

## $E'$ Centers in $\alpha$ Quartz in the Absence of Oxygen Vacancies: A First-Principles Molecular-Dynamics Study

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The displacement of an oxygen atom in pure  $\alpha$  quartz is studied via first-principles molecular dynamics. The simulations show that when an O atom in a Si-O-Si bridge is moved away from its original equilibrium position, a new stable energy minimum can be reached. Depending on the spin state and charge  $Q$  of the system, this minimum can give rise to either a threefold oxygen (singlet ground state and  $Q = +1$ ) or to an unsaturated Si atom carrying a dangling bond (triplet state). In the latter case, the hyperfine parameters associated with the  $^{29}\text{Si}$  dangling bond are in rather good agreement with electron paramagnetic resonance/electron nuclear double resonance experiments.

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The importance of point defects in  $\text{SiO}_2$  stems from the wide application of the material in a variety of electronic and optical devices. In particular, the  $E'$  centers in  $\alpha$  quartz or  $E'_\gamma$  in amorphous  $\text{SiO}_2$  ( $a\text{-SiO}_2$ ), generated by irradiation and detected as typical electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) signals, represent a prototype point defect. This kind of defect plays a role both in the degradation of  $\text{SiO}_2$ -based devices [1] and in the change of refractive index in glass fibers [2]. Hence, it has attracted particular attention by experimentalists [3–8] and theoreticians [9–17]. To our surprise, however, a unique identification of the  $E'$  centers is still missing. A microscopic picture was given by Feigl, Fowler, and Yip in terms of a positively charged oxygen vacancy in which the two Si atoms relax asymmetrically [9,10]. Such an oxygen-deficient center (ODC) model was later corroborated by density functional theory [12,13] calculations and the computed hyperfine (Hf) parameters nicely agree with the experiment [12]. Yet, experimental data [18,19] indicate that several different atomic geometries are possible. Thus, alternative models have been proposed, involving the trapping of a hole at a triangular ODC [20] or at different types of puckered configurations [21]. The microscopic identification of  $E'$  has become even more complicated in that radiation-induced  $E'$ -like centers in  $\alpha$  quartz were identified as triplet states [22,23]. This seems to be consistent with the one-photon UV irradiation experiments [24].

In this work, we study via Car-Parrinello molecular dynamics (CPMD) [25] to see what happens when an oxygen atom in a  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  bridge is displaced away from its equilibrium position, without being removed. We find that the structure undergoes a local modification, resulting in new stable local minima. In these minima, the dislodged O atom is incorporated in a three-membered ring structure and the remaining Si atom is either fourfold or threefold coordinated, depending on

the spin state. In the neutral spin-triplet state, the formation energy is about 7 eV, similar to that of an ODC, and the calculated Hf parameters agree reasonably with the experimental data for the  $E'_1$  center [7].

We performed Car-Parrinello simulations [25,26] within local spin-density approximation, including gradient corrections on the exchange and correlation, after Perdew *et al.* [27]. The core-valence interactions are described by a Troullier-Martins norm-conserving pseudopotential [28] for Si and by a Vanderbilt ultrasoft pseudopotential [29] for O. Valence wave functions are expanded in plane waves with an energy cutoff of 25 Ry. The system consists of an  $\alpha$  quartz tetragonal supercell of  $9.832 \times 8.514 \times 10.811 \text{ \AA}^3$ , corresponding to the experimental lattice parameters [30], and containing 24 f.u. Periodic boundary conditions are applied and the Brillouin zone is sampled only at the  $\Gamma$  point. Dynamical simulations were performed on an  $(N, V, T)$  ensemble in which the temperature ( $T = 300 \text{ K}$ ) was controlled via a Nosé-Hoover thermostat [31]. The reaction path for the oxygen displacement was sampled within the Blue Moon approach [32], assuming as a reaction coordinate the displacement  $\xi(t) = |\mathbf{R}_\text{O}(t) - \mathbf{R}_\text{O}(0)|$  of the selected oxygen atom from its initial equilibrium position  $\mathbf{R}_\text{O}(0)$ . At each sampled  $\xi$ , the system was equilibrated for about 2.0 ps, sufficient to stabilize the running averages of both the total energy and the constraint force. An integration time step of 5.0 a.u. and a fictitious electron mass of 900 a.u. ensured good control of the conserved variables. The Hf coupling parameters, given in terms of eigenvalues of the  $^{29}\text{Si}$  hyperfine matrix  $A_{ij} = a\delta_{ij} + b_{ij}$ , are

$$a = \frac{2\mu_0}{3} g_e \mu_e g_{\text{Si}} \mu_N \rho_{\text{spin}}(\mathbf{R}), \quad (1)$$

$$b_{ij} = \frac{\mu_0}{4\pi} g_e \mu_e g_{\text{Si}} \mu_N \int \frac{3r_i r_j - r^2 \delta_{ij}}{r^5} \rho_{\text{spin}}(\mathbf{r}) d^3 r, \quad (2)$$

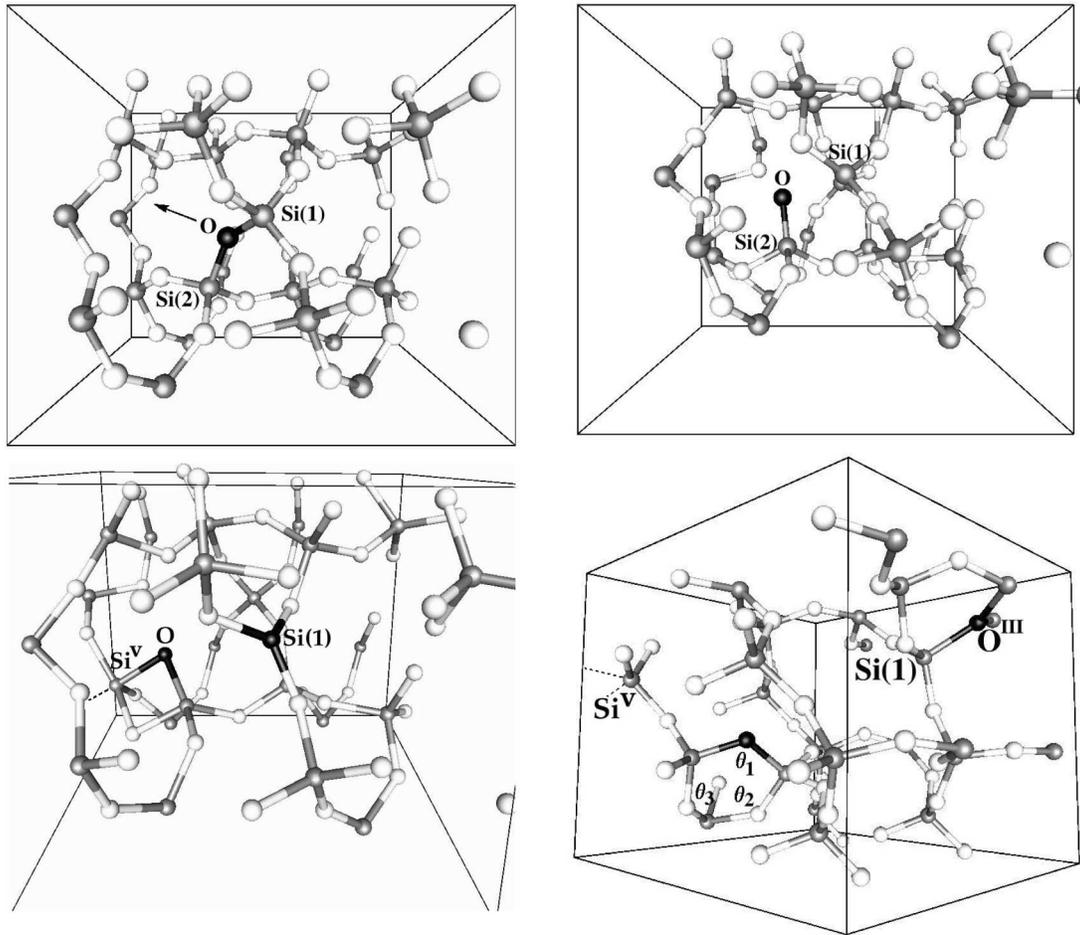


FIG. 1. (a) The  $\text{SiO}_2$  system. Si and O atoms are the gray and white balls, respectively. The O in black is the one displaced in the direction of the arrow. (b) The transition state. (c) A subsequent step with the floating bond  $\text{Si}^{\text{v}}$ . (d) The final minimum with the threefold oxygen ( $\text{O}^{\text{III}}$ ) in black and the three-membered ring. The floating bond displaced to a Si site second neighbor of  $\text{O}^{\text{III}}$  in this snapshot. Dashed lines indicate the bonds not visible due to periodic boundary conditions.

where  $g_e$  is the free-electron  $g$  factor,  $\mu_e$  the Bohr magneton, and  $g_{\text{Si}}$  and  $\mu_N$  the nuclear  $g$  value and the nuclear magneton, respectively. The value of the net spin density  $\rho_{\text{spin}} = \rho_{\uparrow} - \rho_{\downarrow}$  in the core region is given by the van de Walle–Blöchl scheme [33].

We started our simulation with a neutral spin-singlet  $\alpha$  quartz, preequilibrated for  $\sim 1.2$  ps at 300 K, and then imposed a constraint on the O atom of the  $\equiv\text{Si}(1)\text{—O—Si}(2)\equiv$  bridge [Fig. 1(a)], in order to move it away from its original position  $\mathbf{R}_O(0)$ . The chosen direction, indicated by an arrow in Fig. 1(a), was the one toward which the electrostatic repulsion and the bond stress were minimal.

By increasing the distance  $\xi$ , the Si-O long bond breaks and a transition state  $\equiv\text{Si}(2)\text{—O}^{\bullet} + \bullet\text{Si}(1)\equiv$  is reached [Fig. 1(b)] at  $\xi \approx 2.84$  Å, identified by the zero crossing of the constraint force. The total and free energy barriers for this process are  $\Delta E = +7.47$  eV and  $\Delta F = +7.22$  eV, respectively (Table I) and they are close to the formation energy of an ODC [13,15]. The entropic contribution  $T\Delta S = \Delta E - \Delta F = 0.25$  eV accounts for the thermal

motion of the system at 300 K and for the increased number of degrees of freedom of  $\equiv\text{Si}(2)\text{—O}^{\bullet}$  (O stretching and bending) and  $\equiv\text{Si}(1)^{\bullet}$  [Si(1) stretching and out-of-plane modes]. After overcoming the barrier, the system drops to a configuration in which the dangling oxygen forms a new bond with a neighbor Si atom [Fig. 1(c)]. The Si atom is then fivefold coordinated and carries the floating bond. During the subsequent O displacement, the floating bond migrates away onto a nearby Si and the displaced O is included in a three-membered ring structure [34]. Simultaneously, the  $\equiv\text{Si}(1)^{\bullet}$  relaxes

TABLE I. Energetics (in eV) of the O displacement for the neutral, charged ( $Q = +1$ ), and triplet systems. ‡ refers to the activation energy, quench refers to the final quenching.

	Neutral	Charged	Triplet
$\Delta E^{\ddagger}$	+7.47	+7.13	+6.39
$\Delta F^{\ddagger}$	+7.22	+6.97	+6.12
$\Delta E^{\text{quench}}$	+4.12	+3.64	+1.51

slightly beyond the plane formed by its three bonded O atoms and oscillates around a quasiplanar configuration. Shortly after the  $\equiv\text{Si}(1)\text{—O—Si}(2)\equiv$  bond breaking ( $\xi \approx 4.02 \text{ \AA}$ ), the constraint force drops to zero, indicating that the distance  $\xi(t)$  is no longer a good reaction coordinate [35]. Thus, we released the constraint and the system to equilibrate freely with zero average hyperfine parameters, since  $\rho_{\uparrow} = \rho_{\downarrow}$ . However, this was only a metastable object: the system relaxed to the configuration of Fig. 1(d) upon quenching [36]. This structure is located above the unperturbed crystal in energy by 4.12 eV (Fig. 2 and Table I). The  $\equiv\text{Si}(1)^{\bullet}$  undergoes a puckering and forms a bond with a nearby O atom, that becomes threefold bonded. This new bond has a length of 1.83  $\text{\AA}$ , while the former two Si—O bonds with its original Si nearest neighbors have lengths of 1.77 and 1.80  $\text{\AA}$  for the long bond (LB) and the short bond, respectively. Because of the large energy barrier, this structure does not revert back to the original configuration.

An analogous simulation was repeated for the  $Q = +1$  state. The reaction path is similar to the neutral case. Only the barrier is lower by  $\sim 0.3 \text{ eV}$  (see Table I). Also in this case, the structure equilibrates with a quasiplanar threefold  $\equiv\text{Si}(1)^{\bullet}$  and a three-membered ring. After the release of the constraint, we sampled ten configurations, for 1.8 ps, at regular intervals  $\Delta t = 0.18 \text{ ps}$  and computed the average Hf parameters  $\langle A_j \rangle$  of Si(1) and their fluctuations  $\Delta A_j = \sqrt{\langle A_j^2 \rangle - \langle A_j \rangle^2}$ . Instead of one large axial and two equivalent longitudinal components, as expected for an  $E'_1$  center, we found one small axial and two larger equivalent eigenvalues (Table II), similar to the inequivalent  $E'$  center discussed in Ref. [14], characterized by large oscillations and values lower than both experimental data [7] and theoretical estimates [12]. Indeed, also

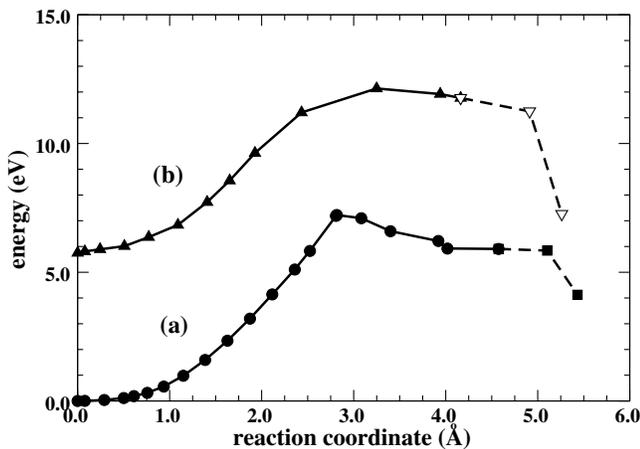


FIG. 2. Energetics of the O displacement as a function of the reaction coordinate. The lower curve (a) refers to the singlet ground state and (b) to the triplet state. The filled symbols indicate the sampled values of the reaction coordinate. The final empty symbols on the dashed line refer to the quench.

this structure is metastable and, upon quenching, forms a threefold O similar to the previous case. Both in the neutral and in the charged state, the three-membered ring structure has average  $\angle\text{SiOSi}$  angles of  $\theta_1 = 119.3^\circ$ ,  $\theta_2 = 132.2^\circ$ , and  $\theta_3 = 139.8^\circ$  [Fig. 1(d)] in agreement with Ref. [34].

For the spin-triplet state, the simulations have been performed in the same way described above. Prior to any O displacement, the relaxed triplet is located 5.75 eV above the singlet (Fig. 2) in energy. The structure, however, is geometrically similar to that of the ground state and  $\rho_{\text{spin}}$  is roughly equally distributed on all the O atoms of the simulation cell.

By displacing the same O selected in the former simulations, the LB breaks apart and a transition state is reached at  $\xi = 3.25 \text{ \AA}$ . The corresponding barriers amount to  $\Delta E = +6.39$  and  $\Delta F = +6.12 \text{ eV}$  for the total and free energies, respectively (Fig. 2). Contrary to the singlet state, no metastable configurations could be found. The release of the constraint and the subsequent quench stabilized the system in the configuration shown in Fig. 3. A three-membered ring is again formed and Si(1) stabilizes in a  $sp^3$  dangling bond (DB) configuration. This configuration is stable and located only at 1.51 eV above the initial spin-triplet structure. This corresponds to a formation energy of 7.26 eV with respect to the perfect  $\alpha$  quartz and is similar to the formation energy of an ODC, indicative of the relative abundance of the present spin-triplet object. In this configuration,  $\rho_{\text{spin}}$  is no longer delocalized, but localized on the O atoms of the three-membered ring structure and on the  $\equiv\text{Si}(1)^{\bullet}$  in the  $sp^3$  DB. This has a small effect on the average  $\angle\text{SiOSi}$  angles of the ring that read  $\theta_1 = 120.0^\circ$ ,  $\theta_2 = 139.1^\circ$ , and  $\theta_3 = 133.4^\circ$ . This spin distribution is adopted by the system in an attempt at minimizing the electrostatic repulsion between the two spin-up electrons; in fact, the distances of Si(1) from the O atoms composing the three-membered ring range from 4.74 to 7.98  $\text{\AA}$ , which is in accord with the experimental estimate of the two parallel spins in the triplet state [23]. The Hf parameters for this state are remarkably close to the experimental values for an  $E'_1$  center (Table II). Nonetheless, in this case, no O atoms have been removed from the system. This quite surprising result is unprecedented and might offer a clue to understanding the experimental outcome about triplet EPR signals [22,23]. Furthermore, it does not disagree with

TABLE II. Average strong hyperfine parameters and computed fluctuations for the  $^{29}\text{Si}$  DB. The metastable state refers to  $Q = +1$ . Experiment is from Ref. [7]. Data are in MHz.

	Experiment	Metastable state	Triplet state
$A_{\text{strong}}^1$	1269.7	$888.0 \pm 128.9$	$1340.4 \pm 89.9$
$A_{\text{strong}}^2$	1095.0	$1033.7 \pm 122.4$	$1274.5 \pm 74.2$
$A_{\text{strong}}^3$	1094.5	$1028.5 \pm 121.8$	$1269.9 \pm 80.2$

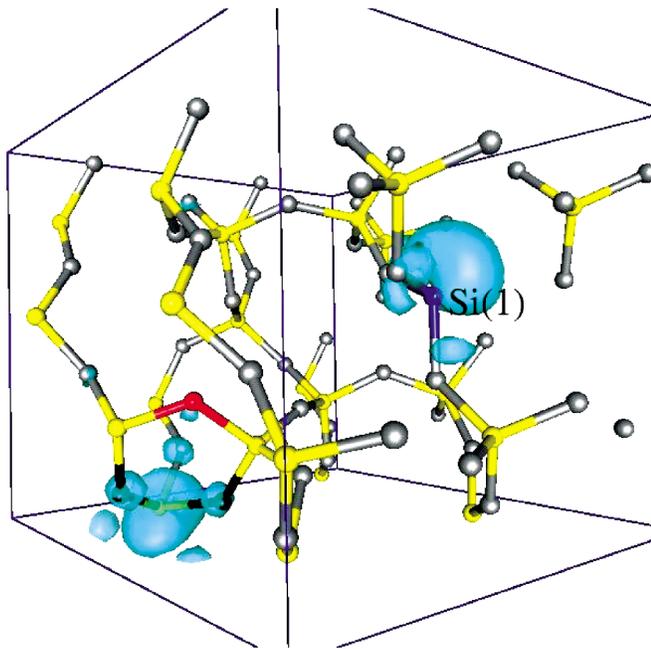


FIG. 3 (color). Spin density distribution in the final structure of the triplet system (yellow: Si, gray: O). The isosurface (light blue) is plotted at  $5 \times 10^{-4} e/\text{\AA}^3$ . Si(1) (blue) is the atom carrying the unpaired DB, the red O is the displaced one, and the other two O (in black) show the three-membered ring.

the reported evidences in which  $E'$  centers are detected in the absence of ionization [24] and it is likely to form during crystal growth or irradiation.

Summarizing, we have shown that, in  $\alpha$  quartz, a displacement of an O atom results in a local distortion that stabilizes as a local minimum. If this O displacement occurs in a triplet state, a DB appears on one Si atom, whose hyperfine parameters agree with experiment. It can also be inferred that those kind of structural modifications can very likely occur in  $\alpha$ -SiO<sub>2</sub>, providing a new guideline for modeling these kinds of defects.

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