Transmission electron microscopy of magnetite at low temperature

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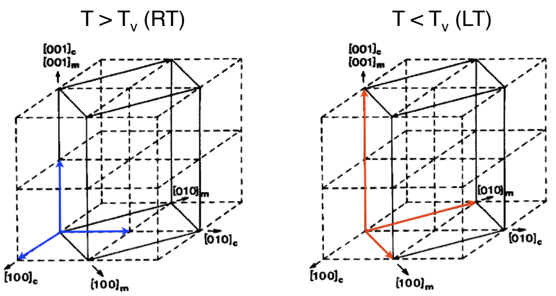
Introduction

The Verwey transition has an enormous impact on the magnetic properties of magnetite at low temperature. Below ~120 K, the magnetocrystalline anisotropy increases by an order of magnitude and the magnetic easy axis switches from the $\langle 111 \rangle_c$ directions of the cubic phase to the $[001]_m$ direction of the monoclinic phase. After cooling through the transition, the $[001]_m$ easy axis of the monoclinic phase can lie along any one of the three $\langle 100 \rangle_c$ directions of the parent cubic phase, resulting in the formation of transformation twins. Numerous studies have proposed that strong interactions exist between ferroelastic twin walls and ferrimagnetic domain walls in magnetite. Nevertheless, the nature of these interactions remains highly controversial. The determination of the crystal structure of the low temperature phase, including the Fe^{2+}/Fe^{3+} distribution, is also essential for understanding both twin formation and the magnetic properties of magnetite below the Verwey transition.

Here, we use off-axis electron holography in the transmission electron microscope (TEM) to study magnetic domain structures in synthetic multi-domain magnetite below the Verwey transition. Electron holography allows magnetic structures to be imaged quantitatively at the nanometer scale. We also use Lorentz TEM to make dynamical observations of the nucleation and motion of transformation twins and magnetic domain walls as the sample is cycled repeatedly through the phase transition. Electron diffraction is used to determine the crystal symmetry. Experimental electron diffraction patterns are compared with simulated patterns obtained using JEMS software. All TEM observations were performed at 300 kV.

Magnetite unit cells above and below the Verwey transition

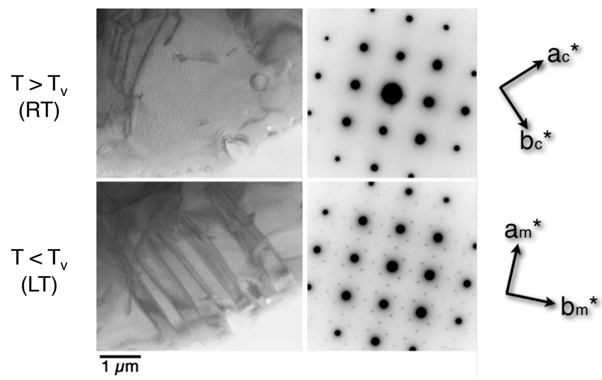


Above the Verwey transition (>130 K):
Inverse spinel structure with space group *Fd-3m.*
Magnetic easy axis parallel to cubic $\langle 111 \rangle_c$.

Below the Verwey transition (<120 K):
Rhombohedral distortion of the unit cell (monoclinic β=90.2˚).
The $[001]_m$ direction of the monoclinic structure is parallel to the cubic $[001]_c$ direction.
The monoclinic $[100]_m$ and $[010]_m$ directions are at 45° to the cubic $\langle 100 \rangle_c$ directions.

The magnetocrystalline anisotropy changes dramatically - below the transition:
Monoclinic $[100]_m$ (*a*-axis) = hard axis
Monoclinic $[010]_m$ (*b*-axis) = intermediate axis
Monoclinic $[001]_m$ (*c*-axis) = easy axis

Diffraction patterns above and below the Verwey transition

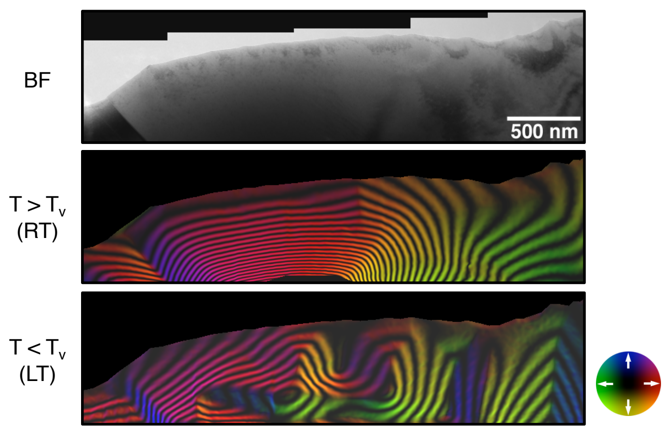


The figures show bright-field images and corresponding [001] diffraction patterns acquired both above and below the transition.

Above the transition, the diffraction pattern corresponds to that of the face-centered cubic structure.

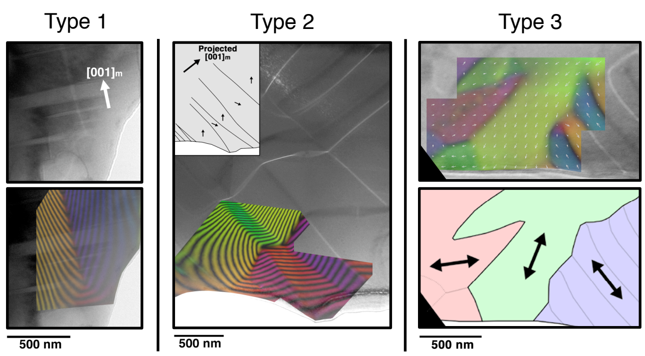
Below the transition, weak extra spots are observed between the strong fundamental reflections. These extra spots are associated with the transition to the monoclinic phase. The ferroelastic twins that are visible in the image are associated with *ab*-plane twinning along the *c*-axis. Diffraction patterns acquired from other orientations of the specimen suggest that the space group is likely to be monoclinic *Cc.*

Magnetic structures above and below the Verwey transition



Electron holography observations show that magnetic domains are large at room temperature and that the magnetic domain structure changes gradually across the specimen. In contrast, below the transition, magnetic domains are smaller and more complicated. The 180˚ and 90˚ magnetic domains that are observed at low temperature are likely to be associated with the strong uniaxial magnetocrystalline anisotropy of the specimen. End-domain closure states form at the specimen edge.

Typical magnetic structures below the Verwey transition



Type 1: 180˚ magnetic domain walls, which are mobile even where they intersect twin walls, although some are pinned at the tips of needle twins.

Type 2: Zig-zag magnetic domains, which are associated with *ab*-plane twinning along the *c*-axis. Slight deviations of the magnetic moments from the *c*-axis towards the intermediate *b*-axis are observed only in thinner regions of the specimen. The small arrows indicate the direction of the monoclinic *b*-axis in each twin domain.

Type 3: Magnetic domains at "strain-contrast-free" twins that are not readily visible in conventional TEM images. The arrows in the schematic diagram show the orientation of the monoclinic *c*-axis in each domain.

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