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Correlative Transmission Electron Microscopy of Highly Perfect Fe_3O_4 Nanocubes

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Magnetite (Fe_3O_4) nanoparticles are attracting considerable interest for applications in ferrofluids, for magnetic separation, as contrast agents for magnetic resonance imaging and magnetic hyperthermia and for information storage technologies. Fe_3O_4 has a cubic inverse spinel structure, in which oxygen anions are arranged on a cubic close-packed lattice, while Fe cations are located in interstitial tetrahedral and octahedral sites. At low temperature, Fe_3O_4 undergoes the so-called Verwey transition to a monoclinic phase, together with a rapid change in conductivity that is associated with charge and orbital ordering of Fe^{3+} ions. The magnetic properties of Fe_3O_4 nanocrystals depend strongly on their composition, morphology, size, defects and arrangement. Here, we combine several transmission electron microscopy (TEM) techniques to characterize the atomic structures, compositions, three-dimensional shapes and magnetic properties of highly perfect cube-shaped Fe_3O_4 crystals. The regular crystal shapes allow the Verwey transition to be studied in the absence of strong shape anisotropy.

Fe_3O_4 nanocrystals were prepared using wet chemical methods [1] and drop-coated onto amorphous C films supported on Cu TEM grids. The sizes of the crystals were in the range 130-160 nm, as measured from bright-field (BF) TEM images (Fig. 1a). Atomic-resolution high-angle annular dark-field (HAADF) scanning TEM (STEM) images, energy dispersive X-ray spectra and electron energy-loss spectra were used to confirm the single crystalline stoichiometric Fe_3O_4 natures of the nanocrystals (Figs 1b, e, f). Spectroscopy and STEM analysis were carried out in a probe-aberration-corrected FEI Titan ChemiSTEM operated at 200 kV. The three-dimensional shape of an individual nanocrystal was reconstructed from a tilt series of HAADF STEM images recorded over +65° to -65°. The reconstructed volume reveals small triangular {111} facets at the edges of a cube of aspect ratio ~1 (Fig. 1c, d). The magnetic configurations of such crystals were measured using off-axis electron holography in an FEI Titan 60-300 TEM operated at 300 kV in magnetic-field-free conditions. The mean inner potential and magnetic contributions to the phase shift were separated for both chains and individual crystals (Figs 1g, h, i). In a chain configuration, magnetostatic coupling was found to align the magnetic fields of adjacent crystals along its main axis. However, at its ends the configuration was more complicated. Magnetic vortices were observed directly in individual crystals. No correlation was found between the directions of vortex cores and the <111> magnetic easy axes of the Fe_3O_4 crystals. Moreover, *in situ* cooling was used to study the Verwey transition in an individual Fe_3O_4 crystal (Fig. 2) in an FEI Tecnai TEM operated at 200 kV. Selected area electron diffraction patterns confirmed monoclinic phase formation below 120 K, although there was no crystalline twin formation (Fig. 2b, c). Preliminary off-axis electron holography results suggest that in Fe_3O_4 crystals the mean inner potential changes abruptly, while the magnetization changes gradually, at the Verwey transition. Further work is needed to confirm and to fully understand these observations [2].

References:

[1] D. Kim *et al*, J. Am. Chem. Soc. **131** (2009), p. 454.
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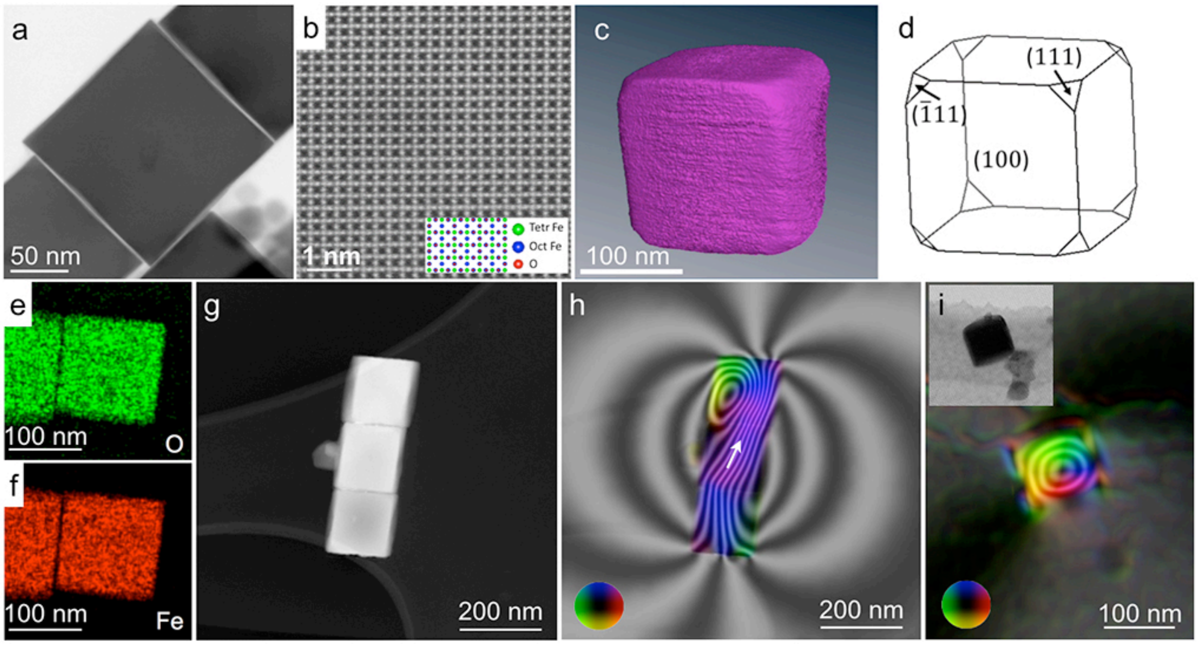

Figure 1. a) Bright-field STEM image of Fe_3O_4 nanocrystals. (b) Atomic-resolution HAADF STEM image showing Fe and O atomic columns in the cubic lattice of an Fe_3O_4 nanocrystal. (c) Reconstructed volume of a single nanocrystal obtained from an HAADF STEM tilt series. (d) Schematic diagram showing the morphology of an Fe_3O_4 nanocrystal based on the reconstruction shown in (c). (e, f) O and Fe EDXS STEM spectrum images. (g, h) Mean inner potential contribution to the phase and magnetic induction map, respectively, of a chain of Fe_3O_4 nanocrystals recorded using off-axis electron holography. The contour spacing in (h) is 0.875 rad. (i) Magnetic induction map of a single Fe_3O_4 nanocrystal showing a magnetic vortex state. The inset shows a BF TEM image of the crystal.

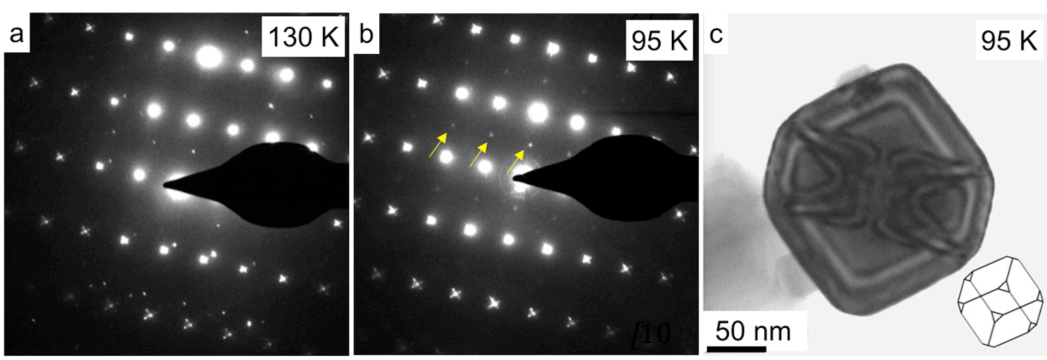

Figure 2. Verwey transition in an individual Fe_3O_4 nanocrystal. (a) SAED pattern of the cubic phase recorded at 130 K, viewed along the <112> direction. (b, c) SAED pattern and BF TEM image recorded at 95 K, viewed along the [101] direction. The extra reflections in (b) indicate monoclinic phase formation. The inset in (c) shows a schematic view of the crystal.

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