HREM of metallized {111} iron oxide nanoparticle surfaces.

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Abstract. Mixed phase Fe\textsubscript{3}O\textsubscript{4} - \(\gamma\)-Fe\textsubscript{2}O\textsubscript{3} (magnetite–maghemite) nanoparticles have been fabricated by colloidal routes. HR(S)TEM images, taken on both aberration corrected and uncorrected (S)TEMs, and indirect reconstruction of images of the nanoparticles show the presence of \{111\} facets that terminate with enhanced contrast. This extra contrast is shown to be real and is due to additional octahedral cations occupying the \{111\} surfaces.

1. Introduction.
Iron oxide nanoparticles play a key role in numerous applications in industry including catalysis, high density data storage and also in medicine, for which the nanoparticles are required to have well characterised structures and properties. The high surface area to volume ratio in nanoparticles can lead to modified surface structures and properties, so there is a great interest in the study of the surfaces of iron oxide nanoparticles, and it becomes crucial to characterise these effects.

Fe\textsubscript{3}O\textsubscript{4} (magnetite) is an inverse spinel and consists of an fcc close packed lattice of oxygen anions. This lattice provides tetragonal (A) and octahedral (B) interstitial cation sites, but only a quarter of the available sites are filled: in a unit cell 8 Fe\textsuperscript{2+} cations sit in the B sites, whilst 16 Fe\textsuperscript{3+} cations are equally distributed between the A and B sites. The \{111\} planes of magnetite consist of layers of anions or cations, but are never mixed. When the model \{111\} surface terminates in octahedral cations as shown in Figure 1, the terminating plane is composed of alternating columns of half occupied and fully occupied octahedral sites.

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\(\gamma\)-Fe\(_2\)O\(_3\) is a defect spinel structure similar to Fe\(_3\)O\(_4\) but with a larger number of cation vacancies, where the number of vacancies depends on the degree of non-stoichiometry. The extra vacancies in the \(\gamma\)-Fe\(_2\)O\(_3\) structure are thought to be found in octahedral positions. It has been suggested that part of the mechanism of \(\gamma\)-Fe\(_2\)O\(_3\) formation from Fe\(_3\)O\(_4\) involves the diffusion of Fe\(^{2+}\) ions from within the particle to the surface, where they oxidise to Fe\(^{3+}\) and leave behind a lattice vacancy [1].

The advent of aberration corrected (Scanning) transmission electron microscopy ((S)TEM) has led to substantial improvements in image resolution, providing additional detail of surface structures in nanomaterials. Conventional HRTEM records the available image intensity which contains information about the phase relationships as it leaves the specimen but this is severely affected by the aberrations present in the objective lens, particularly C\(_S\), and the partial coherence of the electron source. Correctors allow some of the major lens aberrations to be adjusted and hence, the resolution of the image to be improved. An improvement in resolution can also be achieved using reconstruction techniques [2], where it is possible to recover the complex specimen exit wavefunction by indirect reconstruction of a series of images recorded with either differing defocii or beam tilts, and is particularly effective when aberration corrected images are used, as higher order aberrations can then be compensated for, providing a further increase in interpretable resolution.

2. Method

Samples of iron oxide nanoparticles were fabricated using a standard wet chemical route [3], and characterised with electron diffraction techniques and (S)TEM. Particle size data was obtained from bright field TEM images on samples of 200 nanoparticles per specimen. Individual nanoparticles were indexed using Gatan Digimicrograph software. Initial characterisation of the nanoparticles occurred at Leeds, but several microscopes were used during this project: a thermally assisted field emission gun (FEG) FEI CM200 TEM operated at 197 kV with a point resolution of \(\approx\)2.5Å (University of Leeds), a thermionic electron gun with LaB\(_6\) source JEOL 3100 operated at 300kV with an point resolution of 1.7 Å (Cambridge University), a double aberration corrected thermally assisted FEG JEOL JEM-2200FS TEM operated at 200kV and a point resolution of 1.1Å (University of Oxford), a dedicated cold FEG STEM VG-HB501 equipped with a Nion-MarkII-C\(_S\)-corrector operated at 100kV, with a beam diameter of 1Å (SuperSTEM). An exit wave reconstruction technique [2] was used on several focal series of nanoparticles taken on both the Leeds CM200 and the Oxford JEOL JEM-2200FS.

3. Results

![Figure 2](image)

**Figure 2.** Bright field HRTEM images of nanoparticles, taken near the Scherzer defocus, with resolved atomic column edges showing enhanced contrast on the nanoparticle’s \(\{111\}\) surface, as indicated by white arrows. Images taken on a) a FEI CM200 FEGTEM. b) a JEOL 3100 TEM and c) a double aberration corrected JEOL JEM-2200FS FEGTEM.

Initial images were taken using the FEI CM200 FEGTEM. The nanoparticles are single crystalline in nature, and are a mixture of spherical and faceted particles. The average projected particle diameter for all the samples is \(\approx\)8nm, and a near normal distribution is observed. Electron diffraction techniques show the samples to consist of a mixture of Fe\(_3\)O\(_4\) and \(\gamma\)-Fe\(_2\)O\(_3\) phases, although it is unclear from this technique whether this phase mixing occurs on the inter or intra nanocrystal level.
HRTEM images, show that the faceted edges of several particles exhibit atomic column enhanced contrast at their projected surfaces (figure 2). This contrast is present at both Gaussian and Scherzer defocus and does not contrast invert at different negative defocii. HRTEM images were also taken using the JEOL 3100 TEM, and the same enhanced contrast of the atomic columns at the faceted surfaces of nanoparticles is observed. Indexing these high resolution images of individual nanoparticles reveals that the enhanced contrast is only seen to occur on projected surfaces that terminate with \{111\} planes. Particles from the same uncoated batch were also observed in the double aberration corrected JEOL JEM-2200FS FEGTEM. Again, a similar enhanced contrast effect is observed and found to only occur on faceted projected surfaces identified to terminate in \{111\} planes. The fact that this effect can be observed at specific surface facets, even in a microscope corrected for third order spherical aberrations [4], eliminates the probability that the enhanced contrast is induced by such lens aberrations, and suggests that this is a real effect caused by excess cations in columns at the edges of the nanoparticles.

An exit wave reconstruction of several focal series (taken both on the FEI CM200, and on the JEOL-JEM 2200FS) was undertaken [2]. Figure 3 shows an overfocus image from a focal series taken on the JEOL-JEM 2200FS, and the resulting reconstructed phase and modulus of an iron oxide nanoparticle. A clear increase in resolution is apparent in the phase when comparing the focal series image to the phase, and it can now be seen that the \{111\} planes are terminating with octahedrally coordinated cations. The cations at the nanoparticle’s projected surfaces appear white in the phase and in the overfocus focal series image, but dark in the modulus, and all three show clear enhanced contrast on all the octahedral cation columns at the particle’s \{111\} edges. As anions do not significantly contribute to the modulus, the extra contrast can be said to be solely due to cations. In the reconstructed phase, the nanoparticle displays a disordered structure for one to two planes back from the modified edge, before a model ordered structure is visible again (Figure 3a).

![Figure 3](image-url)

**Figure 3.** a) phase and b) modulus exit wave reconstructed maps. c) shows an overfocus bright field HRTEM image of a nanoparticle from the corresponding focal series taken on the double aberration corrected JEOL JEM-2200FS FEGTEM. Cations appear white in a) and c) and dark in b). Enhanced contrast is visible along the surface atomic columns, and a disordered sub surface structure is marked by a black arrow in a).

The same uncoated batch of nanoparticles was also imaged using a dedicated STEM equipped with a Nion-MarkII-C5-corrector at the SuperSTEM facility. HAADF images are highly dependent upon the thickness of the specimen and the atomic number of the atoms within it (so called Z contrast). Figure 4 shows HAADF images taken of the uncoated nanoparticles viewed at or very near to the \(<110>\) direction. The atomic columns seen are consistent with the expected cation lattice, although there is little contrast difference between the various off atomic column positions. This lack of contrast variation could be because the nanoparticles are being viewed slightly off the zone axis, or be due to a reduction in cation order within the nanoparticle.

Integrated line profiles of the image contrast taken along the \{111\} edge of the particle show equal intensity on every atomic column (Figure 4). This suggests that every column along this edge has a similar cation occupation. Line profiles from further within the structure show a lower intensity on alternate columns, suggesting lower cation occupancy. According to the bulk model of Fe$_3$O$_4$ there should only be
50% Fe occupancy of the alternate columns, and 100% occupancy on the other columns of the octahedrally coordinated cation {111} layer. Clearly this indicates near full occupation of Fe on all of the available cation sites at the nanoparticle’s {111} surface, compared to only 75% inside similar octahedral planes inside the ‘bulk’ of the nanoparticle, as would be expected from standard Fe₃O₄ models.

Figure 4. HAADF micrographs taken on the aberration corrected STEM of an iron oxide nanoparticle shown with line intensities taken along {111} planes. Alternate cation sites displaying additional intensity (marked with arrows) are found on the terminating planes, and here the cations appear white.

4. Discussion and Conclusion
Previous image reconstruction techniques require all the octahedral sites at the {111} surface of a Fe₃O₄ nanoparticle to be filled with cations to create contrast effects comparable to experimental images [5]. The alternating columns along the {111} plane of fully occupied octahedral sites, with half occupied columns in between have vacancies in the half occupied columns available for extra cations. Direct evidence of the filling of the available cation vacancies at the octahedral {111} surface has been given within this paper from two aberration corrected electron microscopes (Figures 3 and 4).

Fe₃O₄ nanoparticles tend to form into cube-octahedral morphologies: shapes with low surface area to volume ratios [5]. The exposed face at a particle’s surface is created by a balance between the free energy of individual surfaces, related to their packing, and the need to maintain chemical stoichiometry. It has been theorised that if a low index plane terminates at a nanocrystal surface, then the charge balance of the crystal as a whole is dependent upon whether the surface is terminated by anions or cations [5] because of the higher proportion of atoms at the surface of a nanoparticle. If the nanoparticle is terminated in a cation layer cation vacancies might have to be introduced below the terminating layer in order to maintain the overall stoichiometry of the particle, whilst retaining the anion sublattice. This would create a highly defective γ-Fe₂O₃-type structure below the surface, but γ-Fe₂O₃ forms from Fe₃O₄ by diffusion of cations from within the nanoparticle to the surface. As oxygen anions do not contribute greatly to the overall particle image contrast in current electron microscopy images, a non-stoichiometric cation lattice should be observable as a disordered lattice. Assuming that the enhanced contrast at the surfaces of nanoparticles within the micrographs is a result of additional cations from within the nanoparticle structure, a disordered layer should be apparent in the images just back from the edge. This defect structure is observed in micrographs taken by Jefferson [5], and is also visible in the reconstructed phase map seen in Figure 3a. The presence of excess cations at the nanoparticle’s surface is a modification of the structure from the bulk, and will have significant implications for any applications in industry. It has been proved likely that the enhanced atomic contrast effect seen on the {111} surface edges of several iron oxide nanoparticles is real, and not an artefact caused by lens aberrations, and that the excess contrast is most likely to be caused by excess octahedrally coordinated cations in the surface planes. Evidence was also found of a subsurface cation deficient structure.

References
[1] Stacey, F. and Banajee, S., The Physical Properties of Rock Magnetism, Elsevier, 1974.
[2] Kirkland, A.I. and Meyer, R.R., Microscopy and Microanalysis, 10, p401-413, 2004.
[3] Khalafalla, S.E. and Reimers, G.W., IEEE Trans on Magn, 16, 178-183, 1980.
[4] Hutchison J L et al., Ultramicroscopy, 103, 7-15 2005.
[5] Jefferson, D.A., Phil Trans Royal Soc Lond A, 358, 2683 – 2692, 2000.