Multiscale measurements of magnetic properties and three-dimensional microstructures in magnetite

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Magnetite (Fe_3O_4) is one of the most important magnetic minerals in geological and biological systems (Dunlop and Özdemir, 1997). Magnetite nanoparticles are also of interest for technological and medical applications such as targeted drug delivery (Pankhurst et al., 2009). The Verwey transition in magnetite, which is a first order crystallographic phase transition, has been studied extensively since its discovery (Verwey, 1939) because of its impact on the magnetic and other physical properties of the material. The transition is associated with an order-of-magnitude increase in magnetocrystalline anisotropy and a change in magnetic easy axis from cubic <111> to monoclinic [001] below ~120 K. Although many studies have suggested that magnetic domain walls in magnetite can interact with the ferroelastic twin walls that form at low temperature (e.g., Smirnov and Tarduno, 2002), no direct evidence for such interactions has previously been presented. Here, we show how advanced electron microscopy techniques can be used to characterize magnetic properties in magnetite and three-dimensional microstructures in a magnetite/ilmenite intergrowth across a wide range of length and temperature scales.

Figure 1 shows experimental results obtained from an isolated 50-nm-diameter single crystal of magnetite using off-axis electron holography in the transmission electron microscope (TEM). The magnetic induction maps shown in Figs 1b and c, which were acquired at room temperature and at 90K (below the Verwey transition), respectively, show uniformly-magnetized single domain states, including a characteristic return flux resembling that of an isolated magnetic dipole. At room temperature, the phase contours in the crystal make an angle of ~20° to its [111] elongation direction (Fig. 1b), whereas they make an angle of ~15˚ to the [111] direction at 90 K (Fig. 1c). The in-plane magnetic induction $B_{\perp}$ measured for 90 K is 0.46(±0.09) T, suggesting that the remanent magnetization direction in the crystal is tilted out of the plane by ~40° to the horizontal. This direction corresponds approximately to $[100]_{cubic}$ or $[001]_{cubic}$, which was expected from the prediction that the $[001]_{monoclinic}$ easy axis can lie along any one of the original $<100>_{cubic}$ directions and that the effect of magnetocrystalline anisotropy on the magnetic state of the crystal is predominant in the monoclinic phase below the Verwey transition (Dunlop and Özdemir, 1997).

Figure 2 shows corresponding remanent magnetic states recorded at room temperature and below the Verwey transition from a synthetic magnetite specimen that has a grain size of 10-30 µm. At room temperature, the presence of a magnetic flux-closure domain close to the specimen edge results from minimization of the magnetostatic energy (Fig. 2b). The magnetic state of the specimen below the Verwey transition is significantly different from that observed at room temperature (Fig. 2c). Below the Verwey transition, the magnetic domains are more complicated and their sizes can be as small as several tens of nm. Magnetic domains that are far from the specimen edge have widths of 100-500 nm and are separated by 180˚ domain walls, which result from the strong uniaxial magnetocrystalline anisotropy of the monoclinic phase, as predicted in many previous studies (e.g., Dunlop and Özdemir, 1997) (Antiparallel magnetization directions are shown in purple and yellow on the right side of Fig. 2c). Micromagnetic simulations suggest that the positions of magnetic domain walls in magnetite can be are associated with ferroelastic twin walls, which may not themselves be visible in conventional TEM images such as that shown in Fig. 2a (Kasama et al., 2010).

In order to fully understand the magnetic properties of rocks, in which the constituent minerals have three-dimensional configurations, we have also used focused ion beam (FIB) milling in the scanning electron microscope to characterize the three-dimensional microstructure of a magnetite/ilmenite ($FeTiO_3$) intergrowth sample using electron backscatter diffraction (EBSD) to study the local crystallographic orientation. This study required optimization of the specimen geometry, milling procedure and imaging conditions, due to the effects of charging, damage and redeposition by the electron and ion beams. In particular, low voltage FIB milling was found to be necessary to obtain interpretable EBSD patterns. Ongoing work includes the use of the measured three-dimensional volume in micromagnetic simulations.

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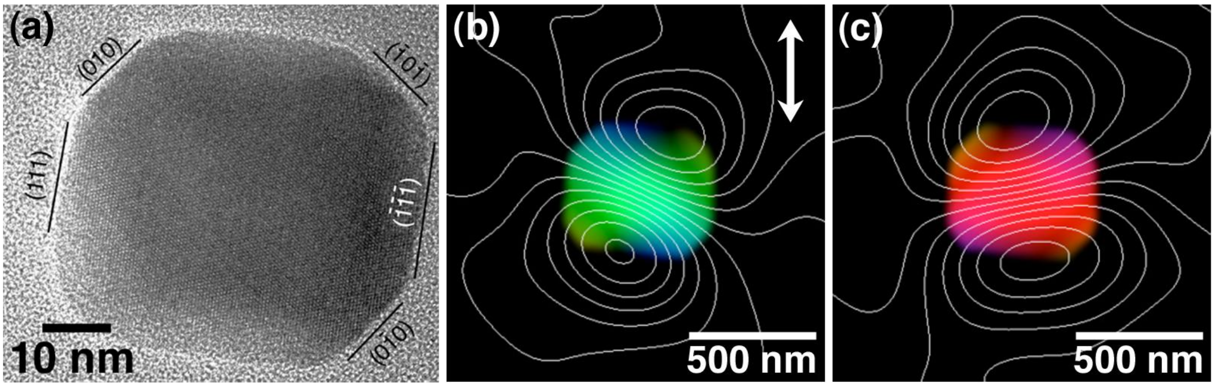

Figure 1. (a) High-resolution TEM image of a 50-nm-diameter magnetite crystal from a magnetotactic bacterial cell (recorded by M. Pósfai). (b, c) Remanent magnetic states recorded from the same particle using off-axis electron holography at room temperature and at 90 K, respectively. The double arrow in (b) shows the direction of the in-plane component of the applied field before reducing the applied field to zero and recording electron holograms.

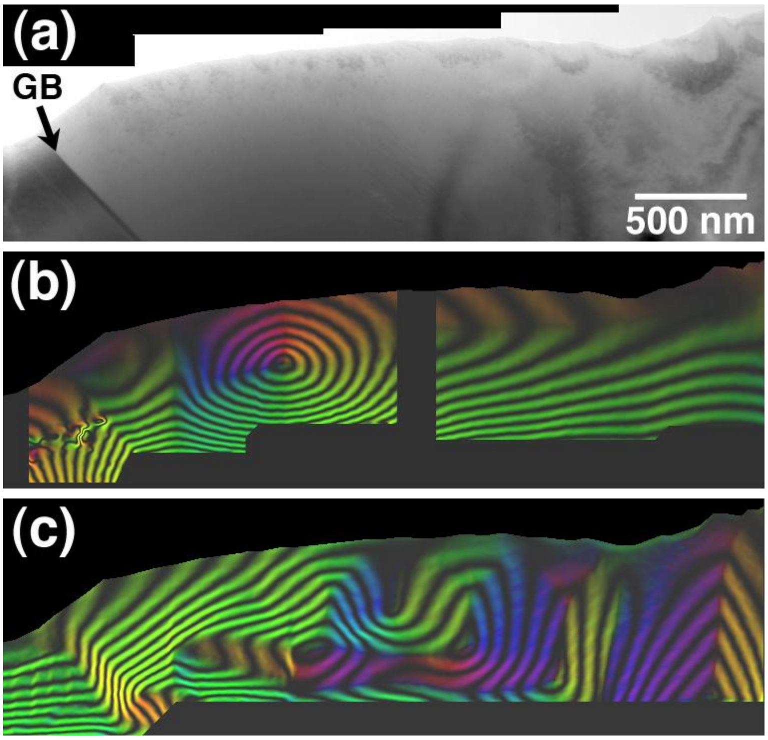

Figure 2. (a) Bright-field TEM image of a synthetic magnetite specimen with a grain size of 10-30 μm, which was prepared for TEM examination using Ar ion milling. (b, c) Remanent magnetic states recorded using off-axis electron holography from the same region at room temperature and below the Verwey transition, respectively. The phase contour spacing is 2π radians. The location of grain boundary (GB) is marked in (a).