔG_{trans} values that are essentially equal at room temperature, we have listed them both.

| Property	BJS	KFBS	JC	JC
a	18.751	19.780	19.265	19.207
b	18.655	19.780	19.219	19.197
c	18.824	19.929	19.140	19.412
α	89.73	90.00	90.47	89.964
β	90.10	90.00	89.85	90.127
γ	89.34	90.00	89.95	89.974
$d_{\text{Si-O}_s}$	1.589	1.595	1.586	1.587
$d_{\text{Si-O}_l}$	1.623	1.616	1.609	1.608
$\langle d_{\text{Si-O}} \rangle$	1.606	1.606	1.599	1.597
$\angle_{\text{Si-O-Si}_s}$	131.6	159.6	143.7	140.8
$\angle_{\text{Si-O-Si}_l}$	155.5	177.1	166.4	175.6
$\langle \angle_{\text{Si-O-Si}} \rangle$	142.7	170.2	153.2	155.1
$\angle_{\text{O-Si-O}_s}$	102.3	107.7	105.2	105.6
$\angle_{\text{O-Si-O}_l}$	115.1	111.4	112.9	113.2
Symmetry	$P\bar{1}$	$I\bar{4}2d$	$P\bar{1}$	$P1$
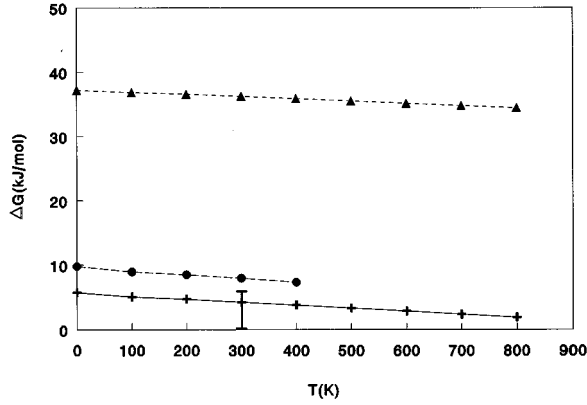
FIG. 2. Predictions for ΔG_{trans} of dodecasil-3C at variable temperatures. Crosses: BJS prediction. Closed triangles: KFBS prediction. Closed points: JC predictions. Vertical bar at 300 K depicts the range of experimental (Ref. 28) ΔG_{trans} values for several all-silica frameworks in which the silicon is tetrahedrally coordinated.

are substantially higher (see Fig. 2). We are not aware of experimental values of ΔG_{trans} for calcined dodecasil-3C. Experimental data[28] on other materials, ranging from the molecular sieve silicalite to the dense coesite, indicate that ΔG_{trans} values of all-silica frameworks with tetrahedrally coordinated silicons lie in a narrow range (vertical bar in Fig. 2). The BJS and JC predictions for the ΔG_{trans} of dodecasil-3C at room temperature are much closer to that range than

the KFBS predictions. Furthermore, the large differences between the KFBS predicted values for ΔG_{trans} and those of the other potentials are mainly due to the predicted value of ΔG_{trans} at absolute zero. The ΔG_{trans} at 0 K is equal to the lattice energy relative to α-quartz, denoted as ΔU_{trans}, because the ΔpV term is negligible for solids at ambient pressure. We have shown in a previous study[33] that BJS and JC calculated values for the ΔU_{trans} of several all-silica polymorphs are much closer to experiment than those of the KFBS potential, the latter values being substantially different. This, as shown earlier,[33] might be due to the fact that the KFBS potential is based on the rigid-ion model, in contrast to both other potentials. The above arguments indicate that the JC and BJS predictions for the stability of dodecasil-3C are more reliable than those of the KFBS potential. The JC potential is only able to model the thermal stability of dodecasil-3C up to 400 K. We conclude that the BJS and JC predictions for the stability of dodecasil-3C without guest molecules are the most accurate below 400 K. Above that temperature, we consider that of the BJS potential as most reliable.

B. Comparison of predicted elastic constants of dodecasil-3C with experiment

In Table III we compare calculated elastic constants of the most stable structures at $T = 300$ K (see Table II) with experimental values, obtained by Friemann and Küppers.[15] The

TABLE III. Predictions for elastic constants of dodecasil-3C at $T = 300$ K compared with experimental data of Freimann and Küppers (Ref. 15). Values not mentioned in the table are zero. Elastic constants are denoted as C_{ij} and are in 10^{10} N m^{-1}. Values in square brackets are elastic constants that have changed significantly due to increase of the cell volume with 1% as discussed in the text.

C_{ij}	Expt.	BJS	KFBS	JC	JC
C_{11}	5.5	5.58 [6.41]	8.62 [9.01]	8.74	7.70
C_{22}	5.5	6.44	8.62 [9.01]	7.99	8.08
C_{33}	5.5	7.93	14.54	7.61	7.48 [6.84]
C_{44}	2.4	2.87	2.12	3.39	3.23
C_{55}	2.4	3.16	2.12	3.30	2.92
C_{66}	2.4	3.12	4.08	3.55	3.65
C_{12}	1.1	1.46 [1.19]	0.50 [0.77]	1.14	1.11
C_{13}	1.1	0.62	3.72	1.07 [1.00]	1.29 [1.59]
C_{14}		−0.07		−0.40	0.02
C_{15}		−0.83		0.13	0.18
C_{16}		0.03		0.03	0.19
C_{23}	1.1	0.63 [0.53]	3.72	1.35 [1.25]	1.79 [1.38]
C_{24}		0.43		−0.10	0.04
C_{25}		0.15		0.08	0.15
C_{26}		0.21		−0.25	−0.07
C_{34}		0.04		−0.23	0.14
C_{35}		0.00		0.28	0.17
C_{36}		0.43		0.00	0.05
C_{45}		0.02		0.02	0.15
C_{46}		−0.01		0.01	0.05
C_{56}		0.02		−0.01	0.12
Symmetry	a	$P\bar{1}$	$I\bar{4}2d$	$P\bar{1}$	$P1$

aFreimann and Küppers have not determined the space group of the compound they used in the elasticity measurements.

elastic constants were measured at ambient conditions for dodecasil-$3C$ with guest molecules N_2 and Ar in the small and $N(CH_3)_3$ in the large framework cages. We are not aware of elasticity measurements on calcined dodecasil-$3C$. First, we notice that the elastic constants were determined from sound velocities measured with Brillouin-zone spectroscopy along the [010], [110], and [111] direction. Equations which hold for cubic crystals,[15,29] the reported symmetry of dodecasil-$3C$ at the time of the experiments, where applied to calculate the elastic constants from the sound velocities. This method yields C_{11}, C_{12}, and C_{14} as independent elastic constants. For crystals with a lower symmetry sound velocities in more directions are needed to determine the elastic constants. (See, e.g., Ref. 30.) Thus, in this experiment it could not be detected if the local symmetry of the sample was perhaps lower than cubic, as indicated by recent ^{29}Si NMR measurements on as-synthesized room-temperature forms of dodecasil-$3C$.[4,11] Also, the symmetry of our calculated structures is lower than cubic. Therefore, we compare the calculated C_{11}, C_{12}, and C_{44} with experiment and consider the remaining computed constants as predictions (see Table III). Furthermore, we compare calculated elastic constants of empty dodecasil-$3C$ with experimental data[15] of dodecasil-$3C$ that contains the guest molecules mentioned earlier. The x-ray powder diagrams of Hofman and Sterzel[31] indicated that as-synthesized dodecasil-$3C$ contracts slightly upon calcination. This might affect our comparison between calculated elastic constants of the empty framework and the experimental data. To estimate this effect, we expanded the unit cells of our calculated structures with 1% by applying a small negative pressure in our minimizations. The latter volume change is above the value obtained from the unit-cell data of calcined dodecasil-$3C$ (Ref. 10) and those of the material used by Freimann and Küppers.[15] For the expanded structures we recalculated the elastic constants. Elastic constants that have changed more than a few percent are listed in Table III. These data imply that the presence of guest molecules has only a small effect on the elastic constants of the framework.

The BJS potential predicts values for C_{11}, C_{12}, and C_{14} that are in reasonable agreement with experiment. Both the KFBS and JC potentials predict these constants less accurately than the BJS potential (see Table III). The worse KFBS predictions for the elasticity of dodecasil-$3C$ seem peculiar when compared with predictions for other silicates. Predictions of the KFBS potential for the elastic constants of coesite and stishovite are more accurate than those of both other potentials. (See Appendix.) Similar results were obtained for predictions on high-pressure elasticity of α-quartz.[32] Therefore, we would not expect that the KFBS predicted elastic constants of dodecasil-$3C$ are less accurate than the JC and BJS predictions, *unless* the KFBS prediction for this structure is less accurate. The following arguments indicate that the latter must be the case. We have seen that the KFBS predicted symmetry for dodecasil-$3C$ differs much from the BJS and JC predictions. The latter potentials predict similar symmetries for dodecasil-$3C$, although they are parametrized in completely different ways: The JC potential is derived from empirical data on α-quartz, whereas the BJS potential is solely derived from *ab initio* data of small silicious clusters. Furthermore, the JC potential pre-

TABLE IV. Predictions for the structure of dodecasil-$3C$ compared with experimental (split position refined) data for calcined dodecasil-$3C$ at $T = 523 \pm 15$ K (Ref. 10). Distances are in Å and angles in degrees.

Property	Expt.	BJS I	KFBS	JC
a	19.369	18.796	19.758	19.239
b	19.369	18.694	19.758	19.247
c	19.369	18.860	19.925	19.455
α	90.00	89.75	90.00	89.98
β	90.00	90.08	90.00	90.13
γ	90.00	89.36	90.00	89.95
$d_{\text{Si-O}_s}$	1.569	1.589	1.595	1.588
$d_{\text{Si-O}_l}$	1.598	1.622	1.616	1.607
$\langle d_{\text{Si-O}} \rangle$	1.581	1.605	1.606	1.597
$\angle_{\text{Si-O-Si}_s}$	150.9	132.6	158.6	141.3
$\angle_{\text{Si-O-Si}_l}$	175.8	156.6	177.0	175.9
$\langle \angle_{\text{Si-O-Si}} \rangle$	163.5	143.5	169.8	156.1
$\angle_{\text{O-Si-O}_s}$	104.3	102.7	107.7	109.5
$\angle_{\text{O-Si-O}_l}$	114.4	115.1	111.4	113.0
$d_{\text{Si-Si}_s}$	3.066	2.989	3.140	3.031
$d_{\text{Si-Si}_l}$	3.156	3.105	3.228	3.176
$\langle d_{\text{Si-Si}} \rangle$	3.123	3.051	3.188	3.113
Symmetry	$Fd\bar{3}m$	$P\bar{1}$	$I\bar{4}2d$	$P1$

dicts a large range of all-silica structures very accurately.[33] Also, for *zsm*-5 and *ssz*-24 it has been shown[33,34] that the KFBS predicted symmetries are not in accordance with experiment, in contrast to the BJS and JC predictions.

C. Comparison of predictions for the dodecasil-$3C$ structure with experiment

The BJS potential predicts that dodecasil-$3C$ without guest molecules is triclinic with space group $P\bar{1}$ for temperatures ranging from 0 to 1200 K. In this temperature range the KFBS predicted structure is tetragonal with space group $I\bar{4}2d$. The JC potential predicts that the structure of dodecasil-$3C$ is triclinic with space group $P1$, which is thermally stable up to 400 K. We compare the predicted structures with (split position refined) single-crystal data of Könnecke, Miehe, and Fuess[10] that were obtained for a calcined sample at $T \approx 523$ K. As we are not aware of single-crystal data on the structure of calcined dodecasil-$3C$ at lower temperatures, we will also compare the JC predicted structure at 400 K with the data of Könnecke, Miehe, and Fuess, thereby assuming that the structure does not change much in the range 400–500 K. Table IV presents the experimental data in comparison with the JC predicted structure at 400 K and the predictions of both other potentials at 500 K. The unit-cell parameters, as predicted by the JC potential, are much closer to experiment than those of the other potentials. All three potentials predict Si-O distances that are considerably larger than the experimental values. The KFBS predicted Si-O-Si bond angles are closest to the experiment, while both the BJS and JC potential seem to underestimate these values. The predictions for dodecasil-$3C$ are peculiar when compared with the performance of the potentials presented in a study on a large number of *other* all-silica structures.[33] According

TABLE V. Calculations of the structure and elastic constants of coesite at room temperature, compared with experiment. Experimental values for the elastic constants are from Ref. 30. Experimental data for the structure are from Ref. 35. Lengths are in Å and angles in degrees. Elastic constants, denoted as C_{ij}, are in 10^{10} N/m^2.

Property	Expt.	BJS	KFBS	JC
a	7.137	6.851	7.157	6.816
b	12.37	12.15	12.51	12.29
c	7.174	7.026	7.275	7.118
β	120.3	120.0	120.7	119.4
d_{Si-O_s}	1.595	1.567	1.581	1.570
d_{Si-O_l}	1.621	1.637	1.621	1.628
$\langle d_{Si-O} \rangle$	1.609	1.614	1.605	1.611
$\angle_{Si-O-Si_s}$	137.2	127.1	145.1	132.8
$\angle_{Si-O-Si_l}$	180.0	179.99	179.99	180.00
$\langle \angle_{Si-O-Si} \rangle$	150.8	140.3	154.6	143.9
$\angle_{O-Si-O_s}$	108.0	104.8	104.3	105.0
$\angle_{O-Si-O_l}$	110.4	114.6	115.6	112.7
C_{11}	16.08	11.97	17.30	9.32
C_{12}	8.21	6.15	8.21	6.26
C_{13}	10.29	6.45	10.60	7.42
C_{15}	−3.62	−1.17	−2.93	0.47
C_{22}	23.04	21.37	24.89	21.05
C_{23}	3.56	5.53	8.72	6.60
C_{25}	0.26	1.78	0.98	2.17
C_{33}	23.16	22.20	27.83	23.96
C_{35}	−3.93	−5.51	−4.80	−6.03
C_{44}	6.78	5.13	2.77	3.36
C_{46}	0.99	1.24	−0.83	0.70
C_{55}	7.33	4.49	5.90	4.77
C_{66}	5.88	4.13	3.92	3.95
Symmetry	$C2/c$	$C2/c$	$C2/c$	$C2/c$

TABLE VI. Calculations of the elasticity and structure of stishovite at room temperature, compared with experiment. Experimental values for the elastic constants and the structure are from Refs. 36 and 37, respectively. Distances are in Å and angles in degrees. Elastic constants, denoted as C_{ij}, are in 10^{10} N/m^2.

Property	Expt.	BJS	KFBS	JC
a	4.177	4.102	4.164	4.034
c	2.665	2.595	2.667	2.776
d_{Si-O_s}	1.757	1.753	1.758	1.784
d_{Si-O_l}	1.809	1.722	1.799	1.733
$\langle d_{Si-O} \rangle$	1.774	1.742	1.771	1.767
$\angle_{Si-O-Si}$	130.7	132.3	130.7	128.9
$\angle_{O-Si-O_1}$	81.3	84.5	81.3	77.8
$\angle_{O-Si-O_2}$	180.0	180.0	180.0	180.0
$\angle_{O-Si-O_3}$	90.0	90.0	90.0	90.0
$\angle_{O-Si-O_4}$	98.7	95.5	98.7	102.2
C_{11}	45.3	67.8	62.5	47.5
C_{12}	21.1	34.8	22.8	30.4
C_{13}	20.3	41.2	26.8	36.1
C_{33}	77.6	98.9	93.3	86.6
C_{44}	25.2	26.8	26.9	14.7
C_{66}	30.2	37.9	26.1	39.6
Symmetry	$P4_2/mnm$	$P4_2/mnm$	$P4_2/mnm$	$P4_2/mnm$

predictions for the nearest-neighbor Si-Si distances differ *not* much from the experimental values. The KFBS and BJS predictions for the Si-Si distances are consistent with those predicted for a large number of all-silica frameworks.[33] This suggests that in the actual structure the O atoms may be further away from the line connecting nearest-neighbor Si-Si atoms, than indicated by experiment. Thus, the experimentally determined O positions in calcined dodecasil-3C may not be well-resolved. Our conclusions agree with the observation[10] that refinement in space group $Fd\bar{3}m$ of the calcined dodecasil-3C structure, with O atoms on split positions, already lowered the average Si-O-Si bond angle and increased the average Si-O bond distances, compared to those obtained from conventional refinement in that space group.

IV. CONCLUSIONS

The shell-model calculations indicate that the local symmetry of dodecasil-3C without guest molecules is triclinic for temperatures between 0 and 1200 K. For the KFBS predictions, that indicate a different structure, we have shown that they are less reliable. The JC potential predicts that the triclinic structure undergoes at $T = 300$ K a small displacive phase transition where the symmetry of the framework changes from $P\bar{1}$ to $P1$. According to the BJS potential, this structure remains a single phase with space group $P\bar{1}$ in the temperature range studied. More experiments are needed to determine the accuracy of these predictions. Our calculations indicate that the experimental values reported for the Si-O-Si bond angle might be too large whereas that for the Si-O bond distances might be too small. This may be due to less accurately measured positions of the O atoms in the framework. Furthermore, the BJS potential predicts elastic constants C_{11}, C_{12}, and C_{44} that are in reasonable agreement with experi-

to that study,[33] predictions of the three potentials for the Si-O distances in the latter frameworks are much closer to experiment than those predicted for dodecasil-3C. Furthermore, for all silicas studied,[33] the Si-O-Si bond angles in those frameworks are overestimated by the KFBS potential, underestimated by the BJS potential, and most accurately predicted by the JC potential. However, *both* the JC and BJS potential seem to underestimate the Si-O-Si bond angles in dodecasil-3C, while the KFBS prediction is closest to experiment. Furthermore, the BJS predicted Si-O-Si bond angles in dodecasil-3C deviate much more from experiment than the predictions for other all-silica polymorphs.[33] If the BJS predicted dodecasil-3C structure really deviates that much from experiment, then it is peculiar that the potential still predicts the elastic constants for this framework reasonably (see Table III). Also, if the KFBS predicted structure is accurate, then it is peculiar that this potential does not predict elastic constants that are in agreement with experiment, which was argued in Sec. III B. The predictions of each potential for the structure of dodecasil-3C would be consistent with those for other all-silica frameworks, when in the *actual* dodecasil-3C structure the Si-O-Si bond angle would be smaller and the Si-O bond distance would be larger than the experimental values that have been reported so far.[10] We notice that JC

mental values. The latter values were obtained by the application of cubic symmetry in the equations that relate the elastic constants to the measured sound velocities. As our calculations indicate that the local symmetry of empty dodecasil-3C might be lower than cubic, it might be interesting to perform additional elasticity measurements on calcined dodecasil-3C and to compare the results with the BJS predictions.

APPENDIX

Tables V and VI present structure and elasticity calculations for stishovite and coesite. The KFBS values for both the structure and elasticity of those silicates are the closest to experiment.

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