

**Migration of O vacancies in  $\alpha$ -quartz: The effect of excitons and electron holes**

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We have used density-functional theory and the nudged elastic-band method to calculate migration pathways and estimated the activation energy for the diffusion of oxygen vacancies in  $\alpha$ -quartz. While the energy barrier for the diffusion of a neutral vacancy is very high, 4.1 eV, the binding of a triplet-state exciton to the vacancy lowers the barrier to 1.7 eV and the attachment of a hole lowers the barrier to 1.9 eV, making the vacancy mobile at commonly used annealing temperatures.

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**I. INTRODUCTION**

Defects in silica play an important role in many situations. Silica is formed as a protective layer on electronic devices, it is the basic component of optical fibers, and it is used to immobilize hazardous waste, such as high-level nuclear waste. The performance is in many cases affected by various kinds of defects in the Si-O network, which can be either crystalline or amorphous. Locally, amorphous silica is quite similar to crystalline quartz and most studies of defects have focused on quartz, a much simpler system. Interstitials have been studied extensively, including theoretical calculations.<sup>1</sup> Another important defect is the oxygen vacancy. It has, for example, been suggested that oxygen vacancies are formed in silica while silicon is oxidized at the same time that Si interstitials are formed in the silicon substrate.<sup>2</sup> Also, voids are often found in glasses after exposure to radiation,<sup>3</sup> possibly because of the agglomeration of vacancies. An important question is how mobile the oxygen vacancies are under various conditions.

Excitons can play an important role in the long-time evolution of the silica network. It has been found that triplet-state, self-trapped excitons (STE) have a long lifetime, on the order of milliseconds.<sup>4,5</sup> Radiation of silica and silicate glasses has been shown to lead to the formation of excitons<sup>6</sup> and it has been speculated that they can lead to Si-O bond breaking and degradation of the silica network. Under certain circumstances radiation can result in densification of silicate glasses.<sup>3</sup> This indicates that defects can be made mobile and/or anneal out in the presence of excitons.

When the Fermi level of silica is shifted by doping, the oxygen vacancies become charged (see, for example, Ref. 7). A (+1)-charged vacancy has been proposed as a model for the intensely studied  $E'_1$  defect in quartz, as well as the  $E'_\gamma$  defect in amorphous silica.<sup>8</sup> Boero *et al.* recently carried out

a density-functional theory (DFT) study of the structure and hyperfine parameters of a (+1)-charged vacancy, providing convincing evidence for the association of this kind of defect with the  $E'_1$  centers.<sup>9</sup>

In this study, we use DFT (Refs. 10,11) to determine the migration path and estimate the activation energy for the diffusion of an oxygen vacancy. We find that the binding of an exciton to the vacancy greatly reduces the activation energy for diffusion, by more than a factor of two. Also, the binding of a hole, which leads to the formation of a positively charged vacancy, reduces the activation energy by a similar amount.

**II. THE COMPUTATIONAL METHODS**

The spin-polarized DFT calculations were carried out with the VASP code,<sup>12</sup> using ultrasoft pseudopotentials<sup>13</sup> and a plane-wave basis set with an energy cutoff of 29 Ry for the wave function and 68 Ry for the electron density. The PW91 (Ref. 14) exchange-correlation functional was used. The importance of using a gradient-dependent density functional rather than the local-density approximation when studying silica has been demonstrated by Hamann.<sup>15</sup> Our calculations were done on a 72-atom cell (eight unit cells) including just the  $\Gamma$  point in the  $k$ -point sampling. Additional  $k$  points were found to have insignificant effect on both structure and singlet/triplet splittings. Two kinds of Si-O bonds are found in alpha-quartz. The DFT calculations predict bond lengths of 1.619 Å and 1.615 Å as compared with experimental estimates of 1.612 Å and 1.607 Å.<sup>16</sup>

We have previously studied self-trapped excitons in quartz by confining the spin-polarized DFT calculations to a triplet state and relaxing the atomic structure.<sup>18-20</sup> This has revealed the existence of three different STEs in quartz. One is quite similar to that found by Fisher, Hayes, and Stoneham

from unrestricted Hartree-Fock (UHF) calculations on small silica clusters.<sup>21</sup> The luminescence calculated by DFT is 2.7 eV in a very good agreement with the experimental value, 2.8 eV (Ref. 6) (while UHF gives 1.6 eV). The self-trapping mainly involves the displacement of an oxygen atom by 1.0 Å, resulting in a broken Si-O bond (2.5 Å). Another STE that turns out to be slightly lower in energy in the DFT/PW91 calculations [but slightly higher in the more accurate DFT/B3LYP (Ref. 22) calculations<sup>18</sup>] involves roughly equally large displacements of two oxygen atoms (by 0.6 Å and 0.5 Å) bonded to the same Si atom, as well as displacements of the adjacent Si atoms (by 0.25 Å), in such a way that Si-O bonds are stretched to 1.76 Å but not broken.<sup>19,20</sup> The calculated luminescence is around 4 eV.<sup>18</sup> This turns out to be close to the observed emission that has been ascribed to vacancies.<sup>6</sup> A detailed comparison of DFT and wavefunction based methods [such as CCSD(T) and CAS-SCF] has shown that the relative energy of different configurations and singlet/triplet splittings for *localized* excitons in silica clusters are represented quite well by the spin-polarized DFT calculations.<sup>20,23</sup> The singlet/triplet splitting of the perfect crystal is, however, calculated to be 6.1 eV, significantly smaller than the experimental estimate of 8.9 eV,<sup>17</sup> consistent with the typical underestimate of band gaps in DFT.

The migration pathway of the vacancy was determined by finding the minimum energy path of a hop from one lattice site to an adjacent site using the nudged elastic-band (NEB) method.<sup>24,25</sup> First, the two endpoint configurations were determined by relaxing the vacancy at the two adjacent sites. Then, a set of intermediate configurations was generated by linear interpolation between the endpoints. The intermediate configurations were then relaxed using an algorithm that ensures convergence to points on the minimum energy path. Harmonic spring interactions are used to connect the different “images” of the system along the path and since all the spring constants were chosen to be equal, the distance between the images along the path become equal. A parallel implementation of this calculation in the VASP code was used and each image was assigned to a separate processor. The NEB calculations parallelize particularly well since for each step, the DFT calculations of each image in the band are independent. Typically the calculation was first carried out with eight images along the path but then the resolution was increased in the relevant regions by inserting additional images and increasing the corresponding spring constants.<sup>24</sup>

### III. MIGRATION OF NEUTRAL VACANCY

When an oxygen atom is removed from the quartz lattice, the two adjacent Si atoms relax towards each other to a distance of 2.5 Å and form a Si-Si bond, see Fig. 1(b).<sup>26</sup> This is a fairly stable configuration, the relaxation energy is 1.1 eV. The formation energy of the vacancy with respect to O<sub>2</sub> in the gas phase is calculated to be 5.2 eV.

The results of the path calculation for the neutral vacancy in the ground state is shown in Fig. 2. The path is fairly direct. It mainly involves motion of an adjacent O atom to fill the vacancy (see inset). The energy barrier for this diffusion hop is high, 4.1 eV. Using a typical prefactor for diffu-

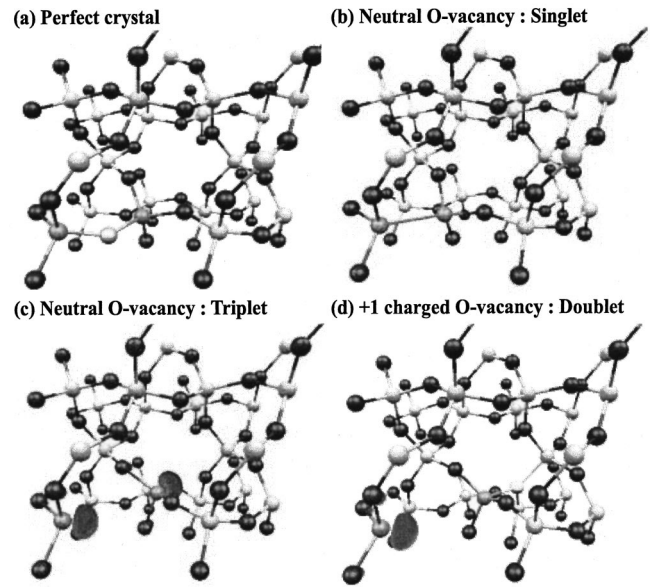


FIG. 1. The 72-atom simulation cell along the (0001) direction for: (a) Perfect  $\alpha$ -quartz crystal; (b) neutral oxygen vacancy in the singlet ground state. The two silicon atoms adjacent to the vacancy (shown with intermediate gray shading) form a covalent bond when the configuration is relaxed, see lower left corner of (b). Panel (c) shows neutral oxygen vacancy in the triplet excited state. When the exciton binds to the vacancy, the Si-Si bond in (b) breaks. The isospin-density surface corresponding to 0.33 electrons/Å<sup>3</sup> is shown and becomes evident at the dangling bonds on the two Si atoms and, to a lesser extent, at the six neighboring oxygen atoms. Panel (d) shows an oxygen vacancy with charge of +1, a doublet state configuration. One of the Si atoms adjacent to the vacancy has moved to a puckered configuration and back bonded to an oxygen atom (shown with light gray), which then becomes three-fold coordinated. The excess spin density is mainly localized in a dangling bond on the Si atom on the other side of the vacancy. The spin-density surfaces are generated in the same way as in (c).

sion,  $10^{12} \text{ sec}^{-1}$ ,<sup>27</sup> this suggests that neutral oxygen vacancies in the ground state are immobile on the time scale of minutes up to a temperature of 1500 K. At the transition state, the Si-Si bond has broken (the distance increased to 2.8 Å) and the two Si atoms have formed bonds to the O atom that moves in to fill the vacancy. One of the Si-O bonds is compressed to 1.60 Å, but the other is stretched to 1.76 Å.

### IV. MIGRATION OF EXCITON-BOUND VACANCY

A neutral vacancy bound to an exciton was simulated by confining the spin-polarized DFT calculation to a triplet state and relaxing the vacancy configuration again. The Si-Si bond then breaks and the distance between the two Si atoms becomes 3.5 Å (compared with 3.06 Å in the perfect quartz lattice), see Fig. 1(c). Both Si atoms are then in a near-planar configuration ( $sp^2$  character) with their three remaining oxygen neighbors. The excess spin density is localized mainly on the two Si atoms adjacent to the vacancy and their oxygen-atom neighbors.<sup>26</sup> As described below, this turns out to be a metastable configuration. The binding energy of the

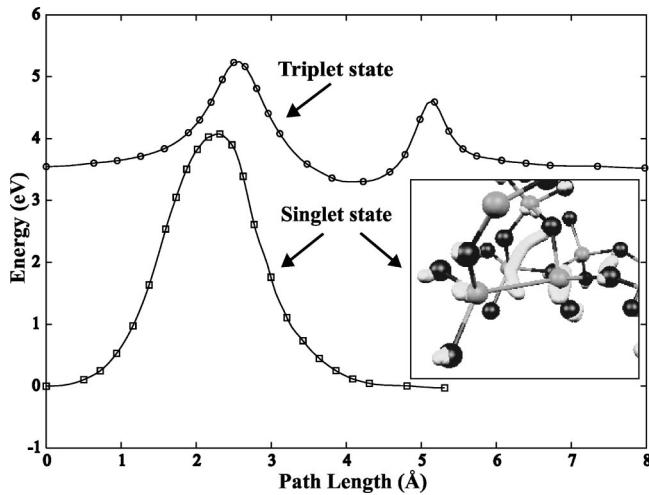


FIG. 2. Migration pathway for a neutral oxygen vacancy in the ground-singlet state (open squares) and in the excited-triplet state (open circles). The path length is the total displacement of all atoms participating in the concerted motion. The inset shows the ground-state migration path that has a high barrier, 4.1 eV. The barrier is reduced greatly in the presence of an exciton, down to 1.7 eV. In the initial and final states of the path the two silicon atoms adjacent to the vacancy are close to being in the plane of the three neighboring O atoms. The NEB method revealed a deeper minimum along the path, where one of the Si atoms has moved through the plane of oxygen atoms to form a puckered configuration. Note that the configurations are not the same for the two paths, but are merely superimposed here. The vacancy relaxed in the triplet state is 3.6 eV higher in energy than the vacancy relaxed in the singlet state.

exciton to the vacancy was estimated by comparing the calculated energy of the excitation (relaxed triplet state vs relaxed singlet state) at a vacancy, 3.6 eV, to the energy of excitation in the absence of a vacancy, 6.5 eV (the oxygen-displaced exciton<sup>19</sup>). This gives a binding energy of 2.9 eV. This large binding-energy suggests that the exciton will remain bounded to the vacancy for several migration hops.

The minimum energy path for a hop from one site to an adjacent site was then calculated with the NEB as before. The results are shown in Fig. 2. The activation energy for diffusion is, now, much smaller than for the ground state, only 1.7 eV. The presence of an exciton, therefore, greatly increases the mobility of a vacancy in quartz. This lowering of the energy barrier is mainly because the initial state is shifted up in energy by 3.6 eV, while the transition state is only shifted by 1.2 eV. The elastic band also reveals that 4 Å along the path, there is an intermediate stable configuration (shown in Fig. 3) that is 0.2 eV lower in energy than the initial configuration of the path. At this stage in the transition, an oxygen atom has already moved to fill the vacancy, leaving a vacancy at the adjacent site. One of the Si atoms, the one that formed the longer Si-O bond with the removed oxygen atom, is placed further away from the vacancy into a puckered configuration (with  $sp^3$  character on the Si atom). The excess spin density in Fig. 3 shows clearly dangling bonds on the two Si atoms adjacent to the vacancy. The distance between the two Si atoms is large, 4.0 Å.

The transition state is characterized by two stretched Si-O

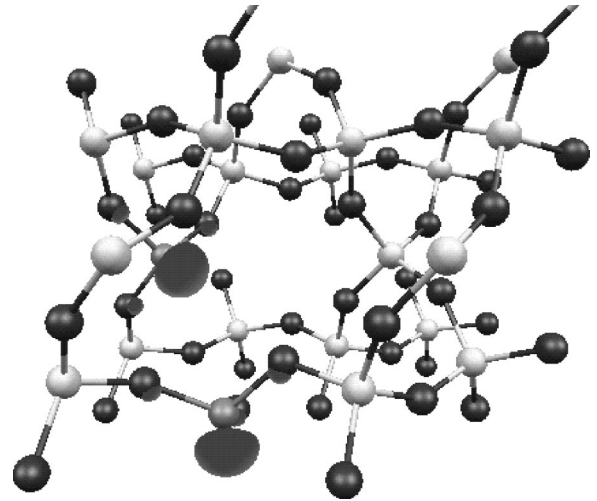


FIG. 3. The intermediate, stable minimum energy configuration that was found from the NEB calculation of the migration of the exciton bound vacancy. This configuration corresponds to the minimum energy (ca. 4 Å along the path) in the path shown in Fig. 2. An oxygen atom has moved into the vacancy shown in Fig. 1(c) and one of the Si atoms has moved through the plane of its three neighboring O atoms into a puckered configuration. The excess spin density is shown as in Fig. 1(c) and clearly reveals the two dangling bonds.

bonds with the displaced O atom, 1.97 Å and 1.69 Å. The distance between the two Si atoms adjacent to the initial vacancy has decreased to 3.0 Å while the distance between the Si atoms adjacent to the new vacancy site has increased to 3.2 Å. The excess spin density is almost as localized in the transition state as it is in the initial and final states of the diffusion hop.

## V. MIGRATION OF CHARGED VACANCY

The ground-state configuration of a positively charged vacancy is shown in Fig. 1(d). In this calculation a neutralizing charge was uniformly distributed over the system in Fig. 4. Here, one of the Si atoms adjacent to the vacancy has moved through the plane of its three oxygen-atom neighbors (a puckered configuration) to back bond (bond length 1.9 Å) to an oxygen atom that already is two-fold coordinated and thereby becomes three-fold coordinated. The distance between the two Si atoms adjacent to the vacancy becomes large, 4.3 Å. This kind of configuration was first suggested by Rudra and Fowler<sup>28</sup> as a model for the  $E'_1$  defect. Our calculations based on the PW91 functional are in good agreement with the LDA calculations of Boero *et al.*<sup>9</sup> who pointed out that this puckered configuration is only slightly lower in energy than a more planar configuration ( $sp^2$  character). In our calculations the energy difference is 0.1 eV.

Figure 3 shows the calculated migration path for the positively charged vacancy. The path first involves a conversion of the puckered to the planar configuration, then a hop to a planar configuration at an adjacent site, and finally a conversion back to a puckered configuration. The barrier for this configurational change is calculated to be 0.4 eV while the



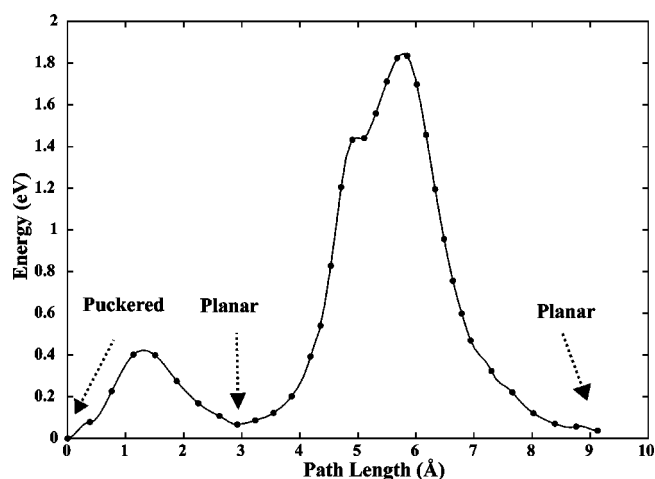


FIG. 4. Migration path for an oxygen vacancy with a charge of +1, doublet state. The optimal configuration has one of the adjacent Si atoms in a puckered configuration backbonded to an oxygen atom [see Fig. 1(d)]. Along the path, this Si atom first moves through the plane of its three other O-atom neighbors. The activation energy for this transition is 0.4 eV. Then, one of the oxygen atoms moves to fill the vacancy, a process with activation energy of 1.8 eV. Finally, the new planar configuration would be transformed to the lower-energy puckered configuration, with a barrier again of 0.4 eV, but this part of the path is not shown. The path is somewhat asymmetric because of the asymmetry in the  $\alpha$ -quartz crystal.

barrier to hop from a planar configuration to an adjacent site is 1.8 eV. The attachment of a hole to the vacancy, therefore, greatly reduces the activation energy for diffusion, down to less than half of its original value. The transition state for the positive vacancy is quite similar to the transition state of the vacancy/exciton complex, the moving O-atom forms Si-O

bonds stretched to 1.99 Å and 1.68 Å, and the distance between the pairs of Si atoms is 3.5 Å and 2.8 Å.

## VI. CONCLUSIONS

In conclusion, we have shown that a neutral oxygen vacancy is much more mobile when bound to a triplet-state exciton than in the ground state. Also, a positively charged vacancy is almost as mobile as exciton-bound vacancy. Assuming a typical prefactor for diffusion,  $10^{12} \text{ sec}^{-1}$ , the onset of mobility (on the time scale of minutes) of the positive and exciton-bound vacancies would be around 600–700 K, while the neutral vacancy would remain immobile up to 1500 K. Diffusion of combined exciton/vacancy defects may play an important role in the structural changes that occur in silica and silicates upon irradiation. Our results also show that impurities that shift the Fermi level and can strongly affect the mobility of oxygen vacancies by changing the charge state of the vacancy.

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