

Nonstoichiometric Twin Defects in Fe₃O₄(111) Thin Films: Atomic and Electronic Structure

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Twin defects, prevalent in face centred cubic stacked materials, are observed across a wide range of natural and synthetic specimens. Such defects are essential to the mechanical behaviour of materials e.g. shape memory alloys and mediate stress and strain in both functional and mechanical materials. Fe₃O₄ is a prototype material for spinel metal oxide structure systems, particularly the ferrite spinels. Recently magnetite has attracted a lot of attention due to its 100% spin polarisation at the Fermi level, hence large interest for spintronic applications. Antiphase domain boundaries are the most studied defects in magnetite and their correlation to magnetic properties is reported extensively [1,2]. However twin defects in magnetite has not been studied on atomic level, and in particular their effect on spin polarisation and overall magnetic properties is not known. In this we have observed twin defects in Fe₃O₄(111) thin films grown on Ytria stabilized ZrO₂, determined their atomic structure, and modelled their electronic properties by using Density Functional Theory (DFT).

The twin boundary is on (111) growth planes and it is formed by the breaking of symmetry of a Fe_A-Fe_B-Fe_A layer. Aberration-corrected STEM-HAADF imaging shows that the boundary is non-stoichiometric with a missing Fe_B plane. Electron energy loss spectroscopy shows changes in Fe and O core edges as well as depletion of the Fe at the boundary, which compliments the HAADF results (Fig.1). The DFT calculation of this non-stoichiometric boundary structure was modelled by introducing electron holes as a charge-compensation mechanism to realise the ionic nature of Fe₃O₄, Fig. 2. The electronic calculations show that majority band gap is significantly reduced with a presence of the interface states. Atomic bond counting from the DFT-optimised geometrical coordinates shows no presence of high-angle Fe-O-Fe bonds hence the absence of AFM superexchange interactions at this boundary in comparison to antiphase domain boundaries in ferrite spinels. The ferromagnetic (FM) coupling between the twin grains was also confirmed by the DFT calculation which found that AFM coupling is less energetically favourable compared to FM coupling. This work clearly shows that the (111) oriented non-stoichiometric boundaries are energetically stable and their effect is more subtle in comparison to the antiphase domain boundaries [3].

References:

[1] KP McKenna et al. Nature communications **5**, doi:10.1038/ncomms6740 (2014).

[2] D Gilks, et al. J. Phys. Cond. Matt. **25**(48):485004 (2013).

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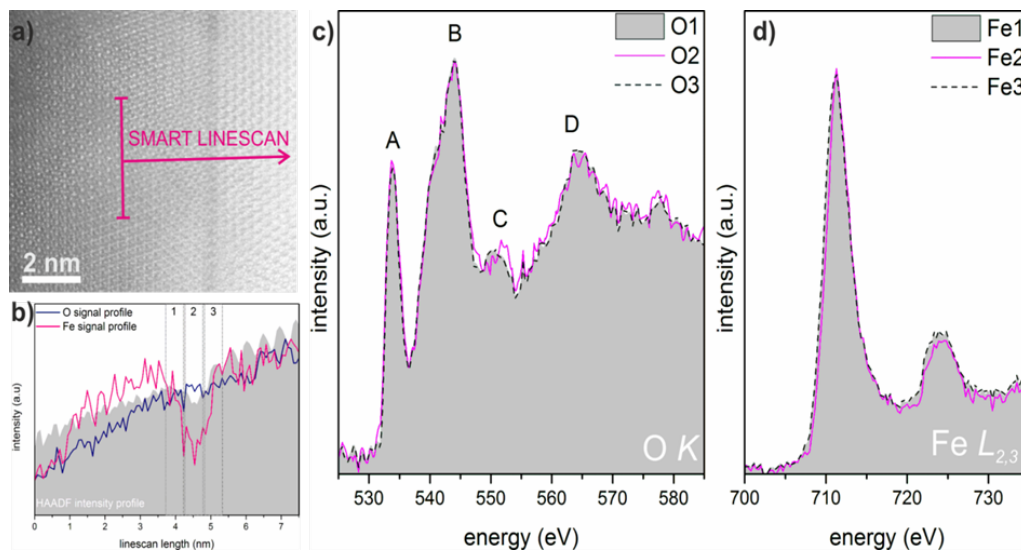


Figure 1. (a) HAADF STEM image and schematic of the SMART EELS scan [20] across the twin boundary: EEL spectra are acquired serially along the direction marked with the arrow while the beam is distributed along the perpendicular direction; (b) plots of the Fe $L_{2,3}$ (pink) and O K EELS (blue) signals along the linescan, plotted against the HAADF image intensity profile (grey). The drop in the Fe signal along with the small drop of the HAADF image intensity are indicative of Fe depletion at the twin boundary. (c) O K and (d) Fe $L_{2,3}$ spectra acquired at (pink) and adjacent to (grey/blue) the twin boundary (marked with dashed lines in panel (b)) The small shift of peak C in the O K edge to higher energies and a small increase of the I_{L_3}/I_{L_2} ratio at the interface corroborate a slight increase of the Fe oxidation state (also manifested by the drop of the Fe signal)

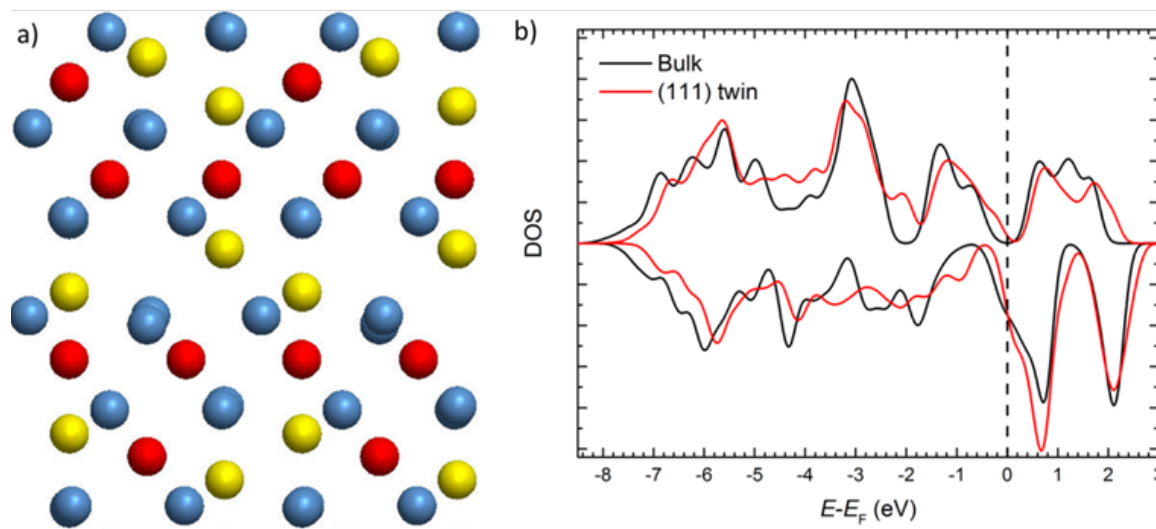


Figure 2. a) Structural model of the non-stoichiometric (111) twin defect stabilized with electron holes to maintain the ionic charge ordering on the interfacial Fe_A and Fe_B sites as expected in the bulk of Fe₃O₄. b) Spin-resolved density of states of the hole compensated (111) twin.