The Fe$_3$O$_4$ origin of the “Biphase” reconstruction on α-Fe$_2$O$_3$(0 0 0 1)

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The so-called Biphase termination on α-Fe$_2$O$_3$ has been widely accepted to be a structure with a ~40 Å unit supercell composed of coexisting islands of Fe$_1$-O and α-Fe$_2$O$_3$. Based on thermodynamic arguments and experimental evidence, including transmission electron diffraction, imaging, magnetic and spectroscopic information, it is found that the previously proposed structure model is inaccurate. The actual Biphase structure is instead a layered structure related to the reduction of α-Fe$_2$O$_3$ to Fe$_3$O$_4$. A model for the Biphase termination is proposed which does not contain islands of Fe$_1$-O but instead consists of bulk α-Fe$_2$O$_3$ and a Fe$_3$O$_4$-derived overlayer. The proposed model is consistent with all current and previously reported experimental findings.

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1. Introduction

α-Fe$_2$O$_3$ and its surface structure are of great interest in fields such as catalysis, geochemistry, water purification, and magnetic recording media. Of all the dehydrated iron oxides, α-Fe$_2$O$_3$ is the most prevalent in soils and sediments, playing a role in many geochemical cycles [1,2]. α-Fe$_2$O$_3$ has been investigated as a catalyst for the removal/decomposition of soil and air pollutants, including 2-chlorophenol [3], aminophenol [4], and SO$_2$ [5,6].

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to scattering across an interface between Fe₂O₃ and its reduction products is the study by Kim et al. [22]. There it was found that the surface of a post-sputtered sample was non-stoichiometric, but upon annealing at low temperatures and high oxygen pressure the outer-most surface recovered to α-Fe₂O₃ while a sub-surface region remained as remnant Fe₃O₄. In effect, the outer α-Fe₂O₃ acted as a barrier for propagation of the oxidation front to the Fe₃O₄ remnant below. The authors proposed that the remnant Fe₃O₄ sub-surface phase could be regarded as a defect layer in the α-Fe₂O₃ crystal, and that full reoxidation of the crystal required segregation of the reduced defect layer to the outer-most surface. As soon as the sample was heated to 745 °C, a LEED pattern with hexagonally symmetric satellite spots was observed, which the authors interpreted to be the structure that exists once the defect phase (presumably related to Fe₂O₃) has segregated to the top surface.

Differing from the previous studies, Condon et al. [11] attributed the hexagonally symmetric satellite spots observed in their LEED pattern following annealing at 800 °C in 7.75 x 10⁻⁷ Torr O₂ to the coexistence of α-Fe₂O₃ and Fe₁₋ₓO phases on the surface of α-Fe₂O₃. This interpretation was based on the corrugation spacing observed by STM. Specifically, domains of 5 Å and 3 Å periodicity were attributed to α-Fe₂O₃ and Fe₁₋ₓO, respectively. These were arranged in a 40 ± 5 Å superlattice cell rotated 30° relative to the α-Fe₂O₃ 1 x 1. The authors coined the term “Biphase ordering” to describe that structure and proposed a model for its formation, suggesting that a close packed layer of oxygen with Fe₁₋ₓO coexisting island structure model by Condon et al., the Biphase termination has been discussed in more detail later, if the sample is in equilibrium with the gas phase oxygen under such conditions bulk Fe₃O₄ is the stable phase and a far more reducing atmosphere of 10⁻¹² to 10⁻¹⁰ Torr of oxygen is needed to produce FeO in the bulk, see Fig. 1. (Details of how the phase diagram was calculated are given later.) Second, in several of the cases the structure was observed on oxidation of Fe₂O₃.

As in most oxides, oxygen is preferentially sputtered from α-Fe₂O₃ when Ar⁺ ion-milled, and the ion milling-induced reduction of pure α-Fe₂O₃ is well-known [23–25]. Upon heat treatment, the presence of a reduced layer at the surface of α-Fe₂O₃ could act as a nucleation site for the growth of Fe₃O₄ at the surface, and further, serve to lower the activation barrier for the propagation of Fe₃O₄ domains into the bulk of the material. The reducing effects of ion milling are enhanced by the presence of contaminants in the α-Fe₂O₃ crystal. Not only does the surface preferentially lose oxygen, a spinel phase can form on the near-surface region of impure α-Fe₂O₃ after Ar⁺ ion bombardment [26] with no heat treatment required. In fact, impurity levels as low as 0.2 at.% have been shown to stabilize the formation of the spinel phase. This impurity level is just at the 0.1–0.5 at.% detection limit of Auger electron spectroscopy (AES), which is commonly used in conjunction with LEED. Because the spinel structure is not exactly coincident with the underlying Fe₂O₃ one easily obtains a “floreted” diffraction pattern by simple double-diffraction. Unlike contamination-induced spinel phases which arise from lower concentrations of impurities, this particular spinel phase – and thus the floreted diffraction pattern – persisted even after annealing.

In nearly two-thirds of the reported cases, the Biphase termination is observed on contaminant-containing samples, either natural minerals [9,11,15,19,22,27] or doped CVT crystals [10] that have been Ar⁺ sputtered prior to annealing. As nearly all mineralogical samples contain impurities (in the case of the doped CVT

### Table 1

Summary of previous reports and details of the Biphase termination on α-Fe₂O₃.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Temperature (°C)</th>
<th>Pressure (Torr)</th>
<th>Time (min)</th>
<th>Sample type</th>
<th>Method</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO/Fe₂O₃</td>
<td>677</td>
<td>1.0 x 10⁻⁶</td>
<td>N/A</td>
<td>FeO₄</td>
<td>SM</td>
<td>Berdunov et al. [50]</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>Oxidized FeO₄</td>
<td>LEED</td>
<td>Huang et al. [29]</td>
</tr>
<tr>
<td>Biphase</td>
<td>550</td>
<td>7.5 x 10⁻⁶</td>
<td>120</td>
<td>Thin film on Pt (1 1 1)</td>
<td>LEED</td>
<td>Leist et al. [21]</td>
</tr>
<tr>
<td>Biphase</td>
<td>612</td>
<td>UHV</td>
<td>30</td>
<td>Mineralogical</td>
<td>LEED</td>
<td>Herman et al. [15]</td>
</tr>
<tr>
<td>Biphase</td>
<td>627</td>
<td>7.5 x 10⁻⁷</td>
<td>N/A</td>
<td>Thin film on Pt (1 1 1)</td>
<td>LEED</td>
<td>Huang et al. [29]</td>
</tr>
<tr>
<td>Biphase</td>
<td>773</td>
<td>3.75 x 10⁻⁷</td>
<td>30</td>
<td>Mineralogical</td>
<td>STM, LEED</td>
<td>Ketteler et al. [18]</td>
</tr>
<tr>
<td>Biphase</td>
<td>745</td>
<td>2 x 10⁻⁷</td>
<td>30</td>
<td>Mineralogical oxidized FeO₄</td>
<td>X-ray scattering, LEED</td>
<td>Kim et al. [22]</td>
</tr>
<tr>
<td>Biphase</td>
<td>800</td>
<td>7.5 x 10⁻⁷</td>
<td>N/A</td>
<td>Mineralogical</td>
<td>SM, LEED</td>
<td>Condon et al. [11]</td>
</tr>
<tr>
<td>Biphase</td>
<td>800</td>
<td>7.5 x 10⁻⁷</td>
<td>N/A</td>
<td>Thin film on Pt (1 1 1)</td>
<td>LEED, SM, LEED, Shaikhutdinov and Weiss [17]</td>
<td></td>
</tr>
<tr>
<td>Biphase</td>
<td>900</td>
<td>1 x 10⁻⁶</td>
<td>30</td>
<td>Mineralogical</td>
<td>LEED, XPS</td>
<td>Lad and Henrich [9]</td>
</tr>
<tr>
<td>Biphase and FeO₃</td>
<td>900</td>
<td>1 x 10⁻⁶</td>
<td>N/A</td>
<td>Mineralogical</td>
<td>SM, LEED</td>
<td>Lad and Henrich [9]</td>
</tr>
<tr>
<td>Biphase and FeO₃</td>
<td>927</td>
<td>1 x 10⁻⁶</td>
<td>5</td>
<td>CTV, germanium-doped, FeO₃ overlayer</td>
<td>XPS, Barbiere et al. [10]</td>
<td></td>
</tr>
<tr>
<td>Biphase and FeO₃</td>
<td>927</td>
<td>UHV</td>
<td>N/A</td>
<td>Mineralogical</td>
<td>LEED, XPS</td>
<td>Barbiere et al. [10]</td>
</tr>
<tr>
<td>Biphase</td>
<td>957</td>
<td>5 x 10⁻⁵</td>
<td>2</td>
<td>Mineralogical</td>
<td>LEED</td>
<td>Camillone et al. [19]</td>
</tr>
<tr>
<td>Biphase</td>
<td>957</td>
<td>UHV</td>
<td>15</td>
<td>Mineralogical</td>
<td>LEED</td>
<td>Camillone et al. [19]</td>
</tr>
</tbody>
</table>
crystal, Ce was intentionally present at levels up to 0.02 at.%, and ion milling was always employed to prepare the Biphase samples, one must keep in mind the implications of the impurity-stabilized near-surface spinel phase on the interpretation of the Biphase surface.

For the remaining studies listed in Table 1, the iron oxide specimens were grown as thin films on Pt(1 1 1) with thicknesses reported to be several ML (monolayers) up to 50 nm [17,21,28,29] and the films were not sputtered prior to annealing. In these studies the Pt substrate was assumed to have no role in the structural dynamics of the iron oxide film. However, the effects of the Pt substrate cannot be ignored based on work by Nahm et al. [30] Liu et al. [31] and Dieckmann [32,33]. Nahm et al. observed the formation of ferrimagnetic phase near the surface which does not form with the very pure single crystals, the later serve as an important check against impurity dependent artifacts. No difference was observed in the behavior of the two types of samples, as an important check against impurity dependent artifacts. No difference was observed in the behavior of the two types of samples, as an important check against impurity dependent artifacts. No difference was observed in the behavior of the two types of samples.

Transmission electron microscopy specimens were made from the iron–oxygen system calculated from Ref. [46]. Marked on the phase diagram are the conditions previously reported for the formation of the Biphase structure on $\alpha$-Fe$_2$O$_3$.

Fig. 1. Phase diagram for the iron–oxygen system calculated from Ref. [46]. Marked on the phase diagram are the conditions previously reported for the formation of the Biphase structure on $\alpha$-Fe$_2$O$_3$.

The samples were milled with 3.8–5 keV Ar$^+$ ions for approximately 2–5 h until electron transparent.

Owing to the possibility of the near-surface spinel phase [26], samples were subjected to a pre-treatment anneal in flowing O$_2$ for 0.5–2 h at 850 °C to remove the spinel phase (if present), repair damage imparted to the specimen upon preparation, and obtain a 1 × 1 surface reconstruction of $\alpha$-Fe$_2$O$_3$. These samples were transferred to a UHV-electron microscope (base pressure 1 × 10$^{-10}$ Torr) with an attached UHV side chamber (SPEAR). Mimicking the traditional surface science preparation regimes, the samples were cyclically milled with 1 keV Ar$^+$ ions at ~60° from the surface normal for approximately 5 min on each side, then annealed with a low-voltage electron gun in pressures ranging from UHV to 1 × 10$^{-6}$ Torr O$_2$; the temperatures of the samples measured with an optical pyrometer. X-ray photoelectron spectroscopy (XPS) spectra were acquired before and after each Ar$^+$ milling or annealing treatment and were used to check for the presence of carbon and qualitatively monitor the oxidation state of the iron.

Transmission electron microscopy was performed in the attached Hitachi UHV-H9000 operated at 300 keV; information on using transmission electron microscopy to study surfaces has been given elsewhere [35–40]. An in situ test for the presence of magnetism in the single crystal TEM specimens, as a way to empirically identify possible phases, was developed based on the attraction of unfixed specimens to the strong magnetic field of the objective lens of the microscope. In most modern conventional TEMs, the objective lens is an electromagnetic immersion lens split into an upper and lower pole. In normal operation, the specimen sits in the gap between the two poles, rigidly fixed inside of a stage or holder. Due to the unique design parameters and sample loading procedures of the UHV microscope, the objective lens pole gap can be viewed easily through a UHV compatible window in the side of the microscope and specimens can be brought near to the pole pieces while not rigidly affixed to the specimen stage. By slowly and carefully moving an unconstrained TEM sample near to the lens gap (with the lens current on), a movement or attraction of the sample to the lens, if observed, indicates the presence of a ferrimagnetic or ferromagnetic phase in the specimen. Since the specimens were all subject to a reducing anneal, the possibility that the apparent magnetism results from the presence of ferrimagnetic $\gamma$-Fe$_2$O$_3$ (where all the iron is fully oxidized in the 3+ state) can be ruled out. The presence of a nonequilibrium amorphous ferrimagnetic phase can be ruled out given the fact that diffraction spots corresponding to a known crystal structure were always observed. Ferromagnetic iron can be ruled out because iron was never observed to be present in the 0+ oxidation state as verified by XPS. $\alpha$-Fe$_2$O$_3$ is antiferromagnetic and was never observed to be attracted to the magnetic pole piece. Similarly, FeO is antiferromagnetic and not expected to interact with the magnetic field.

Therefore, an attraction to the magnetic field of the pole piece in the electron microscope is indicative of the presence of ferrimagnetic Fe$_2$O$_3$ or a related crystalline phase in the TEM specimen.

2. Experimental method

Two different types of raw-material specimens were used in this work. The first were mineralogical samples obtained from naturally-occurring high-purity “iron rosette” crystals (Brazil), and the second were pure single crystals grown in an optical image furnace [34]. Because upon ion milling impure crystals (e.g. mineralogical in origin) can form a spinel phase near the surface which does not form with the very pure single crystals, the later serve as an important check against impurity dependent artifacts. No difference was observed in the behavior of the two types of samples, so this can be ruled out.

Transmission electron microscopy specimens were made from oriented single crystals cut into 3 mm disks using a rotary disc cutter, thinned by hand to ~100 μm using fine grit silicon carbide sandpaper, and dimpled such that the center part of the disk was >15 μm and the outer rim of the sample remained at ~100 μm.

3. Results

We initially attempted to reproduce the Biphase surface by copying the conditions reported in the literature with sputter-cleaning/annealing cycles. In nearly 30 experiments, the characteristic floreted diffraction pattern was never observed although the specimens were often observed to be attracted to the magnetic field of the pole piece, indicating ferrimagnetism. For reference, further background details as well as diffraction data not included here can be found in the PhD theses of Chiaramonti [41] and Lanier [42]. More useful was a systematic search, performed by annealing in different pressures of O$_2$, the results of which are summarized in Table 2.
At low temperatures (650 °C), Fe$_3$O$_4$ was present on the surface of $\alpha$-Fe$_2$O$_3$ owing to insufficient diffusion (for this time and temperature) to drive the recovery of the surface from the ion-milled or reduced state. At higher temperatures (700–800 °C), the 1 × 1 surface of $\alpha$-Fe$_2$O$_3$ was formed. TEM images showed that the surface was starting to facet and diffraction patterns showed streaking, which indicates that the surface was evolving towards a flat, equilibrium structure.

A sample annealed for 20 min in 1.1 × 10$^{-7}$ Torr O$_2$ at 810 °C did form a “floreted” diffraction pattern (shown in Fig. 2), the nominal fingerprint of the Biphase, however these conditions were not exactly the same as those reported in the literature.

At 850 °C, the sample transformed (in part or entirely) to Fe$_3$O$_4$ or another ferrimagnetic cubic spinel phase, as evidenced by an extremely strong attraction of the sample to the magnetic pole piece of the TEM.

Focusing on Fig. 2, the intensity of the floret was not uniform as there were two bright spots per floret shown with arrows. Note that the distance between the paired bright spots increases with increasing distance from the center of the pattern. In LEED diffraction is dynamical and it can be tricky to differentiate between spots present due to double-diffraction and those due to a superstructure. With TEM this is far easier, because a near kinematical diffraction condition can easily be reached by simply tilting the specimen away from the zone axis. Fig. 2 is a textbook example of double-diffraction from two epitaxial crystals [43], here hexon-hex epitaxy. Diffraction from the crystalline overlayer (the inner spots in Fig. 2) indicates that the structure is simple, as it has a simple hexagonal pattern with weak intensity modulations.

A brief explanation is appropriate to emphasize the difference between what LEED, STM and TED show in problems like this. As is well-known, LEED involves scattering primarily from the atomic core potential, but is strongly dynamical so one can rarely say whether satellite spots (e.g. the floret spots) are reciprocal lattice vectors with appreciable structure-factors, or very weak structure factor reflections appearing due to dynamical diffraction. As is also well-known, STM only shows the joint density-of-states, not the atomic sites; sometimes they are similar, but often they are not. Done correctly with an off-zone tilt, TED from a surface is >95% kinematical so we can unconditionally state that the floret spots are due to dynamical diffraction. Omitting these spots, all one has is a simple hexagonal surface structure which can be inverted to the potential almost by hand (e.g. [44]), although this would not add more information so is not included here. The “Biphase” structure with domains of 5 Å and 3 Å periodicity due to both $\alpha$-Fe$_2$O$_3$ and Fe$_{1+x}$O would have a much more complicated diffraction pattern and can be unconditionally ruled out.

X-ray photoelectron spectroscopy was performed on this $\alpha$-Fe$_2$O$_3$ sample before and after the formation of the floreted diffraction pattern and the results are shown in Fig. 3. Prior to annealing the Fe$^{3+}$ satellite peak (marked with a dashed line) is observed before the anneal, but is lower in intensity after the anneal, indicating reduction to Fe$^{2+}$.

![Fig. 2. Off-zone transmission electron diffraction pattern from a $\alpha$-Fe$_2$O$_3$ TEM sample annealed in 1.1 × 10$^{-7}$ Torr O$_2$ at 810 °C for 20 min exhibiting a floreted pattern. Strong diffraction indicating hex-on-hex epitaxy is observed (arrowed). Relatively weak spots at the locations of the 1 × 1 surface lattice are present, one of which is marked; these should rigorously be interpreted as higher-order Laue zone reflections.](image)

### Table 2

Results for a systematic search for the Biphase surface: temperature, pressure, and observed bulk phase.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (Torr O$_2$)</th>
<th>Time (min)</th>
<th>Observed phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>5 × 10$^{-7}$</td>
<td>20</td>
<td>Fe$_3$O$_4$</td>
</tr>
<tr>
<td>700</td>
<td>5 × 10$^{-7}$</td>
<td>20</td>
<td>$\alpha$-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>750</td>
<td>5 × 10$^{-7}$</td>
<td>20</td>
<td>$\alpha$-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>800</td>
<td>1 × 10$^{-8}$</td>
<td>20</td>
<td>$\alpha$-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>810</td>
<td>1.1 × 10$^{-7}$</td>
<td>20</td>
<td>Biphase</td>
</tr>
<tr>
<td>850</td>
<td>1 × 10$^{-6}$</td>
<td>15</td>
<td>Fe$_3$O$_4$</td>
</tr>
</tbody>
</table>

Possibly a phase mixture of Fe$_3$O$_4$ and $\alpha$-Fe$_2$O$_3$.

### Fig. 3.

X-ray photoelectron spectra of the surface of $\alpha$-Fe$_2$O$_3$ before and after the annealing. The Fe$^{3+}$ satellite peak (marked with dashed line) is observed before the anneal, but is lower in intensity after the anneal, indicating reduction to Fe$^{2+}$.

4. **Model for the Biphase**

In this section a model is proposed for the Biphase structure based upon both consideration of the bulk thermodynamics as well as the diffraction, XPS and the magnetization tests described above.

The Fe–O bulk phase diagram, shown in Figs. 1 and 4, was calculated from thermodynamic free energy data [46], and is similar to those presented by Muñoz [47], Miser et al. [48], and Ketteler et al. [18]. The pressure is plotted as log(pO$_2$) (Torr) and temperature in degrees Celsius, such that the lower right corner of the diagram is nominally oxidized relative to the upper left corner. In general, increasing temperature or decreasing pressure results in
a relatively more reducing environment. Thus, moving from the lower right to the upper left, $\alpha$-Fe$_2$O$_3$ (iron as Fe$^{3+}$) reduces to Fe$_3$O$_4$ (iron as Fe$^{2+}$), then reduces to Fe$_{1-x}$O (iron as Fe$^{2+}$), and finally Fe metal (iron as Fe$^0$) is formed.

Superimposed upon Fig. 1 are the conditions where the Biphase surface structure has been reported herein. From this plot it is apparent that the surface structure occurs under conditions where in the bulk $\alpha$-Fe$_2$O$_3$ is being reduced to Fe$_3$O$_4$; this is consistent with the current XPS and magnetism results.

A simple model (Fig. 5) to explain the above results is a slab of Fe$_3$O$_4$ less than one unit cell thick on the oxygen termination of $\alpha$-Fe$_2$O$_3$. The surface unit cell of the Fe$_3$O$_4$ slab is 6.238 Å, the surface unit cell of $\alpha$-Fe$_2$O$_3$ is 5.038 Å (size of the (1$\times$1) unit cell), and the cells are rotated $30^\circ$ in order to preserve the alignment of the similar oxygen sublattices; preservation of oxygen sublattices is a well-known phenomenon in bulk oxides. Placing the Fe$_3$O$_4$ slab on $\alpha$-Fe$_2$O$_3$ produces a supercell with $a = 43.6$ Å, rotated $30^\circ$ from the $\alpha$-Fe$_2$O$_3$ (1$\times$1).

Separate domains of structure within the unit cell can be seen in Fig. 5, consistent with previous STM reports of island-like contrast within a 40 ± 5 Å superlattice cell rotated $30^\circ$ relative to the $\alpha$-Fe$_2$O$_3$ (1$\times$1). Three domains have been marked I, II, and III in Fig. 5. The iron atoms in the surface layer (indicated with an arrow at the top of Fig. 5) are approximately distorted octahedra in domain I, tetrahedra in domain II, and non-standard six-coordinate in domain III. Recall that both $\alpha$-Fe$_2$O$_3$ and Fe$_{1-x}$O bulk contain only octahedrally coordinated iron cations, and only bulk Fe$_3$O$_4$ (and $\gamma$-Fe$_2$O$_3$) contain tetrahedrally coordinated iron cations. To maintain charge neutrality, the iron atoms in the surface layer are nominally Fe$^{2+}$. This is consistent with the experimental XPS measurement of the Biphase surface.

A simulated kinematical diffraction pattern for this model is shown in Fig. 6 and strongly resembles the experimentally observed pattern. Note that the florets in the experimental pattern are a result of dynamical scattering and thus are not observed in the kinematical simulation since it only takes into account single scattering events.

5. Discussion

A combination of experimental data with an analysis of the thermodynamic conditions where the Biphase forms as well as a simple model which explains the results has been presented here. The results are consistent with all the published experimental data, and points to the original interpretations of the floreted (LEED) diffraction pattern as resulting from simple double-diffraction as being correct. Perhaps most importantly, the current results are completely consistent with the bulk thermodynamics, which it will be argued they have to be since a surface is always exchanging material with the underlying bulk, albeit slowly. The reduction of $\alpha$-Fe$_2$O$_3$ to Fe$_3$O$_4$ in the bulk is a topotactic and crystallographically reversible transformation [49]. Upon nucleation of the Fe$_3$O$_4$ slab on the surface of $\alpha$-Fe$_2$O$_3$, growth of the domain can readily occur.

Fig. 4. Phase diagram for the iron–oxygen system calculated from Ref. [46]. Marked on the phase diagram are the conditions where Fe$_3$O$_4$ was observed (blue squares), Fe$_2$O$_3$ (yellow circles) and the Biphase diffraction pattern (red triangle). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. Model for the Biphase structure. Top: side view. Bottom: plan view showing four of the Biphase unit cells with a 43.6 Å cell marked.

Fig. 6. Simulated kinematical diffraction pattern from the Biphase model, showing both the strong spots (from the bulk) as well as weaker ones (from the surface); this should be compared to Fig. 2. The increasing of distance between the spots here and in Fig. 2 is a characteristic of a simple hex-on-hex configuration, with double-diffraction leading to a fully floreted pattern.
into the bulk. That is why domains of Fe₃O₄ are observed to coexist with the so-called Biphase termination and why prolonged annealing in the formation regime lead to a full transformation to Fe₃O₄. According to the model presented here, the only difference between the Biphase and Fe₃O₄ is the thickness of the surface slab (bulk Fe₃O₄ has infinite slab thickness).

The proposed structure herein likely represents a simplified version of the true structure of the so-called Biphase surface. With higher quality diffraction data it is plausible to produce a more accurate model, however the magnetic properties of the sample make this something which cannot be done to the required accuracy using TEM; a better choice might be to use surface X-ray scattering. 

6. Summary

The so-called Biphase termination on α-Fe₂O₃ was previously believed to be islands of Fe₃O₄ and α-Fe₂O₃ arranged in a ~40 Å periodic unit cell based upon a simple interpretation of STM images. This is an inadequate model, and is contradicted by electron diffraction, XPS, and magnetism as well as being in disagreement with the expected bulk thermodynamics. Instead, it is found that the Biphase structure is related to a thin Fe₃O₄-type layer at or near the α-Fe₂O₃ surface, and is a simple hex-on-hex overlayer with double-diffraction leading to the characteristic floreted diffraction pattern that has previously been used as the fingerprint to identify this structure.

Acknowledgments

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References