**Oxidation of Magnetite(100) to Hematite Observed by in Situ Spectroscopy and Microscopy**

Kevin F. McCarty,*† Matteo Monti,** Shu Nie,† David A. Siegel,† Elena Starodub,†⊥ Farid El Gabaly,† Anthony H. McDaniel,† Andrey Shavorskiy,§ Tolek Tyliszczak,∥ Hendrik Bluhm,§ Norman C. Bartelt,⊥⊥ and Juan de la Figuera‡

†Sandia National Laboratories, Livermore, California 94550, United States
‡Instituto de Química-Física "Rocasolano", CSIC, Madrid 28006, Spain
§Chemical Sciences Division and ‡Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

**ABSTRACT:** We study where and how hematite (α-Fe₂O₃) nucleates and grows during the oxidation of magnetite(100) single crystals. Hematite inclusions grow along ⟨110⟩ directions of the magnetite (Fe₃O₄), leading to a biaxial array of hematite slabs in an electrically conducting matrix of magnetite. The slab arrays form in both bulk single crystals and thin films of magnetite. Atomic force microscopy reveals that the surface growth of magnetite that accompanies hematite formation is faster adjacent to the hematite slabs. In situ X-ray photoelectron and X-ray absorption spectroscopies at 600 °C in an oxygen environment reveal that the conversion of the Fe²⁺ in magnetite to Fe³⁺ in hematite occurs without the formation of the metastable phase maghemite (γ-Fe₂O₃). We offer an explanation of why Fe₃O₄(100) oxidizes faster than Fe₂O₃(111).

1. **INTRODUCTION**

The iron oxide phases magnetite, Fe₃O₄, and hematite, α-Fe₂O₃, are ubiquitous in nature, and important chemistries occur on their surfaces. Magnetite catalyzes a variety of surface chemistries, including Fischer–Tropsch synthesis,¹ the water–gas shift reaction,²–⁵ and water splitting.⁶ Magnetite also has intrinsic enzymatic activity in biological systems.⁷ Its ferrimagnetism enables magnetic manipulation of particles in biological applications⁸ and heterogeneous catalysis.⁹ Hematite is an effective catalyst for the photo-oxidation of water,⁰¹⁻¹¹ Key to these catalytic activities are oxidation/reduction (redox) cycles where iron at the surface cycles between different oxidation states.⁴,¹⁰⁻¹³⁻¹⁵

Another important concept in catalysis is that the catalyst itself can serve as a reservoir of reactive species.³ An example is reversible oxygen storage in nonstoichiometric oxides such as ceria.¹⁶ Magnetite also accommodates variable stoichiometry by forming defects on its Fe sublattice.¹⁷ Thus, its bulk can serve as a source or sink of Fe that is exchanged with the surface as environmental conditions like the oxygen partial pressure change. Iron oxides can act as larger oxygen reservoirs through phase transitions between the different iron oxide phases. These phase transitions can produce chemical (“solar”) fuels using heat from the sun.¹⁸⁻²¹ In these processes, H₂O or CO₂ are split on the oxide surface, generating H₂ or CO. The liberated oxygen reacts with the reduced iron oxide, storing oxygen in its solid state. Heating liberates oxygen and regenerates the initial (reduced) oxide. (An additional reaction between a stronger oxidizer such as KOH and Fe₂O₄ is needed to cycle between Fe₂O₄ and Fe₃O₄.¹⁹) Despite all these important applications, little is known about the precise atomic mechanisms through which these oxides undergo oxidation and reduction. For example, where and how does hematite, which contains only Fe³⁺, nucleate and grow during the oxidation of magnetite, which contains a mixture of Fe²⁺ and Fe³⁺? Here we address these questions.

The literature reports that magnetite’s oxidation has strong dependencies on temperature,¹⁷ sample size,²² purity,²³,²⁴ and the crystal face.²⁵⁻²⁷ At temperatures below roughly 300 °C, magnetite oxidizes to the metastable phase maghemite, γ-Fe₂O₃.¹⁷ The reaction occurs by the migration of iron cations to the surface.²²,²³ Since magnetite and maghemite both have cubic crystal structures,¹⁷ the reaction occurs topotactically, with the maghemite forming a coating on the magnetite.²²,²³,²⁸ At higher temperatures, roughly above about 500 °C,¹⁷,²⁴,²⁹ oxidizing magnetite in air leads to hematite. Since magnetite and hematite have different crystal symmetries, hematite domains must nucleate before they can grow.³⁰

Recently we used real-time surface microscopy to provide insight into the mechanism of magnetite oxidation and the nature of redox catalysis on iron oxides.³¹ We found that the high-temperature oxidation of Fe₃O₄(100) occurred by gas-
phase oxygen reacting with iron diffusing from magnetite’s interior, similar to the growth of maghemite at lower temperature.22,23 But the high-temperature oxidation grows magnetite at the surface and hematite in the interior. Namely, different reactions occur in the interior (where hematite forms) and at the surface (where new magnetite forms).24 For every 12 formula units of Fe3O4 created, one unit of Fe3O4 is added to the surface:

\[
9\text{Fe}_3\text{O}_4 + 2\text{O}_2 \rightarrow 12\text{Fe}_2\text{O}_3 + (\text{Fe}_3\text{O}_4)_{\text{surface}}
\] (1)

Eventually, all the Fe3O4 is converted to Fe3O4.

This paper provides further details on the conversion of magnetite to hematite at 600 °C. We find that hematite grows topotactically into the magnetite in a manner that conserves oxygen but liberates iron. The hematite grows along the close-packed oxygen planes of magnetite, consistent with the previously reported crystallography.30 The partially oxidized surface of Fe3O4(100) consists of a two-dimensional array of hematite stripes. This directional growth of the hematite helps explain the observation by Zhou et al. that the Fe3O4(100) surface oxidizes more rapidly than the (110) and (111) surfaces.25 Atomic force microscopy reveals that the surface growth of magnetite that accompanies hematite formation occurs faster near the hematite stripes. The metastable phase maghemite, γ-Fe2O3, is not an intermediate state of the conversion, as revealed in situ by X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) and ex situ by Raman spectroscopy.

2. EXPERIMENTAL SECTION

Three polished natural (mineral) magnetite(100) crystals from Mateck GmbH were examined. The surfaces of all the crystals were prepared in an ultrahigh vacuum (UHV) Elmitec LEEM III instrument, a low-energy electron microscope, using conditions typical for surface science, namely, by sputtering with 1.5 kV Ar ions and then annealing at ~600 °C in O2 at ~1 × 10−6 Torr.32,33 The crystals were examined after varying durations of annealing in O2 by LEEM and low-energy electron diffraction (LEED).

One crystal was further oxidized and characterized by X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) during oxidation at a much higher oxygen pressure, 2.3 mTorr. The XPS and XAS were performed at beamline 11.0.2 of the Advanced Light Source (ALS) using a Specs PHOIBOS 150 differentially pumped hemispherical analyzer.34 Coupled to the analyzer was a custom environmental chamber in which a Fe3O4(100) crystal was heated in a gas environment of regulated composition and pressure.35 The energy analyzer measured the XPS spectra directly. It was also used as a partial yield detector for X-ray absorption spectroscopy. This partial electron yield (PEY) measurement is sensitive to the surface region (approximately a few nanometers). XAS from deeper in the crystal (approximately several tens of nanometers) was obtained by using a silicon diode to measure the X-ray induced fluorescence yield (FY). To ensure the stability of its photocurrent, the diode’s temperature was regulated within a water-cooled enclosure. The hot sample’s thermal radiation was rejected by a thin Al film on the diode and an Al foil placed over the diode. The X-ray spectroscopies were performed in an environment of flowing gas at a total pressure of 230 mTorr. Two environments were examined: pure argon flowing at 60 standard cubic centimeters per minute (sccm) and argon (60 sccm) plus oxygen (0.6 sccm), giving an oxygen partial pressure of 2.3 mTorr.

The Fe 2p, O 1s, and valence-band photoelectron spectra were obtained using photons of 1005, 755, and 300 eV, respectively. The XPS and XAS spectra were calibrated using photoemission from a gold probe in electrical contact with the crystal by fixing the Au 4f/2 XPS peak to 84 eV.36 The XPS spectra were processed by the CasaXPS software using a Shirley-type background.37 The Fe2+ and Fe3+ components of the Fe 2p spectra were fit by asymmetric lineshapes that simulate the effect of the multiplet splitting.38 The fitted energies of the Fe 2p 3/2 and Fe 2p 1/2 photoemission peaks were from 709.3–709.5 (711.0–711.3) eV and 722.4–722.7 (724.2–724.5) eV, respectively, for Fe2+ (Fe3+). The XAS spectra were processed to make the pre-edge signal flat by subtracting a linear background.

Atomic force microscopy (AFM) and Raman spectroscopy were performed in air. The latter used a backscattering geometry with a 100× objective lens, a frequency-doubled Nd:YAG laser, and a CCD detector cooled by liquid nitrogen. The line scan used a step size of 0.5 μm.

3. RESULTS

3.1. Initial Stages of Hematite Formation. We previously reported that preparing a Fe3O4(100) surface by the typical preparation conditions (annealing at ~600 °C in O2 at ~1 × 10−6 Torr) of surface-science studies led to a low density of linear and L-shaped features that were not present on the as-polished surface. The features are hematite. In ref 31 we presented a LEEM image of a hematite inclusion produced by these processing conditions. Figure 1 provides further characterization of the same region after additional oxidation. Figure 1a shows an AFM image. Raman spectroscopy readily identifies the phase of the linear features. Raman spectrum 1 in Figure 1c is from the point on the L shape marked by a 1 in Figure 1a. The peaks at 222, 242, 288, 407, 493, 608, and 1316 cm−1 are characteristic of hematite, α-Fe2O3.39 Particularly distinctive is the strong peak from second-order phonon scattering at 1316 cm−1.40 The region around the hematite L shape is magnetite, as revealed by the peaks at 301, 535, and 662 cm−1 in spectrum 2 (red), which is from point 2 in Figure 1a. (The weak peak at ~660 cm−1 in spectrum 1 reveals the presence of a small amount of magnetite.) Thus, the majority of the surface is magnetite, with a small fraction being hematite. The spectra do not show the features of maghemite, γ-Fe2O3,41,42 namely, three broad peaks around 350, 500, and 700 cm−1. The AFM image reveals that the hematite region (Figure 1a) is recessed from the surface of the surrounding magnetite. This is readily seen in the cross-sectional profile, Figure 1b, from point X to point Z in the image. The hematite is about 200 nm lower than the surrounding magnetite. The magnetite is peaked adjacent to the recessed hematite in all cross sections through the inclusions. In section 4 we explain how this topography results from the solid-state conversion of magnetite to hematite. LEEM and optical microscopy reveal that the hematite stripes lie along two orthogonal directions on the magnetite(100) surface. We used LEED to determine these directions. Figure 1d gives the LEED pattern from the 2 μm diameter region circled in Figure 1a. The diffraction pattern has ε(2 × 2) symmetry relative to the (1 × 1) symmetry of a bulk-terminated (100) surface. This reconstruction is typical of magnetite(100) surfaces prepared by sputtering/annealing cycles.43,44
patterns or electron restructured regions of hematite do not give well-defined fingerprints that distinguish the different Fe–O phases. In contrast to the majority of the surface, which is magnetite, the linear and L-shaped regions of hematite do not give well-defined LEED patterns or electron reflectivity spectra. We believe that this results from the hematite surfaces being rough or inclined from the magnetite(100) surface.

3.2. Monitoring Further Oxidation Using X-ray Spectroscopies. Further insight into the magnetite-to-hematite conversion was obtained by in situ observations using X-ray spectroscopies. A magnetite(100) crystal was prepared by sputter/anneal cycles and characterized in the LEEM instrument. It was then transported in air to the near-ambient-pressure X-ray spectroscopy system at the Advanced Light Source. There the crystal was introduced into an environment of argon gas and examined initially at room temperature. The crystal was heated to about 400 °C in an argon flow. Then O₂ was introduced, at a partial pressure of 2.3 mTorr. The temperature was increased to 600 °C. Subsequently the oxygen was removed from the environment, and the crystal was cooled in argon. Table 1 summarizes the four conditions (A–D) of temperature and gas composition at which spectroscopy was performed. XPS survey spectra revealed that the initial surface (room temperature in Ar) was greatly contaminated by carbon; the C 1s peak was ~2.5 times more intense than the O 1s peak. After heating to 400 °C in O₂ (condition B), the C 1s peak was ~1/10 as intense as the O 1s peak. After heating to 600 °C in O₂ (condition C), the C 1s peak was not discernible in an XPS survey spectrum. In addition, the surface was contaminated by a small amount of Ca, ~3% after the adventitious C was removed, based on the Fe 2p and Ca 2p peaks. No Si was detected. We note that no valid XAS spectra were obtained for condition A.

3.2.1. Fe 2p Spectroscopy. Figure 2 shows the XPS spectra of the Fe 2p core level during the different stages of the oxidation. The top spectrum (A, 400 °C Ar) agrees with literature results for magnetite, with the main Fe 2p 3/2 and Fe 2p 1/2 photoemission lines at ~709.4 (~711.1) eV and ~722.5 (~724.3) eV, respectively, for Fe²⁺ (Fe³⁺).

Table 1. Sequence of Temperatures and Gas Compositions Used To Oxidize Magnetite

<table>
<thead>
<tr>
<th>Condition</th>
<th>Temperature</th>
<th>Gas Composition</th>
<th>Spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>400 °C Ar</td>
<td>Ar</td>
<td>XPS</td>
</tr>
<tr>
<td>B</td>
<td>400 °C O₂/Ar</td>
<td>PEY</td>
<td>XPS</td>
</tr>
<tr>
<td>C</td>
<td>600 °C O₂/Ar</td>
<td>PEY</td>
<td>XPS</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td></td>
<td>XPS</td>
</tr>
</tbody>
</table>

Cooling in argon did not change the Fe 2p spectrum (D, cooling Ar).

3.2.2. Iron L-edge Spectroscopy. Figure 3 shows absorption spectra of the Fe L₂₃ edge obtained in two ways: partial electron yield (PEY), which is surface sensitive, and fluorescence yield (FY), which probes the bulk. The surface spectrum (solid red line) during the low-temperature oxidation (B, 400 °C PEY) is consistent with the literature characterization of magnetite. Specifically, the L₂ edge with a shoulder at 710 eV is considered to be a fingerprint of magnetite, with the shoulder coming from Fe³⁺. This shoulder grows into a well-separated peak by the end of the oxidation (D, cooling Ar). This is consistent with the oxidation of Fe²⁺ to Fe³⁺. Note that during the initial oxidation, the bulk spectrum (FY, dashed red line) significantly differs from the surface (PEY) spectrum. The presence of a well-resolved peak at 710 eV in the initial FY spectrum (B, 400 °C O₂) suggests that the
bulk is more oxidized than the surface. At the end of oxidation (D, cooling in Ar), the surface and bulk spectra are similar.

3.2.3. Oxygen K Edge Spectroscopy. Figure 4 shows absorption spectra of the oxygen K edge in both surface sensitive and bulk sensitive modes. The surface spectrum during the low-temperature oxidation (B, 400 °C O₂ PEY) has a peak at 531.4 eV, which has a shoulder at 532.5 eV, features characteristic of magnetite. Oxidation at 600 °C increases the size of the shoulder (C, 600 °C O₂ PEY). This shoulder develops into a well-separated peak by the end of the oxidation (D, cooling Ar), which is characteristic of hematite. Consistently the shoulder at ∼545.5 eV is characteristic of hematite but not maghemite. The FY spectrum during the initial oxidation (B, 400 °C) has a stronger peak at 532.5 eV than the surface spectrum. This suggests that the bulk is initially more oxidized than the surface, as also suggested by the Fe XAS results (Figure 3). At the completion of the oxidation (D, cooling in Ar), the two O spectra are essentially the same.

3.2.4. Valence Band Spectroscopy. Figure 5 shows the valence band spectra during the oxidation. During the initial oxidation (D, cooling in Ar), the surface and bulk spectra are similar.
oxidation (B, 400 °C O₂ PEY) the valence band has a broad peak around 5 eV, which is characteristic of magnetite. The peak at ~22 eV is the O 2s level. The spectrum also has a small shoulder, which is marked by an arrow, close to the Fermi level. According to Wandelt, only iron oxides containing Fe²⁺ (e.g., FeO and Fe₃O₄) present this feature. Oxidation at 600 °C (C, 600 °C O₂) removes this shoulder and leads to a sharper peak at ~5 eV and a shoulder at ~2.5 eV. These changes result from converting Fe²⁺ to Fe³⁺, giving a spectrum characteristic of hematite. Cooling in Ar gave two new peaks at about 10.5 and 31 eV, whose intensities scale together. We believe that these peaks result from the adsorption of impurities from the gas phase. We note that the final valence band spectrum is not consistent with hydroxide formation. Namely, α-FeOOH and γ-FeOOH do not have peaks near 10.5 and 31 eV and their O 2s peaks have a distinct shoulder at higher binding energy, a feature absent in Figure 5D. One interpretation is that the two new peaks result from a carbonate species.

3.2.5. Oxygen 1s Spectroscopy. Examination of the O 1s spectra provides additional support that magnetite readily reacts with gas-phase impurities, whose decomposition products accumulate on the surface in the absence of O₂. The top spectrum in Figure 6 is from the magnetite at room temperature (RT) in a low vacuum environment after being transported from the LEEM through air. The component from the lattice oxygen at about 530 eV is dwarfed by the contribution from impurities at about 533 eV. On the basis of the XPS survey spectra discussed above, these impurities are mainly carbonaceous. Heating in O₂ largely removed the impurities (C: 600 °C O₂). This is again consistent with the loss of carbon observed in the XPS survey spectra during heating in O₂. Impurities accumulate during cooling in Ar, as shown by the shoulder with ~1.6 eV high binding energy in the bottom spectrum. (XPS survey spectra were not obtained during or after cooling in Ar.) We note that this shoulder is not
consistent with hydroxide formation; the hydroxyl component of the O 1s core level in $\alpha$-FeOOH and $\gamma$-FeOOH is 1.1 eV from the lattice oxygen peak of magnetite.$^{59}$

To summarize the X-ray characterization, we observe the conversion of magnetite to a phase consistent with hematite. The spectroscopies show no evidence of maghemite formation. Specifically, as the oxidation occurred, the oxygen K edge spectra (Figure 4) developed a shoulder at $\sim$545.5 eV, which is characteristic of hematite but not maghemite. We next show that after the X-ray analysis, the near-surface region consisted of a biaxial array of hematite slabs.

3.3. Raman Spectroscopy of a Partially Oxidized Crystal. After the characterization by in situ X-ray spectroscopies, the oxidized crystal was examined by optical microscopy and Raman spectroscopy. The optical micrograph in Figure 7b shows that the surface consists of a high density of stripes that run horizontally and vertically. Smoother regions separate the stripes. The stripes gave the surface a matte appearance, unlike the mirror finish of the as-polished surface. The black-line Raman spectrum in Figure 7a comes from the position labeled 1 in the optical image and has the characteristic peaks (222, 241, 288, 407, 496, 609, 658, 812, and 1315 cm$^{-1}$) of hematite. The red-line Raman spectrum comes from the position labeled 2 and has the peaks (299, 533, and 661 cm$^{-1}$) characteristic of magnetite. Thus, the stripes are hematite surrounded by magnetite.

Further support that the stripes are hematite comes from the Raman line scan between the two $\times$ marks in Figure 7b. We used the hematite and magnetite peaks at 661 and 1315 cm$^{-1}$, respectively, to quantify the relative abundances of the two phases, accounting for the different scattering strengths apparent in Figure 7a. Panel c plots the ratio of the magnetite to the sum of the magnetite plus hematite. Clearly the stripes are hematite, with magnetite in between. AFM analysis revealed the same topography around the hematite inclusions as shown in Figure 1a,b. Namely, the hematite is recessed relative to the magnetite, which has ridges that run along the inclusions. Thus, oxidation at the higher O$_2$ pressure of the X-ray experiments compared to the LEEM experiments has simply continued the process of nucleating and growing hematite domains within the magnetite crystal.

On the basis of published optical constants, the sampling depths in the Raman spectra are roughly 125 nm for hematite$^{61}$ and 50 nm for magnetite.$^{62}$ (These depths attenuate the emitted backscattered beam to $1/e^2$ of the incident laser intensity.) The Raman sampling depths are considerable deeper than the near-surface region probed by XPS (about 2 nm) and likely are deeper than the depth probed by XAS. As discussed in section 4, the hematite stripes penetrate into the crystal, forming slabs.

3.4. Biaxial Array of Hematite Slabs via Magnetite Film Oxidation. We found that oxidizing a single-crystal magnetite film also produced a biaxial array of hematite slabs. The film was synthesized on a Nd-doped SrTiO$_3$(100) substrate from a hematite target using infrared pulsed laser deposition (PLD). The synthesis and characterization of the Fe$_3$O$_4$(100) films have been previously reported.$^{63}$ Figure 8 shows an optical image of a 160 nm thick magnetite film after oxidation in air at 300 $^\circ$C for 24 h. As confirmed by Raman spectroscopy, the silver/gray stripes are hematite. Note that the stripes again run along two well-defined crystallographic directions, which are the Fe$_3$O$_4$ (110) directions. Thus, magnetite in the form of both thin films and bulk single crystals converts to hematite by the same mechanism.

4. DISCUSSION

As the magnetite(100) surface is oxidized, hematite inclusions nucleate and grow. Initially the inclusions are isolated, as in Figure 1a. Eventually the surface is covered by a biaxial array of hematite stripes (Figure 7b), as observed after the oxidation that occurred during the in situ X-ray spectroscopies. Figure 9 provides a schematic illustration of how hematite forms. Figure 1 informs us that the hematite inclusions (stripes) lie along (110) directions of magnetite. This relationship is consistent with the crystallographic alignment reported by Feitknecht and Mannweiler$^{50}$ and has a simple origin. The common structural motifs in magnetite and hematite are close-packed planes of
oxygen atoms.\textsuperscript{17} In magnetite, these are \{111\} planes, and in hematite, they are the (0001) plane. So magnetite’s \{111\} planes become hematite’s (0001) plane. The magnetite-to-hematite conversion is topotactic; the hematite domains grow along and perpendicular to the magnetite \{111\} planes. Since magnetite’s \{111\} planes contain its $\langle 110 \rangle$ directions, the hematite stripes run along these directions. Because magnetite’s \{111\} planes are inclined from its (100) surface, the hematite inclusions are slabs that are also inclined, as illustrated in Figure 9. While the phase transformation preserves the close-packed oxygen layers, there is a rearrangement of the layers. The oxygen layers of magnetite have a face-center-cubic stacking, i.e., an abcabc... stacking with a three-layer periodicity.\textsuperscript{17} In contrast, the oxygen layers in hematite have a hexagonal-close-packed stacking with a two-layer period (abab...). So converting magnetite to hematite involves a shearing that changes the stacking of the oxygen planes.

We note that the net conversion of magnetite to hematite occurs through two spatially separated reactions.\textsuperscript{31} At the surface, oxygen oxidizes Fe$^{2+}$ to Fe$^{3+}$ and new magnetite forms (reaction 1). The surface reaction that forms magnetite creates iron vacancies ($V_{Fe}^{2-}$) in the magnetite:

$$ 2O_2 + 6e^- \rightarrow Fe_3O_4 + 3V_{Fe}^{2-} \quad (2) $$

These vacancies diffuse into the magnetite to an interior phase boundary between magnetite and hematite, where they are consumed, forming hematite:

$$ 3Fe_3O_4 + V_{Fe}^{2-} \rightarrow 4Fe_2O_3 + 2e^- \quad (3) $$

This topotactic reaction conserves oxygen. So the oxidation mechanism shown in Figure 9 does not involve oxygen diffusion through the bulk of either magnetite or hematite. (In fact, oxygen diffusion through magnetite is known to be slow relative to Fe diffusion.)\textsuperscript{17} But the mechanism requires a flow of
electrons to the surface of the magnetite to balance the iron-vacancy flow to the internal interface between magnetite and the hematite inclusions. Given this transport between the hematite and the surface, we might expect the surface magnetite growth to be faster near hematite. Indeed, the AFM characterization in Figure 1 reveals magnetite ridges next to the hematite inclusions. This locally enhanced growth rate is shown schematically in Figure 9. While the observations we present here are from natural magnetite crystals, we have observed the same phenomena (formation of biaxial hematite inclusions and the surface growth of magnetite through reaction 2) in a synthetic crystal.

We note that the directional growth of hematite inclusions in magnetite may be useful for photochemical applications of hematite. A limitation of hematite is its poor electrical conductivity. But partial oxidation of magnetite leads to a biaxial array of hematite slabs in a matrix of magnetite (Figure 7), which is a good electrical conductor. The fact that hematite arrays can also be made from magnetite films (Figure 8) may offer a scalable approach for synthesizing photocatalysts.

During oxidation at 600 °C, the Fe 2p XPS spectra (Figure 2) and the Fe L edge XAS of the surface (PEY spectra in Figure 3) show the conversion of Fe2+ to Fe3+. After oxidation, the O K edge XAS spectra (Figure 4) and the valence band spectrum (Figure 5) show the characteristic features of hematite. During the initial oxidation under X-ray analysis, the bulk was more oxidized than the surface. This difference is apparent in the top spectra of Figure 3, which compare the Fe L edge obtained from surface-sensitive detection (solid line) and bulk-sensitive detection (dashed line). As the oxidation proceeds, the surface and bulk become similar and show the net oxidation of magnetite to hematite. A similar conclusion is reached by considering the O K edge XAS (Figure 4). An explanation involves the magnetite that forms at the surface as part of hematite formation (see reaction 1 and Figure 9). More specifically, the magnetite crystal had been previously oxidized during the LEEM experiments, forming surface magnetite and hematite in the interior. This would account for the crystal’s initial state during X-ray analysis (condition B, 400 °C O2) having bulk that is hematite rich compared to the surface. As the oxidation proceeds, the surface and bulk become more uniformly hematite rich.

The O K edge XAS spectra (Figure 4) or the ex situ characterization by Raman spectroscopy (Figure 7) shows no evidence of maghemite formation. Indeed oxidizing magnetite at lower temperatures (roughly up to 300 °C) leads to maghemite, even though this phase is metastable. Ketteler et al. proposed that the oxidation of a FeO(111) film to hematite at temperatures and oxygen pressures similar to ours occurred through an intermediate phase similar to maghemite [γ-FεO2(111)]. Since maghemite is the limiting composition of iron-deficient magnetite, its formation does not require nucleation. In contrast, a nucleation event is needed to start hematite formation because it and magnetite have different structures. On a FeO(111) surface, the surface plane contains close-packed oxygen planes. A hematite nucleus can then spread across the surface by growing along the oxygen planes. Once the surface is covered with hematite, oxygen would have to diffuse through this capping layer to react with the Fe that is being liberated at the buried hematite/magnetite phase boundary (see Figure 9). This geometry may explain the observation of Zhou et al. that FeO(111) oxidizes slower than FeO(100).25

Magnetite’s reactive nature is also apparent in the in situ X-ray spectroscopies. After the oxygen is removed from the gas-phase environment with the crystal hot (condition D in Table 1), impurities in the argon gas lead to adsorbates, as evidenced by the component of the O 1s XPS peak at about 531.5 eV in the lower spectrum in Figure 6 and the new peaks at about 10.5 and 31 eV in the bottom valence-band spectrum in Figure 5. The latter may arise from carbonate species.

5. CONCLUSIONS

At temperatures above about 500 °C, we find no evidence in situ X-ray spectroscopies for the formation of the metastable phase maghemite during the oxidation of magnetite to hematite. Instead we observe the conversion of the Fe2+ in magnetite to Fe3+ in hematite. The growth of the hematite proceeds along magnetite’s close-packed oxygen planes. So oxidation of magnetite(100) surfaces leads to hematite inclusions inclined from the surface plane. The growth of magnetite that occurs concurrent to hematite formation occurs faster near the hematite, leading to magnetite ridges along (110) directions. This enhanced growth rate results from the flux of Fe atoms from interior phase boundaries between magnetite and hematite to the surface, as illustrated in Figure 9. Partial oxidation of magnetite single crystals, either films or bulk crystals, leads to a biaxial array of hematite slabs within an electrically conducting matrix of magnetite.

AUTHOR INFORMATION

Corresponding Author
E-mail: mccarty@sandia.gov. Telephone: (925) 443-0223.

Present Address
E.S.: KLA-Tencor, Milpitas, CA 95035.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Our research was supported by the Divisions of Materials and Engineering Sciences (under Contract DE-AC04-94AL8500 for SNL) and Chemical Sciences, Geosciences, and Biosciences (under Contract DE-AC02-05CH11231 for LBNL) of the Office of Basic Energy Sciences, U.S. Department of Energy, and the Spanish Ministry of Science and Innovation through Project MAT2012-38045-C04-01. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract DE-AC02-05CH11231. H.B acknowledges support from the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences and Materials Sciences Division of the U.S. Department of Energy under Contract DE-AC02-05CH11231. We thank the group of Marta Castillejo at the Instituto Química-Física “Rocasolano”, Spain, for providing the magnetite film on SrTiO3:Nb sample and Prof. Gareth Parkinson for lending us a synthetic magnetite crystal.

REFERENCES


