Native point defects in yttria and relevance to its use as a high-dielectric-constant gate oxide material: First-principles study


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Yttria (Y$_2$O$_3$) has become a promising gate oxide material to replace silicon dioxide in metal-oxide-semiconductor devices. Using a first-principles approach the electronic structure, defect structure, and formation energy of native point defects in Y$_2$O$_3$ are studied. Vacancies, interstitials, and antisites in their relevant charge states are considered. We find that within the band gap of Y$_2$O$_3$ oxygen vacancies, oxygen interstitials, yttrium vacancies, and yttrium interstitials can be stable depending on the Fermi level and external chemical potentials. When the Fermi level is constrained to be within the band gap of silicon, oxygen vacancies are the dominant defect type under low oxygen chemical potential condition. A higher oxygen chemical potential leads to oxygen interstitials and ultimately yttrium vacancies.

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range of oxygen and yttrium chemical potentials, defined by the competing phases at other Y/O ratios. The largest possible range for \( \mu_O \) and \( \mu_Y \) is obtained from the stability limits of Y2O3 with respect to metallic yttrium and molecular oxygen. To prevent pure Y formation, the following condition needs to be fulfilled:

\[
\mu_{Y^{2+},3+} < \mu_{O^{2-}},
\]

where \( \mu_{Y^{2+},3+} \) is the chemical potential of Y in Y2O3 and \( \mu_{O^{2-}} \) is the chemical potential of O in pure yttrium metal.

To prevent oxygen loss, the following condition needs to be fulfilled:

\[
\mu_{O^{2-},3-} < \mu_{O^{2-}},
\]

where \( \mu_{O^{2-},3-} \) is the chemical potential of O in Y2O3 and \( \mu_{O^{2-}} \) is the energy of pure O2 gas (per oxygen atom). These chemical potentials are related by the formation energy of Y2O3 from metallic Y and O2 gas:

\[
\Delta E_f^{Y_2O_3} = 2\mu_{Y^{2+},3+} - 2\mu_{O^{2-}} + 3\mu_{O^{2-}} - 3\mu_{O^{2-}}.
\]

Combining Eqs. (2)–(4), we obtain the range of \( \mu_{Y^{2+},3+} \) for which the defect energies should be evaluated:

\[
\mu_{O^{2-}} + \frac{1}{2}\Delta E_f^{Y_2O_3} < \mu_{Y^{2+},3+} < \mu_{O^{2-}}.
\]

The range for \( \mu_{Y^{2+},3+} \) can be found by combining Eqs. (1) and (5).

### B. Defect formation energies

The supercell approach is used to calculate defect energies in this study. A defect \( \alpha \) in charge state \( q \) is placed in a large Y2O3 supercell which is repeated periodically. To calculate the formation energy of charged defects, a neutralizing background charge is applied. The formation energy \( (E_f) \) of a charged point defect \( [\alpha^q] \) in Y2O3 is computed as

\[
E_f[\alpha^q] = E[\alpha^\alpha] + \mu_X - E[\text{bulk}] + q(E_V + \Delta V + \epsilon_p),
\]

where \( E[\alpha^\alpha] \) is the total energy of a supercell containing a point defect \( \alpha \) with charge \( q \), \( \mu_X \) is the external chemical potential of element X with + sign for vacancy and a - sign for interstitial defect, \( E[\text{bulk}] \) is the total energy of a perfect supercell, and \( E_V \) is the valence band maximum (VBM) in the perfect supercell. The Fermi level is taken as the energy of the electron reservoir (electron chemical potential \( \mu_e \)) from (in) which an electron is removed (placed) to form a charged defect. The Fermi level is conventionally taken to be zero at the VBM of the perfect supercell. Because the valence band is displaced in calculations on small supercells with defects, its value needs to be referenced back to the valence band in the perfect crystal by an amount \( \Delta V \).

The shift of the VBM in supercell calculations, \( \Delta V \), can be obtained from the difference between the average electrostatic potential in a bulklike environment of the defect supercell and the average electrostatic potential in the perfect bulk supercell. To calculate the average electrostatic potential, the macroscopic averaging technique\(^{24,25} \) is used to find the shift in the VBM. The three-dimensional electrostatic potential is reduced to a one-dimensional planar average first, and the macroscopic average is calculated over the primitive cell along one direction.

For charged systems, the energy of charged defects converges very slowly with supercell size due to electrostatic interactions between the defects across the periodic boundary conditions. This interaction scales as \( 1/eL \), where \( L \) is the linear dimension of supercell and \( e \) is the dielectric constant.\(^{26} \) To achieve faster convergence, Makov and Payne\(^{26} \) suggested adding correction terms to the energy to account for defect-defect interactions induced by the periodic boundary conditions. Although this approach works well for atomic or molecular systems, it may lead to an overestimation of the correction term for defects in semiconductors due to the increased screening from valence electrons which effectively reduce the strength of the interactions.\(^{23,27,28} \) For this reason, we have not included these correction terms in this study.

Errors in the defect formation energy can come from various sources. Well-converged calculations reduce the error from plane-wave energy cutoff and k-point sampling below 10 meV. The interaction between charged defects can introduce an error on the order of 0.1 eV and this error may become larger for higher-charged defects. The band gap error due to density-functional theory itself would have a significant effect on donorlike defects and is discussed with more details in Sec. IV. In summary, a possible error for defect formation energies of a few tenths of an eV should always be assumed.

The thermodynamic transition between two charge states on the defect \( q_1 \) and \( q_2 \) occurs for the Fermi level at which the formation energy of \( [q_1] \) is equal to that of \( [q_2] \), i.e., \( E_f[q_1] = E_f[q_2] \). Using Eq. (6), it can be shown that the thermodynamic transition level \( q_1/q_2 \) is

\[
e_f[q_1/q_2] = \frac{1}{q_2 - q_1} (E_f[q_1] - E_f[q_2]) + q_1(E_V + \Delta V) - q_2(E_V + \Delta V),
\]

where \( q_1 \) and \( q_2 \) are the initial and final charge states, respectively (including the signs), \( \Delta V_1 \) and \( \Delta V_2 \) are the VBM shift for the initial and final charge states, respectively, and \( e_f[q_1/q_2] \) is the Fermi energy level at which the transition from \( q_1 \) to \( q_2 \) takes place. This thermodynamic transition level can be directly observed in deep-level transient spectroscopy experiments.

### III. RESULTS

#### A. Perfect-Crystal Y2O3

The pseudopotentials have been validated on bulk yttria. Convergence of the total energy to within 10 meV was achieved with a 500 eV cutoff energy for plane wave basis and a Monkhorst-Pack k-point grid of \( 2 \times 2 \times 2 \) for Brillouin zone integration. The calculated parameters, along with experimental values, are shown in Table I. The bulk modulus \( (B) \) is obtained by fitting the energy versus volume curve using a fourth-order polynomial.
TABLE I. Calculated and experimental unit cell parameters and bulk modulus of yttria.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$u$</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$a$ (Å)</th>
<th>$B$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>exp</td>
<td>-0.0314</td>
<td>0.389</td>
<td>0.150</td>
<td>0.377</td>
<td>10.604</td>
</tr>
<tr>
<td>30</td>
<td>exp</td>
<td>-0.0323</td>
<td>0.391</td>
<td>0.150</td>
<td>0.383</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>exp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>150</td>
</tr>
<tr>
<td>32</td>
<td>LDA</td>
<td>-0.0326</td>
<td>0.3907</td>
<td>0.1514</td>
<td>0.3797</td>
<td>10.515</td>
</tr>
<tr>
<td>32</td>
<td>GGA</td>
<td>-0.0327</td>
<td>0.3908</td>
<td>0.1516</td>
<td>0.3799</td>
<td>10.700</td>
</tr>
<tr>
<td>Present</td>
<td>GGA</td>
<td>-0.0324</td>
<td>0.3908</td>
<td>0.1515</td>
<td>0.3798</td>
<td>10.700</td>
</tr>
</tbody>
</table>

The total electron density of states (DOS), as well as their atomic and orbital projected DOS, are shown in Fig. 1. It can be seen that a valence band (VB3) of yttrium 4$p$ is centered around $-20$ eV, a valence band (VB2) of oxygen 2$s$ is centered around $-15$ eV, a valence band (VB1) of oxygen 2$p$ occurs below 0 eV, and a conduction band (CB) of yttrium 4$d$ occurs above 4.1 eV. There is a small intermixing of Y 4$d$ and O 2$p$ states in the valence band near 0 eV, which is consistent with the limited covalent bonding between Y and O atoms. The calculated band gap is about 4.1 eV, which is smaller than the experimental value of 6 eV. The underestimation of the band gap energy value is typical of DFT calculations in the GGA or LDA approximations.

B. Defect formation energies

Yttrium metal has a hexagonal close-packed structure. Using a 20 × 20 × 20 uniform k-space mesh, we calculate equilibrium lattice parameters of $a=3.63$ Å (3.65 Å) and $c=5.70$ Å (5.73 Å). Values in parenthesis are experimental data from Ref. 29. The energy of O$_2$ was calculated from a single molecule in a 10 Å cubic cell. While the calculated formation energy for Y$_2$O$_3$ of $-19.41$ eV/Y$_2$O$_3$ is close to the experimental enthalpy of formation of $-19.62$ eV/Y$_2$O$_3$, this result may be fortuitous given the known problem in calculating the O$_2$ binding energy.

The energy to form a yttrium vacancy on the Y1 site is about 0.2 eV lower than on the Y2 site; thus only Y1 vacancy formation energies are reported. There are two interstitial sites, 8$a$ and 16$c$, in yttria. The interstitial site at 8$a$ is octahedrally coordinated, surrounded by six oxygen atoms and six yttrium atoms. The interstitial site at 16$c$ is surrounded by four yttrium atoms and six oxygen atoms and filling it with oxygen would lead to a fluorite structure. The formation energies for interstitials (both oxygen and yttrium) at 8$a$ are always 0.4–1.2 eV higher than interstitials at the 16$c$ site. Hence only formation energies for interstitials at 16$c$ are reported. For oxygen antisites, the oxygen at Y2 has 2 to 3 eV lower energy than the oxygen at Y1; thus the formation energies for oxygen at Y2 site are reported. The formation energy of these defects in various charge states and at the different extremes of chemical potentials and Fermi levels is given in Table II.

The lower limit for the Fermi level ($\varepsilon_F=0$ eV) corresponds to the top of the valence band while the upper limit ($\varepsilon_F=6$ eV) represents the bottom of the experimental conduction band. The formation energies for different defects as a function of Fermi level for the two limiting yttrium chemical potentials and one intermediate yttrium chemical potential are shown in Fig. 2. The slope of the lines in these figures corresponds to the charge state of the defect. For each defect, the line for a particular charge state has only been drawn over the range where this charge state has the lowest energy of all possible charge states. The changes of slope in the curves correspond to the transitions between charge states (and hence to thermodynamic defect energy levels).

C. Defect structure

The results from our calculations suggest that the most common native point defects are oxygen vacancies ($V_\text{O}$), oxygen interstitials ($O_i$), and yttrium vacancies ($V_\text{Y}$). A summary of relaxed local bond lengths for these defect types is shown in Table III. The changes in bond lengths for each defect can be understood in terms of ionic size and charge effects. When an oxygen atom is removed, the nearest yttrium atoms move slightly away from the vacancy site as they are no longer electrostatically attracted to it, and oxygen atoms move closer to the vacancy site as the electrostatic forces are relieved.
repulsion is reduced. This is different from what is found for oxygen vacancies in ZnO (Ref. 17) in which nearest zinc atoms move closer to an oxygen vacancy. Near a yttrium vacancy, oxygen atoms move farther away from the vacancy site while yttrium atoms move slightly closer to the vacancy site. This is similar to what was observed for zinc vacancies in ZnO.17 For the oxygen interstitial, the neighboring yttrium site. This is similar to what was observed for zinc vacancies move closer to an oxygen vacancy. Near a yttrium vacancy, oxygen atoms move farther away from the interstitial site due to the electrostatic repulsion from the interstitial oxygen.

### IV. DISCUSSION

Under high yttrium partial pressure (or low oxygen partial pressure) [Fig. 2(a)], Y↓ dominates when the Fermi level is close to the VBM of Y₂O₃. As the Fermi level moves up, Vₐ becomes dominant due to its lower positive charge, and finally O↓ dominates when the Fermi level is close to the CBM. Lowering the yttrium partial pressure reduces the stability of the yttrium interstitial so that even for a low Fermi level it is not stable anymore. For the intermediate chemical potentials as shown in Fig. 2(b), Vₐ is stable at low Fermi level. At higher Fermi level, the oxygen interstitial is stabilized because of its higher number of electrons. Only for Fermi levels very close to the conduction band is the yttrium vacancy lowest in energy. Under low yttrium partial pressure [Fig. 2(c)], O↓ dominates when the Fermi level is close to the VBM and Vₐ dominates when the Fermi level is close to the CBM. Hence in general we observe that the Fermi level has a strong influence on which defect can be found. When the Fermi level is near the VBM defects with a low number of electrons are stable, such as the oxygen vacancy or the yttrium interstitial. High electron count defects such as the oxygen interstitial or yttrium vacancy are found for higher Fermi level. Whether an O-rich (O↓ or Vₐ) or Y-rich (O↑ or Y↑) defect situation occurs depends then on the external chemical potential.

The transition Fermi levels for the dominant defect types, Vₐ, O↓, Vₐ, and Y↓, are shown in Fig. 3, within the calculated band gap. The transition energies for both oxygen interstitial (O↓) and yttrium vacancy (Vₐ) are very close to the VBM of Y₂O₃, while the transitions for the oxygen vacancy (Vₐ) are located ~1.2–1.4 eV below the calculated CBM. The yttrium interstitial (Y↓) levels are located about 0.5 eV below the CBM.

As the band gap of Y₂O₃ is underestimated by 1.9 eV in GGA, it is important to estimate how the thermodynamic transition levels shown in Fig. 3 would change with a more accurate band gap. One common method17,23,37 to include corrections to the band gap is to leave the energy levels of the acceptorlike defects near the VBM unchanged, but let the

### Table II. Point defect formation energies (E_i) in Y₂O₃.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Defect site</th>
<th>Charge on defect</th>
<th>Kröger-Vink notation</th>
<th>E_{i,\mu_Y=\mu^0_Y} (eV)</th>
<th>E_{i,\mu_Y=\mu^0_Y+1/2\Delta E_{i,YO}} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ε_F=0 eV</td>
<td>ε_F=6 eV</td>
</tr>
<tr>
<td>V_O</td>
<td>e</td>
<td>0</td>
<td>V_X_O</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>V_O</td>
<td>e</td>
<td>+1</td>
<td>V_{O+1}</td>
<td>-2.46</td>
<td>3.54</td>
</tr>
<tr>
<td>V_O</td>
<td>e</td>
<td>+2</td>
<td>V_{O+2}</td>
<td>-5.21</td>
<td>6.79</td>
</tr>
<tr>
<td>V_Y</td>
<td>b</td>
<td>0</td>
<td>V_X_Y</td>
<td>13.52</td>
<td>13.52</td>
</tr>
<tr>
<td>V_Y</td>
<td>b</td>
<td>-1</td>
<td>V_{Y-1}</td>
<td>13.59</td>
<td>7.59</td>
</tr>
<tr>
<td>V_Y</td>
<td>b</td>
<td>-2</td>
<td>V_{Y-2}</td>
<td>13.75</td>
<td>1.75</td>
</tr>
<tr>
<td>O</td>
<td>c</td>
<td>0</td>
<td>O_X</td>
<td>7.85</td>
<td>7.85</td>
</tr>
<tr>
<td>O</td>
<td>c</td>
<td>-1</td>
<td>O_{X-1}</td>
<td>8.01</td>
<td>2.01</td>
</tr>
<tr>
<td>Y</td>
<td>c</td>
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<td>O_{X-2}</td>
<td>8.38</td>
<td>-3.62</td>
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<tr>
<td>Y</td>
<td>c</td>
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<td>Y_X</td>
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<td>c</td>
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<td>6.63</td>
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<tr>
<td>Y</td>
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<td>Y_{X+2}</td>
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<tr>
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<td>c</td>
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<td>Y_{X+3}</td>
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<td>11.42</td>
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<td>V_X_O</td>
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<td>Y</td>
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<td>V_{O+1}</td>
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<td>7.94</td>
</tr>
<tr>
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<td>e</td>
<td>+2</td>
<td>V_{O+2}</td>
<td>-1.98</td>
<td>10.02</td>
</tr>
<tr>
<td>Y</td>
<td>e</td>
<td>+3</td>
<td>V_{O+3}</td>
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<td>11.66</td>
</tr>
<tr>
<td>O</td>
<td>d</td>
<td>0</td>
<td>O_X</td>
<td>18.37</td>
<td>18.37</td>
</tr>
<tr>
<td>O</td>
<td>d</td>
<td>-1</td>
<td>O_{X-1}</td>
<td>19.27</td>
<td>13.27</td>
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<tr>
<td>O</td>
<td>d</td>
<td>-2</td>
<td>O_{X-2}</td>
<td>21.22</td>
<td>9.22</td>
</tr>
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</table>
donorlike defects near the CBM shift upward as the band gap is opened up. The DOS shown in Fig. 1 indicates that the top of the valence band is mainly formed by oxygen 2p states while the bottom of the conduction band is composed of yttrium 4d states. Thus the defect states derived from oxygen 2p states exhibit valence-band character while the defect states derived from yttrium 4d states have conduction-band character.

The neutral oxygen vacancy (VO) removes three states and four 2p electrons from the top of the valence band. As a result, two electrons from yttrium have to occupy conduction bandlike states which are pulled into the gap by the oxygen vacancy. Thus the defect states from oxygen vacancies exhibit conduction band character and the formation energy of the neutral oxygen vacancy may shift to a higher value if the conduction band were to be moved up from the calculated value since there are two electrons in this defect level. The formation energy of \( \text{VO}^{2+} \) will remain unchanged since this defect level is empty. Therefore the thermodynamic transition energy levels +2/+1 and +1/0 for oxygen vacancies will move upwards.

Since one yttrium interstitial does not introduce additional states near the top of the valence band, new states are created in the band gap to accommodate three electrons \( \left( 5s^24d^1 \right) \). Hence the defect states from yttrium interstitials also exhibit conduction band character. On the other hand, one neutral yttrium vacancy does not change the number of states in the top of the valence band, but it removes three electrons from the top of the valence band. Thus the defect levels from yttrium vacancies exhibit more valence band character. An oxygen interstitial adds three 2p states to the top of the valence band and thus also exhibits more valence band character. The thermodynamic transition energy levels from both defects (i.e., yttrium vacancies and oxygen interstitials) are likely to be only slightly affected by a band gap correction.

Based on the discussion above, we investigate the effect of the defect levels on the operation of devices based on \( \text{Y}_2\text{O}_3 \) gate oxides. When \( \text{Y}_2\text{O}_3 \) is used as a gate insulator material in MOS devices, the electron reservoir to form a charged defect comes from the polysilicon gate or silicon substrate. This limits the range for the electron chemical potential to be between the valence band maximum and the conduction band minimum of Si, which is 2.3–3.4 eV below the conduction band minimum of \( \text{Y}_2\text{O}_3 \).33 Under high yttrium chemical potential or low oxygen partial pressure, the dominant defect types in this range of electron chemical potential are oxygen vacancies. Under inter-

FIG. 2. (Color online) Calculated defect formation energy for native point defects in \( \text{Y}_2\text{O}_3 \) as a function of Fermi level and for (a) \( \mu_\gamma = \mu_\gamma^V \) (high yttrium partial pressure or low oxygen partial pressure), (b) \( \mu_\gamma = \mu_\gamma^V + 1/4\Delta E_{\text{Y}^{2+}} \) (intermediate yttrium or oxygen partial pressure), and (c) \( \mu_\gamma = \mu_\gamma^V + 1/2\Delta E_{\text{Y}^{2+}} \) (low yttrium partial pressure or high oxygen partial pressure). Only the lowest formation energy values for defects in different charge states are shown. The positions of the experimental valence band maximum \( [E_V(\text{Si})] \) and conduction band minimum \( [E_C(\text{Si})] \) of silicon with respect to the conduction band minimum of \( \text{Y}_2\text{O}_3 \) are marked by dashed lines.

FIG. 3. The position of the thermodynamic transition energy levels in the calculated band gap (4.1 eV) of \( \text{Y}_2\text{O}_3 \).
mediate yttrium chemical potential [Fig. 2(b)], charged oxygen interstitials become dominant. Under low yttrium chemical potential (or high oxygen partial pressure) [Fig. 2(c)], charged yttrium vacancies are dominant. The defect levels from oxygen interstitials and yttrium vacancies are close to the VBM of Y₂O₃ and will be negatively charged in most of the range of the electron chemical potential. Thus they will only contribute to the negative fixed charge. However, the defect levels from oxygen vacancies will move upwards when a band gap correction is applied. They may become positively charged and act as electron traps. Experiments have shown the existence of defects generating positive fixed charge and electron traps in the Y₂O₃ films.⁸⁻¹⁰ The positive fixed charge will shift the flatband voltage while the electron traps can cause threshold voltage instabilities. Based on our results, we propose that Y₂O₃ films should be grown under high to intermediate oxygen partial pressure to suppress the oxygen vacancy formation.

V. CONCLUSIONS

A first-principles study of point defects in Y₂O₃ has been carried out. The stable defects can be oxygen vacancies, oxygen interstitials, yttrium vacancies, and yttrium interstitials depending on the Fermi level and external chemical potentials. When the Fermi level is constrained to be within the band gap of silicon, oxygen vacancies are the dominant defect types under low oxygen chemical potential condition. A higher oxygen chemical potential leads to oxygen interstitials and ultimately yttrium vacancies. The oxygen vacancies have transition levels near the conduction band and may be responsible for the positive fixed charges and electron traps observed in experiments. We propose that Y₂O₃ films should be grown under high to intermediate oxygen partial pressure to suppress the oxygen vacancy formation.

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TABLE III. Distances to nearest-neighbor atoms for bulk and defect sites in Y₂O₃. dᵢ is the distance of the i-th nearest neighbor in angstroms. The values in parentheses are the number of neighbors having the same distance.

<table>
<thead>
<tr>
<th>Neighbor type</th>
<th>Y</th>
<th>O</th>
<th>Neutral V_O</th>
<th>Y</th>
<th>O</th>
<th>Neutral V_Y</th>
<th>Y</th>
<th>O</th>
<th>O (before relaxation)</th>
<th>Y</th>
<th>O</th>
<th>Neutral O_i</th>
</tr>
</thead>
<tbody>
<tr>
<td>d_1</td>
<td>2.27(1)</td>
<td>2.94(2)</td>
<td>2.29(1)</td>
<td>2.903(1)</td>
<td>2.47(3)</td>
<td>2.30(1)</td>
<td>2.61(3)</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>d_2</td>
<td>2.29(1)</td>
<td>2.35(1)</td>
<td>2.36(1)</td>
<td>2.907(1)</td>
<td>2.50(1)</td>
<td>2.34(3)</td>
<td>2.65(3)</td>
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</tr>
<tr>
<td>d_3</td>
<td>2.30(1)</td>
<td>2.95(2)</td>
<td>2.39(1)</td>
<td>2.91(1)</td>
<td>2.50(3)</td>
<td>2.34(3)</td>
<td>2.65(3)</td>
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</tr>
<tr>
<td>d_4</td>
<td>2.36(1)</td>
<td>2.92(1)</td>
<td>2.39(1)</td>
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