Ab-initio study of oxygen vacancies in α-quartz

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Extrinsic levels, formation energies, and relaxation geometries are calculated ab initio for oxygen vacancies in α-quartz SiO$_2$. The vacancy is found to be thermodynamically stable in the charge states $Q=+3$, $Q=0$, $Q=-2$, and $Q=-3$. The charged states are stabilized by large and asymmetric distortions near the vacancy site. Concurrently, Franck-Condon shifts for absorption and recombination related to these states are found to be strongly asymmetric. In undoped quartz, the ground state of the vacancy is the neutral charge state, while depending on the charge state of the ground state.

Optical transitions related to the vacancy are predicted around 3 eV and 6.5 eV (absorption) and 2.5 to 3.0 eV (emission), depending on the charge state of the ground state.

More complex defects are likely to be even more rare. A study of lattice vacancies seems therefore timely, also because, although many semiempirical studies have appeared in the past, even these simple defects have not been widely studied at the ab initio level (recent density-functional-theory studies are reported in [4] and [5]). In particular, no systematic study exists, to our knowledge, dealing with the charge states of the O vacancy beyond the neutral and +1 states [4].

II. METHOD

We perform ab initio density-functional theory (DFT) plane-waves pseudopotential calculations, using ultrasoft-pseudopotentials [6], which guarantee a high degree of transferability and a fast convergence in Fourier space of all the relevant quantities [7]. A plane-waves basis is used with a cut-off at 20 Ryd. A conjugate-gradient total-energy minimization [8] is used to obtain the self-consistent electronic ground-state at fixed ions, and an efficient relaxation method [9] is used to reach the minimum energy structure following Hellmann-Feynman forces. We employ 36-atom orthorombic supercells with no imposed symmetry, and one special $\mathbf{k}$ point as Brillouin zone sampling. This setting gives structural properties in agreement with those obtained by Liu et al. [10], matching experiment to better than 1 %, apart from two O internal parameters having a deviation of $\sim 2\%$.

The formation energy for an O vacancy in SiO$_2$ in charge state $Q$ (where, conventionally, $Q$ is the number of electrons transferred from the defect to a reservoir of chemical potential $\mu_e$) is given by

$$E_f(Q) = \Delta E^{\text{tot}}(Q) - \mu_O + Q(\mu_e + E_O^Q),$$

where $\Delta E^{\text{tot}}(Q)$ is the total energy difference between the defected supercell in charge state $Q$ and the perfect bulk supercell, and $\mu_e$ is the electron chemical potential (i.e the Fermi level in our $T=0$ calculation). The zero of $\mu_e$ may be assumed to be the top valence band energy $E_v^Q$ of the defected crystal in the charge state $Q$. The chemical potential $\mu_O$ is one half of the total energy of the spin-unpolarized O$_2$ molecule (calculated in a large supercell). As expressed above, the formation energy depends on the charge state and on the Fermi level. The latter embodies the effects of background doping, competing defect species, or externally injected carriers.
A. Defect levels as total energy differences

The eigenvalues of the hamiltonian of a crystal with a fixed number of electrons have no rigorous relationship to observable optical transition, unless they are many-body quasiparticle energies. This is also the case for defected crystals, and for transitions involving extrinsic levels therein. In particular, transitions to and from extrinsic levels cannot simply be extracted as differences of DFT eigenvalues of e.g. the neutral state of the defect. This is true for any one-body theory, including Hartree-Fock calculations [11], since Koopman’s theorem gives (e.g.) an ionization potential which is not exact even in principle. Within DFT one can resort to total energy differences, since the DFT total energy is exact in principle, apart from the local density approximation (LDA) and other technical issues of practical relevance [12]. In particular, in a DFT calculation one calculates formation (i.e. total) energy differences between the relevant systems. For e.g. the case of \( Q=0 \) and \( Q=-1 \), this difference is, by definition, the energy needed to extract an electron from the \( Q=-1 \) state (ionization of the charged center) leaving behind a \( Q=0 \) center, or to add one to the \( Q=0 \) state (binding to the neutral center) transforming it into a \( Q=-1 \) state. When account for geometrical changes upon occupation is taken, this difference is the thermal excitation level; “thermal” indicates that the structure is allowed sufficient time to rearrange to its new equilibrium position. We concentrate on the calculation of this quantity, and discuss later optical transitions.

Apart from basic choices such as the use of the LDA as opposed to gradient-corrected functionals, the uncertainties in the predicted defect energy levels arise mainly from the alignment of the energy zero of differently-charged supercells. Since we choose conventionally the Fermi level zero at the valence band top, \( Q \neq 0 \) charge states have a constant energy offset \(-QE^Q_{bulk}\) away from the neutral state energy (Eq. 1). We proceed by calculating the bulk valence band top \( E^Q_v \) in a bulk supercell, and express the valence top in the charged supercell as

\[
E^Q_v = E_v + \Delta V, \tag{2}
\]

where \( \Delta V \) is the difference of the macroscopic averages of the local potentials of the charged supercell and of the bulk supercell,

\[
\Delta V = \nabla Q - \nabla_{bulk}. \tag{3}
\]

This quantity is evaluated in an appropriate bulk-like region, i.e. regions of the simulation cell where the local potential is unaffected by the defect. The resulting uncertainties are at most of order \( \pm 0.1 \) eV in the thermal ionization levels.

III. RESULTS

For the neutral state of the vacancy, the formation energy is 6.97 eV. Such large energy is in accord with the need for irradiation to produce vacancies in the first place. As seen from Fig. 1, the vacancy is stable in the \( Q=+3 \) state for Fermi level values of up to 2 eV above the valence band top. Thereafter, the neutral state becomes stable, and remains such for Fermi levels up to about 5.5 eV. The neutral state is therefore the ground state of the oxygen vacancy in nominally undoped quartz, i.e. for the Fermi level at mid-gap (~ 4.5 eV). Increasing further the Fermi level, the vacancy becomes negatively charged. The \( Q = -3 \) charge state is the most stable state for Fermi levels ranging from about 5.5 eV to 8 eV (neglecting the small Fermi level range from 5.5 eV to 5.7 eV, where the \(-2 \) state prevails).

While the thermal level sequence which is usually expected is \( Q = +3, +2, +1, 0, -1, -2, -3 ... \), in the present case we find a negative-U behavior [14] between the triply positive state and the neutral state, and between the neutral and the \( Q = -3 \) state: the \( Q = +2 \) and \( Q = +1 \) states are unstable against the release of a further electron, and the \( Q = -1 \) and \( Q = -2 \) states are unstable towards the capture of a further electron. This is due to a strong electron-lattice coupling, as is discussed below. The realization of large-\( Q \) negative and positive states is not unusual for wide gap materials.

A. Defect electronic structure

The \( Q = 0 \) vacancy is a symmetric combination of Si dangling bonds. The Si neighboring to the vacancy relax almost symmetrically, by 9.5 % of the unrelaxed Si-O bond length, towards the vacant site. In Fig. 2, we display density isosurfaces for the defect state of the neutral vacancy.

The only stable positive charge state is the \( Q=+3 \) state. The two Si atoms neighboring to the vacancy relax strongly away from their original positions in an asymmetric fashion: their distance to the vacancy site increases from 1.62 Å to 2.16 Å, and from 1.61 Å to 2.81 Å, respectively. The two Si atom are three-fold coordinated and close to co-planar with the neighboring oxygens. The charge density of the last occupied state is delocalized, suggesting that the defect level is resonant with the valence band. The thermodynamical instability of the singly positive vacancy signals potential difficulties in previously proposed models [3] of the so called \( E’ \) center.

The \( Q = -1 \) charge state is the antibonding combination of the same dangling bonds as above, as can be seen in Fig. 3 (compare with the previous Figure). Additional relaxations with respect to the neutral state are below 1%. Thus, electronic promotion into this state will require a (rather large) energy of almost purely electronic origin.

In the \( Q = -2 \) charge state, the first antibonding state gets completely filled. In contrast to the \( Q = -1 \), a large, markedly asymmetric relaxation occurs. This can
be seen in the structure model of Fig. 3. In this geometry atom Si$_1$ has moved towards the vacancy by about 20 \% of the pristine unrelaxed bond length, whereas Si$_2$ has moved away from the vacancy by about 3 \%. The tetrahedron centered on Si$_1$ remains essentially undistorted, while that centered on Si$_2$ is distorted concurrently with the neighboring tetrahedron centered on a third Si atom, Si$_3$. This effect is due to a large displacement of the bridging O atom. Due to the large relaxation energy gain and to the associated electronic rehybridization (visible in Fig. 3, where the relevant charge density isosurfaces are displayed), the $Q = -2$ state is lower in energy than the $Q = -1$ (Fig. 4) over most of the $E_F$ range, despite the electron-electron repulsion. Thus a negative-U effect takes place. The $-2$ state becomes favored over the neutral at a Fermi level of 5.5 eV.

At a Fermi level about 0.2 eV higher the $Q = -3$ state charge becomes favored. Si$_1$ moves towards the vacancy site by an additional 7 \% (its distance from the vacancy is about 30 \% shorter than the unrelaxed bond length), while Si$_2$ moves closer by 2 \% (its distance from the vacancy is about 1 \% longer than the unrelaxed bond length). The stability of the $Q = -3$ state over the $Q = -2$ state for a wide range of $E_F$ is somewhat puzzling in view of the large repulsion to be expected among electrons in the center. The prominent feature of this state is indeed that the additional electron minimizes the Coulomb repulsion with the preextant ones by occupying a state in the interstice between the vacancy-adjacent Si$_1$ and Si$_2$ atoms, and the Si$_3$ atom belonging to the tetrahedron neighboring to Si$_2$ and closest to the vacancy. The distance between Si$_2$ and Si$_3$ is reduced to only 4.3 a.u., to be compared with a distance of 5.8 a.u. in the unrelaxed structure. This is due to the aforementioned distortion of the Si$_2$-O-Si$_3$ bridge linking the two tetrahedral units, whereby the corresponding angle decreases from the usual $144^\circ$ to only about $80^\circ$. While this distortion is in fact already qualitatively present in the $Q = -2$ charge state, the additional electron in the $Q = -3$ state is effectively bound by Si$_3$, as can be seen from Fig. 3. In view of its electronic structure, the $-3$ charge state may be a candidate $E'$-like center (see below).

The $Q = -3$ state is stable up to extreme $n$-type conditions (Fermi level $\approx 8.1$ eV), whereby the $Q = -4$ state sets in. The fourth electron fills in the state whose occupation was initiated with $Q = -3$, with marginal additional relaxation. The charge density and geometry are very close to the $Q = -3$.

By the time one gets to extreme $p$ or $n$-type conditions, the formation energies of the vacancy become very small. Vacancy-driven Compensation of acceptor and donor impurities will be very efficient, and we expect that $n$-type doping of quartz will only be achieved with extreme difficulty, if at all.

### B. Franck-Condon shifts

The Franck-Condon (FC) shift $F_{Q,Q'}$ is defined as the total energy difference between the system in charge state $Q$ in its own equilibrium configuration and the same system in the equilibrium configuration of charge state $Q'$:

$$F_{Q,Q'} = E^Q_{\text{tot}}[R_Q] - E^{Q'}_{\text{tot}}[R_Q].$$

(4)

The FC shift is symmetric upon exchange of $Q$ and $Q'$ if the dependence of the total energy on configurational coordinates is quadratic and with identical force constants in the two charge states. However, given the large distortions involved in the present case, the FC shift might be asymmetric (especially for large shifts) both because of anharmonicity and of force-constant differences. These expectations are indeed verified in our calculations. We find large asymmetries for large shifts, which are consistent with force constants differing by factors of up to about $\sqrt{2}$ assuming a single quadratic configurational coordinate. We express for convenience the FC shifts between the non-positive (non-negative) charge states as a matrix $F^{-\text{neg-states}}$ ($F^{\text{pos-states}}$) whose elements $F^{-\text{neg-states}}_{ij}$ ($F^{\text{pos-states}}_{ij}$) are the FC shifts for the $Q = -i$ ($Q = i$) state in the geometry of the $Q = -j$ ($Q = j$) state; this matrix would be symmetric in the symmetric-FC hypothesis, and its diagonal elements are null. For negative states, with $Q$ between 0 and $-3$, we have

$$F^{-\text{neg-states}} = \begin{pmatrix}
0 & 0.60 & 5.20 & 6.38 \\
0.37 & 0 & 1.21 & 1.93 \\
2.51 & 1.81 & 0 & 0.18 \\
3.17 & 2.20 & 0.18 & 0
\end{pmatrix},$$

while for positively charged states ($Q$ between 0 and $+3$) we have

$$F^{\text{pos-states}} = \begin{pmatrix}
0 & 1.35 & 6.23 \\
0.64 & 0 & 1.76 \\
3.78 & 3.81 & 0 & 0.63 \\
4.41 & 2.90 & 0.63 & 0
\end{pmatrix},$$

all energies being expressed in eV. Note that only the $F_{i,i\pm1}$ elements are needed in the discussion to follow.

### C. Optical transitions

The optical transition energy is the total energy difference of the two (differently charged) initial and final systems in a fixed geometry. Alternatively (but equivalently), optical levels can be expressed as combinations of thermal levels and FC shifts. We only consider one-electron (i.e. first-order) processes. This kind of process amounts to transferring only one electron at a time into, or out of, a defect level.

The transitions we consider are absorption (an electron is transferred from the valence states reservoir into the
defect, or transferred from the defect to the conduction band via an internal excitation of e.g. the –3 state into the –2 state, recombination (the electron drops into the defect level from a reservoir of e.g. optically-excited conduction electrons), and single-particle deexcitation of a metastable charged center by recombination of an electron into the valence band. We assume that all processes involved, e.g. successive absorption transitions (0 → −1, −1 → −2, −2 → −3 ...), take place on time scales shorter than those of lattice vibrations, so that (e.g.) absorption occurs in a frozen structure. This assumption seems plausible in view of typical phonon frequencies and optical transition times, especially in large excitation densities. We therefore assume that the structure remain frozen in the equilibrium configuration of a given state $Q_f$ (typically the initial state) throughout the transition cascade.

If the ground state of the defect is charge state $Q$, in terms of thermal levels $\epsilon[Q/Q']$ and FC shifts $\mathcal{F}_{Q,Q'}$, the optical absorption energy for electronic transitions from the valence band into charge state $Q - 1$ is

$$\delta_{Q}^{\text{abs}} = \epsilon[Q/Q - 1] + \mathcal{F}_{Q-1,Q_f} - \mathcal{F}_{Q,Q_f}. \quad (5)$$

For internal absorption excitations (transforming e.g. $Q = -2$ into $Q = -1$ by electron excitation in the conduction band) we have instead

$$\delta_{Q}^{\text{int-abs}} = E_{\text{gap}} - \epsilon[Q - 1/Q] + \mathcal{F}_{Q,Q_f} - \mathcal{F}_{Q-1,Q_f}. \quad (6)$$

Within the same assumptions, for the conduction band-to-acceptor recombination we have emissions at

$$\delta_{Q}^{\text{em}} = E_{\text{gap}} - \delta_{Q}^{\text{abs}} \quad (7)$$

with $E_{\text{gap}} = 8.9$ eV, the experimental gap of $\alpha$-SiO$_2$. Once again we implicitly assumed that subsequent recombinations are instantaneous on the scale of ionic relaxation.

Deexcitation is slightly more complicated. Suppose that the vacancies have been occupied with a number of electrons e.g. between 1 and 4. Assume further that the lifetimes of each charge states are larger than the inverse of typical phonon frequencies ($\sim 10$ THz). This assumption seems again admissible in view of typical decay constants of observed luminescence bands in silica being of order $10^{-5}$ to $10^{-10}$ sec. Then, each charge state can relax to its own ground state before deexcitation. For each vacancy in a given charge state, a cascade of deexcitation processes occurs, whereby each charge state (between the initial one, say $Q = 3$, to $Q = 0$) is occupied in sequence, and it loses one electron to the valence band while in its own equilibrium geometry. Expressing again total-energy differences in terms of thermal levels and FC shifts, we obtain the deexcitation emission energies from charge state $Q$ as

$$\delta_{Q}^{\text{deex}} = \epsilon[Q/Q - 1] - \mathcal{F}_{Q,Q-1}. \quad (8)$$

For internal deexcitation the formula reads

$$\delta_{Q}^{\text{int-deex}} = E_{\text{gap}} - \epsilon[Q/Q - 1] + \mathcal{F}_{Q-1,Q}. \quad (9)$$

Here we did not consider selection rules possibly preventing some of the transitions involved, and remain with an open question on this issue.

As mentioned above, quantitative predictions depend on which ground state is actually realized. This makes the optical properties of this system quite rich and complex. In Table I we summarize the main groups of absorption and emission transitions involving different ground states. If the Fermi level is at mid-gap (i.e. the solid is undoped), the ground state is the neutral state. In moderate $n$-type conditions, the ground state will typically be the –3 state. The relevant thermal levels are $\epsilon[0/ - 1] = 6.24$ eV, $\epsilon[-1/ - 2] = 5.47$ eV, and $\epsilon[-2/ - 3] = 5.82$ eV. The FC shifts have been given previously. In p-type conditions, the ground state will be the +3 state. The relevant thermal levels are $\epsilon[+3/ +2] = 2.48$ eV, $\epsilon[+2/ +1] = 2.69$ eV, and $\epsilon[+1/ 0] = 0.72$ eV (the FC shifts have been given previously).

For the neutral state, the absorption band is centered around 6.6 eV and the emission band at about 2.3 eV. For the –2 charge state there is an absorption band at about 6.3 eV, while the emission one is centered around 3.9 eV. For the $Q = -3$ state, the absorption bands are located around 3.2 eV, 6.0 eV, and 7.1 eV. These correspond to internal excitations $-3 \rightarrow -2$, $-2 \rightarrow -1$, and $-1 \rightarrow 0$ respectively. While calculated line intensities are not available, we speculate that the latter components may give rise to a band centered around 6.3 eV, close to an experimentally observed absorption band (6.2 eV) usually assumed to be related to the $E'$ center.

On the other hand, the emission bands are around 2.7 eV, close to the 2.7/2.8 eV emission band generally attributed to the oxygen vacancy, and at 3.2 eV, where a band is also observed experimentally in silica. For the $Q = +3$ state, absorptions (either normal or internal) are predicted at 2.2 eV, 3.1 eV and 5.0 eV, while emissions are at 1.9 eV and 0.9 eV.

D. The $Q = -3$ as an $E'$-like center

We note at this point that the triply-negative charge state of the oxygen vacancy exhibits several of the characteristic features of the $E'$ center in $\alpha$-quartz. Both the transition generating the center (if the starting ground state is the neutral vacancy) and that characteristic of the center itself are correctly predicted around 6 eV. While such transition energies appear also in the predicted spectra of other possible ground states, only the electronic structure of the $Q = -3$ state seems compatible with hyperfine-field and EPR measurements. These experiments indicate the presence of two weak hyperfine interactions and a strong one associated with the oxygen vacancy. In our –3 state the weak signals can be attributed to Si$_1$ and Si$_2$, while the strong signal comes from the unpaired electron prevalingly bound to Si$_3$. 

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Such attributions could not be made for the $Q=+3$, 0, and $-2$ ground states. The unpaired electron lobe is approximately directed along the direction of the “short bond” $\overrightarrow{E'Q}$ in the ideal structure, and as can be seen from Fig. 1 $\Sigma_3$ is close to three fold coordinated, as it is generally accepted that $E'$ should be $[3^8]$.

The main objection to identifying the $Q=–3$ state of the vacancy with $E'$ comes from experiments showing that $E'$ is positively charged in MOS Si/SiO$_2$ junctions $[39]$. However, this result is not always reproduced in other instances $[2]$. It would be interesting to analyze further these experiments in the light of our results, taking into account for instance band offset effects at the Si/SiO$_2$ interface. As to magnetic data, recent calculations $[3]$ of the hyperfine tensor of a distorted variant of the singly positive vacancy have resulted in good agreement with the data pertaining to the $E'$ center $[17]$, giving support to the attribution of $E'$ to a positive charge state of the vacancy. On the other hand our results indicate that the $Q=+1$ vacancy is unstable towards becoming triply charged, and that the $Q=+3$ state appears to be a valence resonance, lacking features which could explain the peculiar magnetic signature of $E'$.

It is clear that additional work is needed to resolve this puzzle. Nevertheless, the 3– oxygen vacancy seems to carry several $E'$-like features, and it may be considered as a possible new variety of $E'$ defect.

IV. SUMMARY

We have presented ab initio results on oxygen vacancies in $\alpha$–SiO$_2$. The ground states for the vacancy as function of background doping are the triply-charged positive, neutral, and triply-charged negative states. The high-charge states are stabilized by large, asymmetric distortions involving at least three tetrahedral units neighboring to the vacancy. In connection with the possible different ground states we predict optical absorption energies in the 3.2 eV and 6-7 eV ranges, and emissions in the 2.3-3.2 eV range. Based on predicted optical transitions, geometry, and electronic structure, we suggested a possible new $E'$-like center, namely the triply-charged negative oxygen vacancy.

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FIG. 1. Formation energy of the oxygen vacancy in $\alpha$-SiO$_2$ as a function of the Fermi level.

FIG. 2. Charge density isosurfaces for the neutral state of the oxygen vacancy. The surface shown corresponds to a density value of 0.02 electrons/bohr$^3$.

FIG. 3. Charge density isosurfaces for the singly-negative charge state of the oxygen vacancy. The surface shown corresponds to a density value of 0.006 electrons/bohr$^3$.

FIG. 4. Relaxed geometry of the $Q = -2$ state of the oxygen vacancy (black atoms and thick connecting lines). The geometry of the neutral vacancy is given for reference (white atoms and thin connecting lines).

FIG. 5. Charge density isosurfaces for the doubly-negative charge state of the oxygen vacancy. The surface shown corresponds to a density value of 0.02 electrons/bohr$^3$.

FIG. 6. Charge density isosurfaces for the triply-negative charge state of the oxygen vacancy. The surface shown corresponds to a density value of 0.0045 electrons/bohr$^3$. 
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