Formation, migration, and clustering energies of interstitial He in α -quartz and β -cristobalite

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Abstract

Precipitation of implanted helium (He) is detrimental to many nuclear materials. A solid in which implanted He does not precipitate, but rather remains in solution and diffuses readily is potentially of interest for applications requiring resistance to He-induced damage. We use density functional theory (DFT) calculations to examine He interstitial formation, migration, and clustering energies in two SiO₂ polymorphs: α -quartz and β -cristobalite. Our findings show greater He solubility and mobility in the latter than in the former. This difference appears to be due primarily to the unlike atomic-level structures of α -quartz and β -cristobalite, rather than their differing densities. Our findings also suggest that He is unlikely to cluster in either material. The behavior of He in α -quartz and β -cristobalite, and similar forms of silica make them promising materials for further investigation for potential use in applications requiring resistance to He-induced damage.

I. Introduction

Implanted helium (He) has a deleterious effect on metals used in nuclear energy [1,2]. In fission reactors, He generated through neutron-induced transmutations embrittles Ni-base alloys [3]. In future magnetic confinement fusion reactors, He-induced surface damage may prove life-limiting for plasma-facing materials [4]. In both cases, the damaging effect of He is due to its insolubility [5]: it precipitates out rapidly, stabilizing void nuclei [6–8] and weakening grain boundaries [9,10]. He is also insoluble in a wide range of ceramics, including oxides, nitrides, and carbides [11]. Similar to He, noble gas fission products such as Kr and Xe are insoluble in UO_2 and accelerate degradation of nuclear fuels upon precipitating out [12,13]. Thus, materials in which implanted noble gasses do not precipitate out are potentially of interest for applications requiring resistance to He-, Kr-, or Xe-induced damage.

Using density functional theory (DFT) calculations, we investigate He interstitial formation, migration, and clustering energies in two polymorphs of crystalline silica (SiO_2): α -quartz and β -cristobalite. Our findings indicate that, in β -cristobalite, He interstitials have high solubility and diffusivity as well as no tendency to bind with each other. Similar to β -cristobalite, pairs of He interstitials do not bind to form stable complexes in α -quartz. However, He interstitial solubility and diffusivity in α -quartz are lower than in β -cristobalite. Differences in He behavior in these materials may be due to different densities or atomic-level structures. However, our results support the view that atomic-level structure—rather than density—plays an overriding role in determining He behavior in silica, motivating further investigations of He in other structural forms of SiO_2 .

Our work is inspired by experiments demonstrating high solubility [14–16] and rapid diffusion [14,17,18] of He in amorphous silica (a-SiO_2). This behavior is thought to be due to the ease of He penetration into and through high-volume

interstices in α -SiO₂ [16]. Experiments on crystalline silica are consistent with this interpretation: low-density (~ 2.28 g/cm³) polymorphs tridymite and cristobalite have high He lattice solubility [19] while He solubility is four orders less in quartz. Moreover, the He diffusion rate scales with dislocation density in quartz, consistent with He segregation to defects due to low solubility in the perfect crystal [20]. The solubility and high diffusivity of He is also considered to account for the anomalously low compressibility of α -SiO₂ under GPa-level He pressures [16,21,22] : rather than simply exerting an external pressure that collapses high-volume interstices, He enters into them and buttresses them from within against the applied load [16,22].

The unique behavior of He in α -SiO₂ has prompted assessments of this material for applications that require resistance to He-induced damage. For example, Mattern *et al.* found that He implantation does not cause blistering or exfoliation of α -SiO₂ over a wide range of temperatures up to $\sim 800^\circ\text{C}$ [23]. Fares *et al.* investigated He implantation into a sodium borosilicate glass and observed rapid He transport and no evidence of He precipitation, blistering, or cracking [24]. Both studies indicate the solubility of He in α -SiO₂ as the underlying reason for lack of He-induced damage.

Perfect crystalline solids contain a small number of distinct types of interstitial sites [25]. By contrast, α -SiO₂ has a continuous distribution of interstitial sites whose structures depend on average density [26]. He solubility and diffusivity in α -SiO₂ are thought to depend on the volumes and connectivity of these sites [27]. Atomic-scale simulations have the potential to elucidate the behavior of He in such interstitial networks in detail. However, due to their high computational cost, first principles models of α -SiO₂ typically contain 100 atoms or fewer [28–30], resulting in discrepancies with experimental measurements [31].

Direct, first principles simulations of He in silica have therefore not yet been performed. Instead, investigators have resorted to other approaches. Boiko and Berezhnoi studied He diffusion in α -quartz and a-SiO₂ using a classical pair potential [32] that represents the polarization-induced interaction of He with oxygen, but neglects the interaction between He and Si [33,34]. They show that He diffuses by passing between adjacent interstitial sites *via* channels formed by silicate rings. Hacırlıoğlu *et al.* performed DFT simulations of He passing through freestanding silicate rings and found that the activation energy for the transition decreases markedly as the number of oxygen bridges in the ring increases from four to eight [35]. These findings support the view that the elevated diffusivity of He in low-density forms of silica is due to their more open atomic structures. However, first principles models of He in structurally accurate, fully three-dimensional models of silica have yet to confirm this interpretation.

In the work presented here, we investigate the formation, clustering, and migration energies of He interstitials in α -quartz and β -cristobalite. Because these materials are crystalline, it is straightforward to construct accurate, fully 3-D models of them that are sufficiently small to allow for DFT simulations. β -cristobalite has a density of ~ 2.2 g/cm³ [36], close to that of a-SiO₂. Indeed, a-SiO₂ has been described as a disordered form of β -cristobalite [37]. α -quartz has a more compact SiO₂ network, with a higher density of 2.6 g/cm³ [36]. Thus, investigating these two structures sheds light on the effect of SiO₂ density and atomic structure on He behavior in silica.

II. Modeling methods

The crystal structures of α -quartz and β -cristobalite are obtained from Refs. [38,39], which report unit cell dimensions and atom coordinates obtained from x-ray diffraction. To ensure that our simulation cells are large enough to allow for network distortions caused by He interstitials, we use supercells consisting of 2x2x2

unit cells for both crystals (trigonal in the case of α -quartz, cubic for β -cristobalite). Our α -quartz models contain 24 Si and 48 O atoms while for β -cristobalite, there are 64 Si and 128 O atoms.

The local density approximation is known to overestimate the cohesive energy of SiO_2 markedly [40]. We therefore perform first principles calculations with the PBE (Perdew, Burke, and Ernzerhof [41]) version of the generalized gradient approximation within the plane-wave pseudopotential scheme using the Quantum-ESPRESSO package [42]. We use Rabe-Rappe-Kaxiras-Joannopoulos ultrasoft pseudopotentials [43] for Si and O and the Martins-Troullier norm-conserving pseudopotential [44] for He. The kinetic energy and charge density cutoffs are 544.2 eV (40 Ry) and 4353.8 eV (320 Ry) respectively. We use a 2x2x2 Monkhorst-Pack (MP) k-point grid. These parameters were determined based on careful tests of energy and force convergence with larger cutoffs and denser MP k-points. We find that the energy difference is less than 5 meV/atom (0.0004 Ry/atom) and the force difference is less than 0.005 eV/a.u. (0.0004 Ry/a.u.) when compared to higher cutoffs and k-point densities. For models containing He, we perform calculations both with and without a van der Waals (vdW) dispersion correction. Such corrections are commonly used when dealing with inert gases in DFT calculations. They are applied by adding a semi-empirical dispersive force [45]. Unless stated otherwise, the results reported herein refer to calculations without the dispersion correction.

To validate our DFT settings, we use them to compute the volume per formula unit, cohesive energy, and bulk modulus of α -quartz. Similar experimental data for β -cristobalite are not available since it is not thermodynamically stable at room temperature. Table I compares our results with experimental values, previous DFT calculations, and the predictions of several classical potentials. Our calculations agree with experiments, confirming that our choice of energy cutoff and pseudopotential are optimal for SiO_2 networks.

Table I. Bulk modulus (B_0), volume per SiO_2 formula unit (V_0), and cohesive energy per SiO_2 formula unit (E_0) for α -quartz.

	B_0 (Gpa)	V_0 ($\text{\AA}^3$)	E_0 (eV)
Present work	30.7	40.36	-19.68
Experiments [46,47]	34-37	37.7	-19.23
MEAM [48]	35	34.7	-29.08
ReaxFF [49]	64.2	37.5	-19.29
LDA [50]	37	N/A	-22.42
GGA [51,52]	31.3	N/A	-19.74 [51] -23.83 [52]

To relax the crystal structures, we first investigate how their energies change when the volume is varied isotropically. Then, starting from the lowest energy volume, we use the BFGS (suggested independently by Broyden [53], Fletcher [54], Goldfarb [55], and Shanno [56,57]) quasi-newton algorithm to relax both the ion positions and the cell dimensions. For α -quartz, the optimized supercell dimensions are $10.056 \times 8.709 \times 11.061$ $\text{\AA}$ and for β -cristobalite they are $14.905 \times 14.905 \times 14.905$ $\text{\AA}$. From these cell sizes, we compute the volume per formula unit, V_0 , of each structure. The calculated lattice parameters for both crystals are slightly higher than reported experimental values [46,47]. When investigating He impurities in these models, we relax only the ion positions and not the simulation cell shapes.

As observed by Flocke *et al.* [58], the potential energy surface for α -quartz is rather flat with respect to small-scale atomic displacements about their equilibrium positions. Thus, allowing atomic positions to adjust during the structure relaxation results in slight deviations from the ideal perfect crystal sites. These deviations may be suppressed by fixing atomic positions during the simulation cell shape relaxation.

However, we choose to retain them as they give rise to a more representative sampling of He migration energies, to be described in section V.

Cohesive energy, E_0 , is the energy required to pull a formula unit of the crystal apart into a set of free atoms: $\text{SiO}_2 \text{ (crystal)} \rightarrow \text{Si (atom)} + 2\text{O (atom)}$. Thus, to compute E_0 , we subtract the energies of standalone spin-polarized Si and O atoms from the energy of crystalline SiO_2 . We obtain the bulk modulus, B_0 , by fitting the Birch-Murnaghan equation of state [59],

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B'_0 + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\} \quad (1)$$

to the energy-volume curve per formula unit near the lowest energy volume of the crystal structure.

To compute He interstitial formation energies, we first locate the stable interstitial sites in the crystal structures of interest. The canonical interstitial sites for β -cristobalite are already known [60]. To locate interstitial sites in α -quartz, we decompose the SiO_2 network into Voronoi cells using the Voronoi tessellation algorithm [61] (using the VORO++ code library [62]). Each Voronoi cell is centered on either a Si or O atom. Candidate interstitial sites are located at the vertices, the centers of edges, and centers of faces of the Voronoi polyhedra. We test the mechanical stability of He interstitials at each site by inserting one He atom at the site, relaxing the atomic model, and determining whether the He moved to a different site. We also determine which sites are thermodynamically stable by finding the ones with lowest interstitial formation energy.

Formation energies, ΔE_{He} , of He interstitials are computed as

$$\Delta E_{\text{He}} = E(\text{SiO}_2 + \text{He}) - E(\text{SiO}_2) - E(\text{He}). \quad (2)$$

Here, $E(\text{SiO}_2 + \text{He})$ is the energy of the relaxed atomic model containing a He atom, $E(\text{SiO}_2)$ is the energy of the atomic model prior to insertion of a He atom, and $E(\text{He})$ is the energy of an isolated He atom in vacuum. Positive ΔE_{He} means that the insertion of a He impurity is endothermic, i.e., there is an energy penalty to solvate the He atom. Negative ΔE_{He} means that solvation is exothermic.

The tendency of He interstitials to cluster is characterized by computing the interaction energy of a di-He cluster. We investigate configurations where individual He atoms occupy two adjacent interstitial sites as well as ones where two He atoms (a He dimer) occupy a single interstitial site. In the latter case, we initially place the He atoms 1.6 Å apart with the midpoint between them at the interstitial site. The interaction energy, ΔE_{int} , of the di-He cluster is the difference between its formation energy and that of two isolated He interstitials:

$$\Delta E_{\text{int}} = \Delta E_{2\text{He}} - 2\Delta E_{\text{He}}. \quad (3)$$

Here, $\Delta E_{2\text{He}}$ is the formation energy of a di-He cluster, computed as

$$\Delta E_{2\text{He}} = E(\text{SiO}_2 + 2\text{He}) - E(\text{SiO}_2) - 2E(\text{He}). \quad (4)$$

According to the definition in Eqn. 2, positive ΔE_{int} signifies that the di-He cluster is thermodynamically unstable with respect to decomposition into isolated interstitials.

To compute He migration energies, ΔE_{mig} , we find minimum energy paths (MEPs) between adjacent interstitial sites using the climbing image nudged elastic band method (CI-NEB) [63]. The migration energy is the difference between the maximum energy along the MEP and the energy of the interstitial site from which migration commences.

III. He interstitial solubility

Fig. 1 shows the two canonical interstitial sites of β -cristobalite [60]: the Si tetrahedral site (Fig. 1.a) and a site between adjacent Si tetrahedra (Fig. 2.b). In the former, the interstitial is 4-fold coordinated by Si atoms with equal distance to each. Following Mariani and Hobbs [64,65], the atomic bonding topology of SiO_2 networks may be described in terms of primitive rings. In the case of β -cristobalite, four 6-membered rings pass through every Si atom [37]. Fig. 2 shows one such ring from three different perspectives. The interstitial site in Fig. 1.b is located at the midpoint of a 6-membered primitive ring of β -cristobalite.

Fig. 1: He interstitial sites (gray spheres) in a 1×1 β -cristobalite cell. Yellow, red, and white beads represent Si, O and He atoms. (a) Tetrahedral site. (b) 6-membered primitive ring center site.

Fig. 2: The 6-membered primitive ring in β -cristobalite. Yellow beads are Si atoms and red beads are O atoms. (a), (b) and (c) show three orthogonal projections of the same ring.

We find that He interstitials in β -cristobalite are only stable at the tetrahedral site shown in Fig. 1.a. If a He atom is placed at the ring center site in Fig. 1.b and perturbed slightly from its initial position, then upon relaxation of the atomic structure, it will move to one of the adjacent tetrahedral sites. As will be shown in section V, the ring center site in Fig. 1.b is in fact the saddle point configuration for He migration between adjacent tetrahedral sites.

The formation energy of a He interstitial in β -cristobalite is 0.035 eV. The smallest distance between He and other atoms in this configuration is the 3 Å He-O distance. Using the vdW dispersion correction described in section II yields a tetrahedral He interstitial formation energy of -0.039 eV. The experimentally determined He solvation energy in β -cristobalite is 0.1 ± 0.026 eV [19], suggesting that the DFT calculations without the vdW correction might be more representative for the atomic configurations of interest here. However, in both α -quartz and β -cristobalite, the vdW corrections on He interstitial formation energy, He-He binding energy, and He migration energy are less than 100 meV, 10 meV, and 20 meV, respectively. These energy differences fall within the range of uncertainty of the DFT calculation itself and therefore cannot be considered as significant.

For α -quartz, we use the Voronoi tessellation to find interstitial sites. Due to the slight displacements of atoms from the exact equilibrium positions mentioned in section II, the Voronoi polyhedra found for different Si and O atoms are not identical. We choose to investigate five unique, contiguous Voronoi cells: three centered on Si atoms and two on O atoms, as shown in Fig. 3. Among the possible interstitial sites identified from these polyhedra, there are eight regions—shaded in Fig. 3—that have lowest He interstitial energies, all within the range 0.52-0.53 eV (0.40 eV with

the vdW correction). All initial interstitial positions in each of these regions in fact relax to the same stable He interstitial configuration.

Fig. 3: Contiguous Voronoi polyhedra for five connected atoms in α -quartz. Red spheres are O atoms. Cyan spheres are Si atoms. The lines represent individual Voronoi polyhedra for each atom. Vertices (where lines connect), edge centers (crosses), and face centers (solid squares) of the polyhedra are candidate sites for He interstitials. Sites within each of the shaded regions give rise to identical interstitial structures upon relaxation.

As in the case of β -cristobalite, the locations of lowest-energy He interstitials in α -quartz may be understood in terms of 6-membered primitive rings. Figure 4 shows such a ring from several perspectives. Comparing them with Fig. 2, we see that they have a different, more compact configuration than in β -cristobalite. Figure 4.b

shows the location of a He interstitial with respect to one of these rings. The interstitial occupies the high volume region encircled by the silicate ring.

Figure 4. A 6-membered primitive ring in α -quartz viewed from three perpendicular directions. (b) illustrates the location of one He interstitial with respect to the silicate ring. Yellow: Si, red: O, white: He.

Table II summarizes the He interstitial formation energies calculated in β -cristobalite and in α -quartz. The formation energy in β -cristobalite is considerably lower than in α -quartz. Comparing Fig. 2 and Fig. 4 suggests that this difference may be due to the more closely planar conformation of primitive rings in β -cristobalite, resulting in a more spacious site for the He interstitial and greater He-O nearest neighbor distances. Indeed, the distance between the He interstitial and the nearest O atom in α -quartz is ~ 2.5 Å, significantly lower smaller than the ~ 3.0 Å He-O distance for interstitials in β -cristobalite tetrahedral sites.

Table II. He interstitial formation energies in β -cristobalite and α -quartz.

SiO ₂ polymorph	ΔE_{He} without vdW (eV)	ΔE_{He} with vdW (eV)	Experiment (eV)
β -cristobalite	0.035	-0.039	0.1 ± 0.026 [19]
α -quartz	0.52-0.53	0.40	N/A

IV. Interaction of He interstitials

We conduct two types of di-interstitial calculations in β -cristobalite. In the first, we place two He atoms in one tetrahedral interstitial site. We investigate three different orientations of this He dimer: along the x-, y-, and z-axes, illustrated in Fig. 1. For dimers oriented along the x- and z-directions, the He atoms move apart and eventually occupy ring center sites on opposite sides of the original tetrahedral interstitial site. As will be shown in section V, these sites are not stable equilibrium points. However, the energy landscape in their vicinity is sufficiently flat so that the energy minimization nevertheless terminates at this stage. The dimer oriented along the y-direction continues to occupy the same interstitial site after relaxation. In the second type of calculation, we place He atoms in two adjacent tetrahedral interstitial sites. The atoms remain in these sites upon relaxation.

Table III summarizes the outcome of these calculations. We obtain the highest (positive) interaction energy for two He atoms in one interstitial site. The next highest interaction energy is for two He atoms at ring center sites. Finally, the interaction energy for He atoms at adjacent tetrahedral interstitial sites is negligibly small. These calculations show that binding of He atoms to form di-interstitials in β -cristobalite is always endothermic and therefore unlikely to occur. Moreover, the interaction energy decreases as the distance between He atoms increases, indicating that the He atoms experience a repulsive thermodynamic driving force. Thus, the nucleation of He precipitates by aggregation of He interstitials appears unlikely in β -cristobalite, since the first step in that process (the formation of a di-interstitial) is thermodynamically unfavorable.

Table III. He interstitial binding energies in β -cristobalite.

Initial configuration	Initial He-He separation ($\text{\AA}$)	Final configuration	Final He-He separation ($\text{\AA}$)	He di-interstitial formation energy (eV)	He binding energy (eV)
Dimer in tetrahedral site along x-direction	1.9	He atoms occupy ring center sites on opposite sides of a	2.2	0.13	0.201

		tetrahedral interstitial site			
Dimer in tetrahedral site along y-direction	1.9	Same as initial	1.8	0.42	0.452
Dimer in tetrahedral site along z-direction	1.9	He atoms occupy ring center sites on opposite sides of a tetrahedral interstitial site	2.2	0.13	0.210
He atoms occupy adjacent tetrahedral interstitial sites	3.23	Same as initial	3.23	-0.07	0.005

In α -quartz, we construct two types He dimers: ones oriented perpendicular or parallel to the SiO_2 ring shown in Fig. 4. Both dimers start with a separation distance of 1.6 Å. The calculation is summarized in Table IV. After structure relaxation, both dimers have positive He binding energies. During the relaxation for the dimer perpendicular to the ring, the He atom closer to the ring center pushes the further He atom away. Concurrently, the surrounding cage of oxygen atoms expands, making space for this second He atom. The first He atom settles at the interstitial site. The second one ultimately resides in the middle of a 8-membered ring (Fig. 5), despite the fact that the center of an 8-membered ring is not a stable interstitial site for isolated He interstitials. In the case where the dimer is parallel to the ring, both He atoms settle at the center of adjacent 8-membered rings.

We also investigated He atom pairs occupying adjacent interstitial sites shown in Fig. 4 and found that the He atoms and the SiO_2 network remain nearly unaltered during structural relaxation. The binding energy ranges from -0.025 to 0.030 eV among the possible pairs. The negligible interaction of He atom pairs with separations above ~ 3.0 Å in α -quartz is similar to that in β -cristobalite. Thus, as in β -cristobalite, He binding is endothermic at all locations in α -quartz and there is no di-interstitial complex that represents a viable first stage in the formation of a He precipitate nucleus.

Fig. 5: An 8-membered ring in α -quartz. The transparent part and atoms connected to it form a primitive, 6-membered ring.

Table IV. He interstitial binding energies in α -quartz

Initial configuration	Initial He-He separation (Å)	Final configuration	Final He-He separation (Å)	He di-interstitial formation energy (eV)	He binding energy (eV)
Dimer perpendicular to ring	1.6	One He at interstitial site, the other at the center of adjacent 8-membered ring	~ 2.1	1.26	0.199
Dimer parallel to ring	1.6	He atoms at centers of adjacent 8-membered rings	~ 2.1	1.52	0.449
Dimer at adjacent interstitial sites	~ 3.3 -5.5	Remains at the locations	~ 3.2 -5.5	~ 1.1 -1.2	-0.025-0.030

To assess the effect of density and crystal structure on He interstitial formation and binding energies in α -quartz and β -cristobalite, we re-scale the volume of models containing isolated He atoms as well as He atoms at adjacent interstitial sites while keeping their crystal structures fixed. We then recalculate the He interstitial formation and binding energies in these modified simulations cells and plot them in Fig. 6 as functions of volume per formula unit. We find that there is very little change in either energy with changing volume. In particular, the difference between He interstitial energies in α -quartz and β -cristobalite remains approximately the same even when both structures are scaled to the same volume. We therefore conclude that atomic-level structure—not density—is most directly responsible for differences in He behavior in different structural forms of silica. We also find that

van der Waals (vdW) corrections do not make a qualitative difference in the energies of these He defects.

Fig. 6: He interstitial (a) formation and (b) binding energies as a function of formula unit volume in α -quartz and β -cristobalite, computed with and without vdW corrections.

V. He interstitial migration

We compute the MEP connecting two contiguous tetrahedral sites in a 2x2x2 supercell of β -cristobalite using the CI-NEB, as illustrated in Figure 7. The path leads through a ring center site, of the type illustrated in Fig. 1.b. As the He interstitial migrates, the surrounding Si and O atoms hardly move at all, i.e. no distortion of the SiO_2 network is needed to accommodate He migration. Figure 7.b shows that the migration energy barrier is 0.11 or 0.13 eV, depending on whether the vdW correction is used. This barrier is comparable to self-interstitial migration energies in metals [25] and is easily overcome at room temperature. The ring center site is the saddle point for He interstitial migration.

Fig. 7: (a) He interstitial migration path in β -cristobalite. Arrows indicate passage of the interstitial from a tetrahedral site, to a ring center cite, and finally to a neighboring tetrahedral site. Yellow: Si, red: O, white: He, cyan: tetrahedral sites at the endpoints of the MEP. (b) Energy along the MEP.

Each of the interstitial sites in α -quartz identified in Fig. 3 has three adjacent interstitial sites to which He may migrate. We perform NEB calculations on ten potential migration paths, illustrated in Fig. 8. Unlike in β -cristobalite, He migration in α -quartz forces nearby Si and O atoms to displace, resulting in more complex migration paths and higher migration energies. Although the interstitial sites in Fig. 4 and 8 appear similar, we find a wide range of migration energy barriers, from ~ 0.21 to ~ 0.52 eV. The MEPs are not identical: depending on the initial and final sites assigned, some pass through the primitive, 6-membered rings (Fig. 4) while others pass through 8-membered rings (Fig. 5). The latter structure is relatively spacious and thus the energy barrier is lower. Nevertheless, the energy barriers are not sharply divided into two categories, but rather exhibit a broad spectrum, as demonstrated in Fig. 8. These results suggest that He migration in α -quartz is very sensitive to local structure and small variations in the SiO₂ network may cause large changes in He migration energy.

Fig. 8: Black arrows indicate He interstitial migration paths in α -quartz. Corresponding migration energy barriers are listed on the right. The number 6 or 8 in parenthesis indicates which ring type the He passes through. Yellow: Si, red: O, white: He interstitial sites.

VI. Discussion

We have shown that He interstitial formation energies in β -cristobalite are negligibly low, suggesting a high He solubility in this material. Moreover, there is an effective repulsive interaction between adjacent He interstitials, making di-interstitial cluster formation and He precipitation unlikely. He interstitial migration energies in β -cristobalite are on the order of 0.1 eV, indicating rapid He diffusion in this material, even at room temperature. He di-interstitial behavior in α -quartz is similar to that in β -cristobalite, suggesting that He clustering is also unlikely in the former. However, He has higher He interstitial formation energies in α -quartz than β -cristobalite, indicating reduced He solubility. He migration energies are also higher in α -quartz, approaching 0.6 eV in some cases. Although a He interstitial is likeliest to follow a path with the lowest migration energy barriers (0.25 eV, in our calculation), long-range diffusion may require it to pass over higher energy barriers, as well. Therefore, we expect that the effective activation energy for long-range

diffusion in α -quartz will lie between the extremes listed in Fig. 7. The behavior of He in α -quartz and β -cristobalite make them and similar forms of silica promising materials for further investigation for potential use in applications requiring resistance to He-induced damage.

We also found that atomic structure has a more direct effect on He solubility in α -quartz and β -cristobalite than does density. Thus, atomic structure is the deciding factor for whether a certain form of silica is to be considered “similar” to α -quartz or β -cristobalite, from the standpoint of He behavior. One way to describe this atomic structure is in terms of primitive rings—such as those illustrated in Fig. 2, 4, and 5—and their conformations. Density is likely to play an indirect role by changing the relative energies of competing atomic structures, thereby favoring one over the other.

Activation energies for He diffusion in α -quartz have been determined experimentally by observing He release with a mass spectrometer [66]. The activation energy is found to be in the range 0.26-0.52 eV at 200°C, consistent with our calculations. The same experimental technique was also used for high-purity fused quartz (amorphous silica), in which the activation energy for He diffusion is 0.24-0.29 [14]. Although fused quartz has the same density as β -cristobalite (2.2 g/cm³), the activation energy for He diffusion in it is almost twice that of β -cristobalite (0.11~0.12 eV). This difference may be due to the non-uniform distribution of silicate rings in an amorphous structure. All He migration paths in β -cristobalite pass through identical 6-membered rings. By contrast, in vitreous SiO₂ there are different sizes of silicates rings, ranging from 4-membered (4 Si-O pairs) to 8-membered [67]. Moreover, each of these rings may take on complex, non-planar conformations. Therefore, unlike in β -cristobalite, not all migration paths in amorphous silica allow for easy He migration.

A major difference between the two SiO₂ polymorphs investigated here is that α -quartz exhibits far greater structural variability upon introduction of He than does β -cristobalite. When He interstitials are introduced into α -quartz, adjacent Si and O cages expand. He migration in α -quartz forces further structural rearrangements. These rearrangements are likely due to the higher density of α -quartz, leading to stronger interactions between He and the surrounding silica network. By contrast, these interactions are comparatively weak in β -cristobalite due to its lower density and therefore more open atomic structure.

He-induced structural changes in α -quartz may be related to degrees of freedom arising from rigid unit modes (RUMs) [68,69]. The silica polymorphs investigated here as well as other crystalline and non-crystalline forms of silica may be viewed as connected networks for corner-sharing SiO₄ tetrahedra [70]. These tetrahedra are relatively stiff, due to the strong directional bonding between Si and O. On the other hand, the joints between neighboring tetrahedra are comparatively compliant. Thus, SiO₂ networks may undergo easy structure changes through relative rotations of SiO₄ tetrahedra about their joints. Such changes are known as RUMs and are thought to be responsible for phase transitions among the silicates, including highly complex ones, such as those occurring through incommensurate Dauphiné twinning [70,71]. RUMs also give rise to a dynamic disorder structure in β -cristobalite [46,72], which may in turn affect point defect behavior at elevated temperature.

Consistent with previous *ab initio* calculations [35], we find that He migration energies are negligible for approximately planar silicate rings composed of 6 or more siloxanes. Both α -quartz and β -cristobalite contain 6-membered primitive silicate rings. However, only the latter has 6-membered rings with nearly planar conformation (see Fig. 2). The 6-membered rings in α -quartz are folded into a curved conformation (see Figure 4c). Our study suggests that not only does the size of silicate rings matter for He diffusion, but also the minimum He-O distance

encountered as the He migrates through the ring. This distance, in turn, depends on the conformation of the ring.

Finally, our work only considers He behavior in charge-neutral SiO₂. The presence of charged defects or self-trapped electrons [73] may alter He behavior in this material. Because of its closed shell electronic structure, He prefers to occupy interstitial sites with relatively low electron density. Thus, charged defects may cause local modifications to lowest energy He interstitial configurations: He may prefer to occupy hole-trapping defects while avoiding electron-trapping defects.

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