Ilmenite (0001) surface investigated using hybrid density functional theory

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The ilmenite (0001) surface is examined using the hybrid density functional B3LYP. A number of surface configurations are studied, with the Fe–O3–Ti– terminated surface computed to have the lowest cleavage energy, and also computed to be the most stable surface at high vacuum. Under oxygen-rich conditions, the O3–Ti–Ti– terminated surface is computed to be most stable. The calculated geometries of the surfaces, when compared to experimental measurement, suggest that experimentally cleaved ilmenite at low oxygen partial pressures can form a metastable O=Fe–O3– terminated surface.

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I. INTRODUCTION

Ilmenite is the naturally occurring phase of FeTiO3, and forms an end member of the Fe2O3–FeTiO3 solid solution. It is an economically important mineral, used as a source of TiO2, and its wide band gap of about 2.5 eV (Refs. 1 and 2) has led to it being investigated for optoelectronic, chemical, catalyst, and photocatalystic applications. Ilmenite is also an interesting system to study from a theoretical point of view, as it contains two transition-metal cations that allow partially occupied d shells, with different cation charge orderings (Fe2+Ti4+ and Fe3+Ti3+) being consistent with O2– anions. However, there is little published information on the structure of ilmenite surfaces in the literature. Only two experimental studies have been performed to determine the structure of FeTiO3 surfaces, and these two experimental studies fail to unambiguously describe the surface termination.

The ilmenite structure is based on a hexagonal-close-packed oxygen lattice, with metal atoms occupying two-thirds of the available octahedral sites. A low-energy electron diffraction (LEED) study by Fellows et al. demonstrated that clean ilmenite (0001) surfaces are stable at ambient temperature in ultrahigh vacuum and can relax in an unreconstructed (1 × 1) termination. There are several possible ways to terminate the (0001) surface with a (1 × 1) periodicity, as shown in Fig. 1. Along the [0001] axis, ilmenite can be viewed as a stack of layers, comprised of either O3–, Ti, or Fe (where the subscript gives the number of atoms in a layer in the unit cell), and the ordering of these layers can be described as ···Ti–O3–Fe–Fe–O3–Ti–···. Depending on the cleavage position, the possible ilmenite surfaces can then be labeled as Fe–Fe–O3–, Fe–O3–Ti–, O3–Ti–Ti–, Ti–O3–Fe–, and O3–Fe–Fe–. In addition to these cleaved surfaces, one can consider the more reduced surfaces that can be formed from the O3–Fe– and O3–Ti– surface, namely the O2–Fe–Fe–, O3–Fe–Fe–, O3––Ti–, and O3––O3– surfaces, and the oxidation of the Fe–O3– and Ti–O3– surfaces to form ferryl (O=Fe–O3–) and titanyl (O=Ti–O3–) surfaces.

Fellows et al. in a scanning tunneling microscopy (STM) investigation of the (0001) ilmenite surface, found that after cleaving and annealing, a terraced surface is formed with two surface types, each having distinct atomic arrangements. These two surface areas were labeled X and Y, with the X-type surface having the largest surface area, and the Y terraces being smaller. Height steps between two X terraces were measured to be 4.4 Å, and steps between X and Y terraces were measured at 2.2 Å. From atomic resolution images on the Y terrace, features were observed arranged in hexagonal arrays, with a measured separation of 4.8 Å, matching the cation, but not the anion spacing. Atomic resolution imaging of the X surfaces were unsuccessful. From these measurements and a consideration of the bulk geometry, Fellows et al. attributed the surfaces to have either a Fe–O3–Ti– or Ti–O3–Fe– termination, however they were not able to determine which of these terminations were the X and Y surfaces.

While there have been no published theoretical investigations of the surface of ilmenite, there have been a number of theoretical and experimental studies on the (0001) surface of hematite. Hematite is crystallographically similar to ilmenite (replacement of the Ti in ilmenite with Fe gives the hematite structure), which makes hematite surfaces relevant for comparison with ilmenite in the absence of any other calculations. However, differences are to be expected when comparing similar surfaces (e.g., the Fe–O3–Ti– in ilmenite and the Fe–O3–Fe– in hematite) due to the different valence values of the cations, with Fe3+ in hematite, as opposed to the Fe2+ and Ti4+ in bulk ilmenite. Periodic density...
functional theory (DFT) calculations were first used by
Wang et al. 12 to study the (0001) surface of hematite within
the generalized-gradient-approximation (GGA) formulation,
examining the Fe–Fe–O3–, Fe–O3–Fe–, O3–Fe–Fe–, O3–Fe–,
and O3–Fe–Fe– surfaces. Within the GGA formulation,
the O3–Fe–Fe– surface was found to be the most stable surface
under oxygen-rich conditions, while the Fe–O3–Fe– surface
became the most stable under more reducing conditions.
Bergermayer et al. 13, in a later GGA study, considered the
O=Fe–O3– surface in addition to those studied by Wang
et al. 12 and found that within a particular temperature and
oxygen pressure range, the O=Fe–O3– surface was more stable
than either the O3–Fe–Fe– or Fe–O3–Fe– surfaces. This ferryl
(O=Fe–O3–) termination of hematite was later experimentally
verified by infrared reflection absorption spectroscopy. 8

DFT methods such as the local density approximation
(LDA) and the GGA fail to correctly treat d orbitals in
transition-metal oxides due to unphysical self-interaction, and
in the case of ilmenite both the LDA and GGA incorrectly
predict a metallic state. The mixing of nonlocal and semilocal
exchange in the B3LYP functional has been shown to reduce
this error and give a reliable representation for transition-
metal–oxide solids. 14–18 and has been shown to perform well
in the prediction of structural, elastic, and electronic properties
of ilmenite. 19,20 This study examines the structure and stability
within the B3LYP approximation of the various possible terminations for the unreconstructed (1 x 1) (0001) ilmenite
surface. This paper is organized as follows. Section II contains
a description of the computational method used, structural
relaxation data and electronic density of states are reported in
Sec. III and discussed in Sec. IV, with conclusions given in
Sec. V.

II. COMPUTATIONAL METHOD

All calculations were performed using the CRYSTAL06
ab initio software package, 21 with Becke’s three-parameter
hybrid functional (B3LYP) (Ref. 22) used for the treatment
of electron exchange and correlation in the calculations. The
basis sets used here were developed and optimized in previous
calculations on rutile TiO2 and bulk surfaces 23–27 and studies of
hematite Fe2O3. 28

The five cutoff tolerances for the evaluation of the Coulomb
and exchange series were set to 10−8, 10−8, 10−8, 10−8, and
10−16. The reciprocal space integration was performed by sam-
ping the Brillouin zone using the Monkhorst-Pack 29 scheme
with a shrinking factor of 8. The internal coordinates of the
surfaces were optimized using analytical energy gradients 30,31
to a tolerance on the maximum and rms forces of 0.00045
and 0.0003 Hartree/Bohr, respectively. The energy difference
between the ferromagnetic and antiferromagnetic solutions
of ilmenite is small, at less than 0.03 eV per formula unit, and
so in this investigation the ferromagnetic solutions have been
used for computational efficiency.

When working with localized basis-set calculations, some
consideration for basis-set superposition error must be given
when comparing different surfaces. Basis-set superposition
error comes about because unused basis functions of one atom
can augment the basis functions of a second atom and lower
its energy compared to a calculation of the second atom alone.

For high-quality basis sets, this effect is small. In the case
of the Fe–O3–Ti– and Ti–O3–Fe– surfaces, calculations were
performed with the basis functions for an extra oxygen atom
on top of the surface for comparison with the O=Fe–O3– and
O=Ti–O3– surfaces. The effect of this correction is small, and
was not carried out for the other surfaces, and should not alter
the ordering of the surface energies.

To allow for a comparison of the stability of the various
surfaces and an understanding of the effect of nonvacuum
conditions on the various surfaces, the Gibbs free energy can be
considered, following the approach of Reuter and Scheffler. 32
The Gibbs free energy of a slab at temperature T and pressure
p is given by

\[ \Omega = G - N_{Fe} \mu_{Fe} - N_{Ti} \mu_{Ti} - N_{O} \mu_{O}, \]  

where \( \mu_{Fe}, \mu_{Ti}, \) and \( \mu_{O} \) are the chemical potentials of Fe, Ti,
and O, respectively, and \( G \) is given by

\[ G(T, p) = E(0, 0) + TS + pV, \]  

where \( T \) is the temperature, \( S \) is the entropy, and \( p \) is the
pressure. At \( T = 0 \) and \( p = 0 \), this simplifies to

\[ \Omega = E_{slab} - N_{Fe} \mu_{Fe} - N_{Ti} \mu_{Ti} - N_{O} \mu_{O}. \]  

If ilmenite is chosen as the chemical reservoir for both iron
and titanium, then

\[ \mu_{FeTiO3} = \mu_{Fe} + \mu_{Ti} + 3 \mu_{O}. \]  

For surface slabs with \( N_{Fe} = N_{Ti}, \) Eq. (3) can be written as

\[ \Omega = E_{slab} - N_{Fe} \mu_{FeTiO3} + (3N_{Fe} - N_{O}) \mu_{O}. \]  

For surface slabs in which \( N_{Ti} \neq N_{Fe}, \) \( \mu_{FeTiO3} \) cannot be
used as the chemical reservoir for both Fe and Ti. Instead, the
range of the chemical potentials can be examined by using
either TiO2 for the chemical reservoir for Ti or Fe2O3 for
the chemical reservoir for Fe. If TiO2 is used for the chemical
reservoir for Ti, then

\[ \mu_{TiO2} = \mu_{Ti} + 2 \mu_{O}. \]
The chemical potential of Fe can then be calculated from the ilmenite chemical potential
\[ \mu_{\text{Fe}} = \mu_{\text{FeTiO}_3} - \mu_{\text{TiO}_2} - \mu_{\text{O}}. \]  
(7)

which gives a 0 K surface energy
\[ \Omega = E_{\text{slab}} - N_{\text{Fe}} \mu_{\text{FeTiO}_3} + (N_{\text{Fe}} - N_{\text{Ti}}) \mu_{\text{TiO}_2} \]
\[ + \left( \frac{1}{2} N_{\text{Fe}} + \frac{3}{2} N_{\text{Ti}} - N_{\text{O}} \right) \mu_{\text{O}}. \]  
(8)

Using Fe$_2$O$_3$ for the chemical reservoir for Fe leads to a surface energy
\[ \Omega = E_{\text{slab}} - N_{\text{Ti}} \mu_{\text{FeTiO}_3} - \frac{1}{2} (N_{\text{Fe}} - N_{\text{Ti}}) \mu_{\text{FeO}} \]
\[ + \left( \frac{1}{2} N_{\text{Fe}} + \frac{3}{2} N_{\text{Ti}} - N_{\text{O}} \right) \mu_{\text{O}}. \]  
(9)

The surface energies can be plotted as a function of oxygen partial pressure by varying the oxygen chemical potential. As a reference, the chemical potential of oxygen can be taken to be half the total energy of O$_2$.
\[ \mu_{\text{O}} = \frac{1}{2} E^{\text{bulk}}_{\text{O}_2}. \]  
(10)

To be useful in experimental situations, the oxygen chemical potential is better expressed as an oxygen partial pressure ($P_{\text{O}_2}$) at a particular temperature. It is computationally expensive to calculate the entropy term for surfaces, however the 0 K results can be used to get an approximation guide to the oxygen partial pressure at temperature, following the approach outlined in Reuter and Scheffler. The chemical potential can be related to actual pressure and temperature conditions by assuming thermodynamic equilibrium between the surface and the surrounding gas phase. The temperature and pressure dependence for an ideal gas is given by
\[ \mu_{\text{O}}(T, P_{\text{O}_2}) = \frac{1}{2} \left[ E^{\text{total}}_{\text{O}_2} + \bar{\mu}_{\text{O}_2}(T, \rho^0) + k_B T \ln \left( \frac{P_{\text{O}_2}}{\rho^0} \right) \right], \]  
(11)

where $\rho^0$ is the pressure of a reference state and the chemical potential $\bar{\mu}_{\text{O}_2}(T, \rho^0)$ is taken from thermodynamic tables.

### III. Results

Bulk ilmenite was optimized within the B3LYP approximation and the hexagonal unit cell was determined to have dimensions $a = 5.150$ Å and $c = 14.095$ Å, slightly overestimating the experimental values of $a = 5.0875$ Å and $c = 14.0827$ Å. Cleave energies were computed for slabs of increasing thickness to test for convergence, with convergence found for slabs of 24 atomic layers thick. Symmetric slabs 24 layers thick were then used for the surface relaxations.

Table I gives the cleavage energies for the various surface terminations. The cleavage energies have been calculated using the formula
\[ E_{\text{surface}} = \lim_{N \to \infty} \frac{1}{2A} \left( E^{N}_{\text{slab}} - \frac{N}{N - M} (E^{N}_{\text{slab}} - E^{M}_{\text{slab}}) \right), \]  
(12)

where total energies from two slabs of different thicknesses, $E^{N}_{\text{slab}}$ and $E^{M}_{\text{slab}}$, are used. Calculating the cleavage energy this way has the advantage of calculating all the energies under the same numerical conditions, which leads to a cancellation of any systematic error. When cleaving bulk ilmenite, either two identical or a pair of different surfaces will be formed, depending on where the bulk is cleaved. For the paired surface terminations (Ti–Ti–O$_3$–/O$_3$–Fe–Fe–Fe–Fe–Fe–O$_3$–/O$_3$–Ti–Ti–O$_3$–Fe–Fe–Fe–O$_3$–/O$_3$–Ti–Ti– and O$_2$–Fe–Fe–/O$_3$–Fe–Fe–Fe–/O$_3$–Ti–Ti–), both surfaces in the pair arise simultaneously under cleavage and so the cleavage energy has been distributed evenly between the pair. Table I shows that the Fe–O$_3$–Ti– terminated surface was found to have the lowest cleavage energy at 1.92 J/m$^2$. This is similar to calculated values for other (0001) surfaces in corundum-like structures, such as hematite (2.3 J/m$^2$), $\alpha$-Al$_2$O$_3$ (1.76 J/m$^2$), and Cr$_2$O$_3$ (1.60 J/m$^2$). The highest cleavage energy belongs to the Ti–Ti–O$_3$–/O$_3$–Fe–Fe–Fe–/O$_3$–Ti–Ti– pair at 10.8 J/m$^2$.

Surface relaxations were performed on the 12 different surface terminations outlined in the Introduction. For the Ti–O$_3$–Fe–Ti–Ti–O$_3$– and Fe–Fe–O$_3$– surfaces, initial relaxations found local minima structures (i.e., no forces on any atom, but not the lowest energy structure), but subsequent relaxations were able to find geometries for these surfaces with a lower energy. Table II gives the change in interlayer spacing after relaxation for the lowest-energy structure found for each surface. The interlayer relaxations are expressed as percentage change from the bulk interlayer distances, given by the equation
\[ \triangle d_{i,i+1} = \frac{d_{i,i+1}^{\text{relaxed}} - d_{i,i+1}^{\text{bulk}}}{d_{i,i+1}^{\text{bulk}}} \times 100, \]  
(13)

where $i$ is the layer number and a positive sign indicates an expansion and a negative sign a contraction between layers.

Mulliken population analysis was performed on the relaxed surfaces, and the net charge and spin of the outer layers are given in Tables III and IV. For all the surfaces, the inner layers had a Mulliken analysis that was consistent with a Fe$^{2+}$/Ti$^{3+}$ solution, in agreement with values from bulk calculations.

#### A. Fe surfaces

Relaxation of the Fe–O$_3$–Ti– surface [Fig. 2(a)] found a large (~0.72 Å) inward movement of the surface Fe atom, resulting in the Fe atom sitting only 0.24 Å above the O$_3$ layer, coordinated with three oxygen atoms, while there is computed to be a small (7%) expansion of the O–Ti distance. The inward movement and final geometry of the Fe atom is qualitatively similar to that found in Fe–O$_3$–Fe– terminated hematite (0001) surface, where calculations within the GGA give a large
TABLE II. Interlayer relaxations (in %) of the different surface terminations considered relative to the corresponding bulk spacing. Positive values indicate an expansion of the layer, while negative values denote a contraction. Negative values greater than 100% indicate a contraction that has reversed the order of the layer.

<table>
<thead>
<tr>
<th></th>
<th>Fe–O3–Ti–</th>
<th>O=Fe–O3–</th>
<th>O1–Fe–Fe–</th>
<th>O2–Fe–Fe–</th>
<th>O1–Fe–Fe–</th>
<th>Fe–Fe–O3–</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3/2/3 Ti–Fe</td>
<td>−26.1</td>
<td>−9.3</td>
<td>−7.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe–Fe</td>
<td>−64.8</td>
<td>−53.7</td>
<td>3.9</td>
<td>197</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe–O3–Ti</td>
<td>7.0</td>
<td>0.5</td>
<td>8.5</td>
<td>22.5</td>
<td>21.8</td>
<td>17.6</td>
</tr>
<tr>
<td>Ti–Ti</td>
<td>−29.2</td>
<td>−22.0</td>
<td>21.2</td>
<td>18.2</td>
<td>16.7</td>
<td>5.8</td>
</tr>
<tr>
<td>Ti–O3–Fe</td>
<td>10.4</td>
<td>6.2</td>
<td>−6.3</td>
<td>−8.7</td>
<td>−6.3</td>
<td>−5.6</td>
</tr>
<tr>
<td>O3–Fe</td>
<td>3.3</td>
<td>3.5</td>
<td>−0.8</td>
<td>0.4</td>
<td>2.3</td>
<td>39</td>
</tr>
<tr>
<td>Ti–O3–Fe–O</td>
<td>−23.9</td>
<td>4.1</td>
<td>25.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti–O3–Fe–O=Ti–O3–</td>
<td>−62.1</td>
<td>−40.5</td>
<td>−25.4</td>
<td>58.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti–O3–Fe–O=Ti–O3–</td>
<td>−191</td>
<td>−6.7</td>
<td>64.1</td>
<td>−19.8</td>
<td>−56.6</td>
<td>−78.4</td>
</tr>
<tr>
<td>O1–Fe–Fe</td>
<td>−126</td>
<td>−35.4</td>
<td>−39.7</td>
<td>−11.4</td>
<td>−49.0</td>
<td>24.4</td>
</tr>
<tr>
<td>Fe–Fe</td>
<td>143</td>
<td>23.1</td>
<td>14.8</td>
<td>3.8</td>
<td>−65.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Fe–O3–Fe</td>
<td>21</td>
<td>0.6</td>
<td>12.1</td>
<td>−0.4</td>
<td>−25.3</td>
<td>−6.4</td>
</tr>
</tbody>
</table>

inward movement of the Fe, placing it 0.4 Å above the oxygen layer with an expansion of the O-Fe distance.

The electron density of states (DOS) of the Fe–O3–Ti–surface (Fig. 3) resembles that of bulk ilmenite, except for a splitting of the Fe state at the top of the valence band, with the surface Fe contributing a state 0.5 eV lower in energy than the bulk Fe state. The overall band gap remains the same as in the bulk at 2.5 eV. Mulliken population analysis of the Fe–O3–Ti–surface (Table III) finds there is little change in the computed net spin of the surface Fe at 3.68[e] from the bulk value of 3.76[e].19

For the relaxed Fe–O3–Ti– surface, the surface Fe sits above a cavity in the lower Ti-bilayer, as shown in Fig. 2(a). Computations performed on the Ti–O3–Fe–surface (the results of which are given in Sec. III) found a lower energy structure when the surface Ti was placed in the cavity within the lower Fe bilayer. As a test for local minima, an alternate geometry was minimized where the surface Fe was placed below the surface oxygen layer into the cavity within the Ti bilayer, giving a mixed Ti-Fe layer. A stable structure was found with this configuration, however it was computed to be 3.8 eV higher in energy than with the Fe above the surface oxygen.

Oxidizing the Fe–O3–Ti– surface to form the O=Fe–O3–surface lessens the inward contraction of the surface Fe layer to −0.22 Å, with the O atom sitting atop the Fe at a distance of 1.62 Å [Fig. 2(b)]. Again, the relaxed geometry for this ilmenite surface is similar to that found in calculations on the hematite O=Fe–O3– surface within the GGA,8 where the O=Fe distance was found to be 1.58 Å. The net spin of 3.39[e] on the outermost Fe has changed little from the bulk, remaining consistent with a Fe2+ solution, and the net spin of the other atoms is also very similar to their bulk values.

TABLE III. Mulliken population analysis of net charge (α+β) and net spin (α−β) for the relaxed Fe-terminated surfaces, computed using the B3LYP functional.

<table>
<thead>
<tr>
<th></th>
<th>Fe–O3–Ti–</th>
<th>O=Fe–O3–</th>
<th>O1–Fe–Fe–</th>
<th>O2–Fe–Fe–</th>
<th>O1–Fe–Fe–</th>
<th>Fe–Fe–O3–</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>23.90</td>
<td>24.21</td>
<td>24.37</td>
<td>24.42</td>
<td>24.42</td>
<td>24.42</td>
</tr>
<tr>
<td>O</td>
<td>9.09, 9.09, 9.09</td>
<td>9.07, 9.05</td>
<td>9.432</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>19.64</td>
<td>19.65</td>
<td>19.65</td>
<td>19.78</td>
<td>19.78</td>
<td>19.78</td>
</tr>
<tr>
<td>O</td>
<td>0.250, 0.250, 0.250</td>
<td>0.50, 0.34</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>4.07</td>
<td>2.83</td>
<td>3.60</td>
<td>3.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>3.39</td>
<td>3.53</td>
<td>4.05</td>
<td>3.62</td>
<td>−3.48</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>0.08, 0.09, 0.10, 0.10</td>
<td>0.05, 0.05, 0.05</td>
<td>0.06, 0.06, 0.06</td>
<td>0.04, 0.04, 0.04</td>
<td>0.04, 0.04, 0.04</td>
<td>0.04, 0.04, 0.04</td>
</tr>
<tr>
<td>Ti</td>
<td>0.06</td>
<td>0.07</td>
<td>0.06</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Ti</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
</tr>
</tbody>
</table>
The DOS plot (Fig. 4) shows that the surface oxygen introduces a sharp unoccupied state into the band gap that is hybridized with Fe, and the unfilled spin-down Fe states of the surface Fe move down to just below the bulk conduction band.

In the cleaved Fe–Fe–O$_3$– surface, two iron atoms sit above the first oxygen layer [Fig. 5(a)]. Directly below one of these iron atoms is a cavity in the first Ti bilayer, while the other iron atom sits above a titanium. With relaxation, it was found that the surface Fe that was directly above the cavity moved down to fill the cavity [Fig. 5(b)]. This differs from the geometry reported in GGA studies on the Fe–Fe–O$_3$– terminated hematite surface, where both iron atoms remain above the first layer of oxygen atoms, similar to the cleaved geometry. Geometries with both iron atoms above the first oxygen layer were tested here, but proved unstable.

In the fully oxidized O$_3$–Fe–Fe– surface [Fig. 2(c)], the Mulliken analysis (Table III) of the relaxed surface shows the net spin on the outer Fe atom to be $3.76|e|$, greater than the net spin of $3.76|e|$ typical for a Fe$^{2+}$ state, and approaching the $4.26|e|$ calculated for a Fe$^{3+}$ solution in bulk ilmenite. Both the O$_3$–Fe and Fe–Fe interlayer distances have contracted from their bulk spacing, while the Fe–O$_3$ distance has increased. The net result of this is that the surface Fe polyhedra have slightly smaller Fe–O bond distances than in the bulk, with the shorter Fe–O distance lowering from 2.1 to 1.9 Å. There is a narrowing of the band gap (Fig. 6) from the bulk value to 0.83 eV due to...
FIG. 4. (Color online) Electron DOS for the O$_{3}$–Fe–O$_{3}$– surface. Total DOS decomposed to Fe (yellow), Ti (blue), and O (gray) is shown in (a), while (b) shows a decomposition of just the surface Fe, Ti, and O, with (c) showing the decomposition into Fe, Ti, and O of the other layers.

The introduction of unfilled Fe surface states from the outer Fe bilayer, consistent with the picture of the surface Fe having a higher valence.

Removal of an oxygen atom from the O$_{3}$–Fe–Fe– surface forms the O$_{2}$–Fe–Fe– surface. Under relaxation there is an inward movement of the outer O atoms and a contraction of the Fe–Fe bilayer, but to a lesser extent than that found for the O$_{3}$–Fe–Fe– surface. Relaxation of the O$_{1}$–Fe–Fe– surface computes a small inward movement of the surface oxygen and a small expansion of the Fe bilayer. The single surface oxygen is shared between the two surface Fe atoms, with a bond length of 1.83 Å to the higher Fe atom in the higher position bilayer, and 1.84 Å to the Fe in the lower position in the bilayer.

B. Ti surfaces

Initial relaxations of the Ti–O$_{3}$–Fe– surface saw the movement of the surface Ti to a metastable position 0.26 Å above the O$_{3}$ layer, over the cavity in the lower Fe bilayer and coordinated with three oxygen atoms. This geometry is analogous to that found for the Fe–O$_{3}$–Ti– surface [Fig. 2(a)].

A lower energy solution was found by displacing the surface Ti to below the topmost O$_{3}$ layer into the cavity within the lower Fe bilayer, although this proved to be another metastable solution, as a lower energy solution was found by moving the high position iron from the bilayer to a position above the surface O$_{3}$ layer [Fig. 7(a)].

This final geometry has a Fe just above the topmost O$_{3}$ layer, coordinated with three oxygen atoms and above a cavity in the next bilayer. It is $-1.98$ eV lower in energy than the original metastable relaxed geometry with the Ti atom above the first oxygen layer. The final geometry resembles that of the Fe–O$_{3}$–Ti– surface, but with a mixed Fe-Ti bilayer below the O$_{3}$ layer. This mixed bilayer has a similar cation arrangement to that found in the LiNbO$_{3}$ high-pressure structure of ilmenite,\textsuperscript{20} The lowest
energy relaxed Ti–O3–Fe– surface has a DOS (Fig. 8) which shows a narrowing of the band gap, due to the filled Fe beta states in the gap. The net spin on all the atoms is little changed from their bulk values, with the outer Ti remaining close to Ti⁴⁺, and the outer Fe close to Fe²⁺.

The O=Ti–O₃– surface, formed by placing an oxygen atom atop the surface Ti in the unrelaxed Ti–O₃–Fe– surface, relaxed to a geometry with the oxygen atom sitting 1.84 Å above the Ti, with the Ti atom displaced −0.27 Å from its bulk position [Fig. 7(b)]. The net spin on the outermost Ti changed to 0.11 |e|, only a slight change from the 0|e| of a Ti⁴⁺ cation in the bulk. The DOS plot shows that, like in the O=Fe–O₃– case, the surface oxygen introduces a sharp state at the bottom of the valence band.

Initial relaxations of the Ti–Ti–O₃– surface from its cleaved bulk geometry led to a metastable geometry in which both surface titanium atoms remained above the first oxygen layer. A displacement of one of the surface titanium atoms into the cavity below the oxygen layer led to a stable geometry with a lower energy. The outer Ti surface atom contracted to a position 0.3 Å above the oxygen layer and the lower Ti from the surface bilayer relaxed in the vacant site within the Fe bilayer below its initial position, giving a mixed Fe and Ti bilayer. An increase in the net spin and charge on the Ti atoms (Table IV) indicates that their valence has changed from Ti⁴⁺ to Ti³⁺ or less. The lower Ti, which has moved close the Fe bilayer, has perturbed the net spin of the Fe atoms in this layer, but for atoms below this their Mulliken values are close to their bulk values.

For the fully oxidized O₃–Ti–Ti– surface geometry relaxation calculates an inward movement of −0.2 Å of the oxygen layer toward the Ti bilayer, the Ti bilayer contracting by −0.3 Å and a 0.5 Å expansion of the Ti–O interlayer distance (Table II). Reduction of this surface to O₂–Ti–Ti– results in a slight (0.07 Å) expansion of interlayer distance between the surface oxygen and the Ti bilayer. The contraction of the Ti bilayer is slightly less at −0.2 Å, and the expansion of the Ti bilayer to O is smaller at 0.2 Å. Removing another surface oxygen gives the O₁–Ti–Ti– surface, whose relaxation moves the oxygen 0.17 Å from the Ti bilayer. The Ti bilayer still contracts, but only by −0.1 Å.

C. Relative stability of the relaxed surfaces

The relative stability of the relaxed Fe–O₃–Ti–, O=Fe–O₃–, Ti–O₃–Fe–, and O=Ti–O₃– surfaces calculated using Eq. (5) is plotted versus oxygen chemical potential in Fig. 9, using ¹E₀₂ as the reference for the oxygen chemical potential, and FeTiO₃ as the chemical reservoir for Fe and Ti. In oxygen-rich conditions (high partial pressures of oxygen), the oxidized O=Fe–O₃– and O=Ti–O₃– surfaces become more stable than their reduced counterparts Fe–O₃–Ti– and Ti–O₃–Fe–, with the most stable surface in oxygen-rich conditions being the O=Fe–O₃– surface, and the Fe–O₃–Ti– surface being the most stable under oxygen-poor conditions.

The relaxed surfaces other than that shown in Fig. 9 have an unequal number of Ti and Fe atoms, so it is not possible to use FeTiO₃ to determine the chemical potentials of both Fe and Ti. Instead, using O₂ for the chemical reservoir for oxygen, the range of Ti and Fe chemical potentials can be examined by using either TiO₂ as a chemical reservoir for Ti or Fe₂O₃ for Fe, and FeTiO₃ for Fe and Ti, respectively. The relative surface energy for surfaces with an unequal number of Ti and Fe can be obtained via Eqs. (8) and (9), and the surface stability versus oxygen chemical potential calculated this way is shown in Figs 10 and 11. The choice of TiO₂ or Fe₂O₃ as chemical reservoirs has no effect on the stability of the Fe–O₃–Ti–, O=Fe–O₃–, Ti–O₃–Fe–, and O=Ti–O₃– surfaces, as when NFe = NTi, Eqs. (8) and (9) reduce to Eq. (5). Comparing Figs. 10 and 11, it can
be seen that choosing TiO$_2$ as the chemical reservoir has a stabilizing effect on the O$_3$–Fe–Fe–, O$_2$–Fe–Fe–, O$_1$–Fe–Fe–, and Fe–Fe–O$_3$– surfaces and a destabilizing effect on the O$_3$–Ti–Ti–, O$_2$–Ti–Ti–, O$_1$–Ti–Ti–, and Ti–Ti–O$_3$– surfaces, and using Fe$_2$O$_3$ as the chemical reservoir has the opposite effect.

**IV. DISCUSSION**

The stability of the various ilmenite surfaces bears some resemblance to that found in hematite.$^{12,13}$ Under greatly reducing conditions the Fe–O$_3$–Ti– surface in ilmenite and the Fe–O$_3$–Fe– surface in hematite are the most stable. As conditions become more oxidizing, the O=Fe–O$_3$– termination becomes more stable in both ilmenite and hematite, with the hematite O=Fe–O$_3$– surface becoming stable at lower oxygen partial pressures than for the ilmenite surface. At high oxygen partial pressures (0.2 bar at 500 K), the hematite O$_3$–Fe–Fe– surface becomes the most stable, while for ilmenite the O=Fe–O$_3$– surface remains slightly more stable. These results are consistent with the cation in hematite being more positive than the iron in ilmenite. For the titanium surfaces in ilmenite, at very reducing conditions, the Ti–O$_3$–Fe– surface is the most stable, and then as the oxygen partial pressures increase, the O$_3$–Ti–Ti– surface becomes the most stable of all the ilmenite surfaces.

The ilmenite surface with the lowest cleavage energy calculated within the B3LYP approximation is the Fe–O$_3$–Ti– surface, with a calculated cleavage energy of 1.92 J/m$^2$. This is a lower energy than the 2.3 J/m$^2$ of Fe–O$_3$–Fe–

![Graph showing surface energies as a function of oxygen chemical potential](image)

**FIG. 9.** (Color online) Surface energies of selected surface terminations plotted as a function of oxygen chemical potential. O$_2$ used as the chemical reservoir for O, and FeTiO$_3$ used for Ti and Fe. In the top x axis, the chemical potential $\Delta \mu_O(T, p)$ has been converted into pressure scales at fixed temperatures of $T = 300$ and 600 K.

![Graph showing surface energies as a function of oxygen chemical potential, using TiO$_2$ as the chemical reservoir](image)

**FIG. 10.** (Color online) Surface energies of selected surface terminations plotted as a function of oxygen chemical potential, using TiO$_2$ as the chemical reservoir for Ti, FeTiO$_3$ for Fe, and O$_2$ for oxygen terminated (0001) surface of Fe$_2$O$_3$ (Ref. 12) calculated within the GGA, which seems reasonable as the iron in ilmenite has a lower valence (Fe$^{2+}$) than that of hematite (Fe$^{3+}$). With the titanium in ilmenite having a valence of Ti$^{4+}$, it would be expected that the Ti–O$_3$–Fe– surface would have a higher cleavage energy than the Fe–O$_3$–Ti– surface, which it does at 3.73 J/m$^2$. As well as having the lowest cleavage energy, the Fe–O$_3$–Ti– surface is found to be the most stable of the surface terminations under reducing conditions, with the O$_3$–Ti–Ti– surface becoming the most stable termination at higher oxygen partial pressures.

From the results of the B3LYP calculations, some interpretations as to the nature of the surfaces seen in the Fellows et al.$^6$ STM study can be made. In their study, the FeTiO$_3$ (0001) surface was cleaved under high vacuum and then annealed at $10^{-10}$ mbar at 1073 K, followed by annealing in $5 \times 10^{-7}$ mbar...
TABLE V. Step height, surface feature spacing, and surface energies for the relaxed surfaces relative to the relaxed \( \text{Fe–O}_3–\text{Ti}–\) surface, surface energies relative to the \( \text{Fe–O}_3–\text{Ti}–\) surface at \( \mu \text{O} = -1 \).

<table>
<thead>
<tr>
<th>Surface</th>
<th>( X-Y ) step (Å)</th>
<th>Surface (Å)</th>
<th>Energy at ( \mu \text{O} = -1 ) (eV/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_3–\text{Ti}–\text{Ti}– )</td>
<td>2.8</td>
<td>2.7</td>
<td>-0.002</td>
</tr>
<tr>
<td>( \text{O}=\text{Fe–O}_3–)</td>
<td>2.65</td>
<td>4.8</td>
<td>0.024</td>
</tr>
<tr>
<td>( \text{O}_1–\text{Ti}–\text{Ti}– )</td>
<td>2.4</td>
<td>4.8</td>
<td>0.295</td>
</tr>
<tr>
<td>( \text{Ti}–\text{O}_3–\text{Fe}– )</td>
<td>2.3</td>
<td>4.8</td>
<td>0.052</td>
</tr>
<tr>
<td>( \text{Fe–Fe–O}_3– )</td>
<td>0.86</td>
<td>4.8</td>
<td>0.332</td>
</tr>
<tr>
<td>( \text{O}_3–\text{Fe–Fe}– )</td>
<td>0.4</td>
<td>2.6</td>
<td>0.076</td>
</tr>
<tr>
<td>( \text{O}_2–\text{Fe–Fe}– )</td>
<td>0.26</td>
<td></td>
<td>0.059</td>
</tr>
<tr>
<td>( \text{O}_1–\text{Fe–Fe}– )</td>
<td>0.19</td>
<td>4.8</td>
<td>0.094</td>
</tr>
<tr>
<td>( \text{O}=\text{Ti–O}_3–)</td>
<td>0.08</td>
<td>4.8</td>
<td>0.039</td>
</tr>
</tbody>
</table>

\( \mu \text{O} \) is the oxygen chemical potential. The energies are relative to the Fe–O3–Fe– and O2–Fe–Fe– surfaces. The energies of \( \text{Ti}–\text{O}_3–\text{Fe}– \) and \( \text{O}_3–\text{Fe–Fe}– \) surfaces are not shown in the table due to the high energy required for their formation.

FIG. 11. (Color online) Surface energies of selected surface terminations plotted as a function of oxygen chemical potential, using \( \text{Fe}_2\text{O}_3 \) as the chemical reservoir for \( \text{Fe}, \text{FeTiO}_3 \) for \( \text{Ti} \), and \( \text{O}_2 \) for oxygen.

High-resolution imaging of the \( Y \) terraces showed a hexagonal array of features, with a 4.8 \( \pm \) 0.2 Å spacing. From this feature spacing, we can rule out some of the surfaces considered here. The relaxed \( \text{O}_3–\text{Fe–Fe}–, \text{O}_3–\text{Ti}–\text{Ti}– \) and \( \text{O}_2–\text{Fe–Fe}– \) surfaces all have feature spacing of less than 4.8 Å, leaving the \( \text{O}=\text{Fe–O}_3–, \text{O}–\text{Ti}–\text{Ti}–, \text{Fe–Fe–O}_3–, \text{Ti}–\text{Ti}–\text{O}_3–, \text{Ti–O}_3–\text{Fe}–, \text{O}_3–\text{Fe–Fe}–, \text{O}_2–\text{Fe–Fe}–, \text{O}_1–\text{Fe–Fe}–, \text{Ti}–\text{O}_3–\text{Fe}–, \text{O}=\text{Ti–O}_3–\) as possible surfaces for the \( Y \) terrace.

Fellows et al.\(^6\) also measured the height difference between two \( X \) terraces to be 4.4 \( \pm \) 0.5 Å and the step from \( X \) to \( Y \) or \( Y \) to \( X \) was 2.2 \( \pm \) 0.3 Å, and noted that the \( Y \) terraces grew larger with longer annealing times. From the relaxed geometries calculated within the B3LYP functional, Table V gives three possible surfaces for the \( Y \) terrace that have step heights from the \( \text{Fe–O}_3–\text{Ti}– \) surface that are close to experiment: the \( \text{O}=\text{Fe–O}_3–, \text{O}–\text{Ti}–\text{Ti}–, \text{Fe–Fe–O}_3–, \text{Ti}–\text{Ti}–\text{O}_3–, \text{Fe–O}_3–\text{Ti}–, \text{O}_3–\text{Fe–Fe}–, \text{O}_2–\text{Fe–Fe}–, \text{O}_1–\text{Fe–Fe}–, \text{Ti}–\text{O}_3–\text{Fe}–, \text{O}=\text{Ti–O}_3– \) surfaces. From the calculated relative stability of these three surfaces, the \( \text{O}=\text{Fe–O}_3– \) surfaces seems the most likely candidate for the \( Y \) terrace, although its step height at 2.65 Å is slightly larger than the STM determined step height of 2.2 \( \pm \) 0.3 Å. This surface also seems reasonable in light of the experimental results showing that the \( Y \) terrace “grows” from the \( X \), as the \( \text{O}=\text{Fe–O}_3– \) surface is simply the oxidation of the proposed \( X \) terrace surface, \( \text{Fe–O}_3–\text{Ti}– \).

The formation of the \( \text{O}=\text{Fe–O}_3– \) surface instead of the more stable \( \text{O}_3–\text{Fe–Ti}– \) surface can be explained in terms of kinetics, with the \( \text{O}=\text{Fe–O}_3– \) surface requiring only oxidation of the \( \text{Fe–O}_3–\text{Ti}– \) surface, whereas formation of the \( \text{O}_3–\text{Fe–Ti}– \) surface would require a larger atomic rearrangement. The plot of surface stability in Fig. 9 shows that at the experimental conditions, the \( \text{O}=\text{Fe–O}_3– \) surface will still be less stable than the \( \text{Fe–O}_3–\text{Ti}– \) surface; however, this does not rule out the formation of the \( \text{O}=\text{Fe–O}_3– \) surface, but lowers the probability that it will form. In addition, the \( \text{O}=\text{Fe–O}_3– \) surface has been found experimentally to form on hematite surfaces.

V. CONCLUSIONS

A number of possible terminations for the ilmenite (0001) surface have been examined using the B3LYP functional. In addition to the 12 different terminations considered, metastable geometries were found for the \( \text{Ti–O}_3–\text{Fe}–, \text{Ti–Ti}–\text{O}_3–, \) and \( \text{Fe–Fe–O}_3– \) surfaces, illustrating the complex nature of the (0001) surface. The \( \text{Fe–O}_3–\text{Ti}– \) surface was found to have the lowest cleavage energy, and also to be the most...
stable surface at low oxygen partial pressures, suggesting it is most likely to form when ilmenite is cleaved under high vacuum. Based on step heights, surface geometry, and surface energy, it is likely that under slightly oxidizing conditions, the O=Fe–O3− surface is stabilized.

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