Magnetic force microscopy of epitaxial magnetite films through the Verwey transition

A. K. H. Lee,[1] P. B. Jayathilaka,[2] C. A. Bauer,[2] M. C. Monti,[1] J. T. Markert,[1] A. de Lozanne,[1] and Casey W. Miller[2,a)]
[1]*Department of Physics, University of Texas at Austin, 1 University Station C1600, Austin, Texas 78712, USA*
[2]*Department of Physics, Center for Integrated Functional Materials, University of South Florida, 4202 East Fowler Avenue, Tampa, Florida 33620, USA*

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Magnetic force microscopy was performed on 300 nm thick magnetite films grown epitaxially on MgO (001) at temperatures ranging from well below to well above the Verwey transition temperature, T_V. Frequency shift images were acquired at different locations on the sample as temperature was increased through the Verwey transition. The magnetic domain features are persistent at all temperatures, which indicates that the domains are pinned across the phase transition, probably due to antiphase boundaries. An enhancement of magnetic contrast below T_V indicates the moments tilt out of the plane below T_V, which is corroborated by superconducting quantum interference device magnetometry. © *2010 American Institute of Physics*.
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Magnetite, Fe_3O_4, is one of the most widely studied magnetic materials, and is of continued interest in a variety of areas: its proposed half-metallicity is interesting for spintronics applications;[1,2] it has utility in biomedical applications;[3,4] it forms the "backbone" of magnetotactic bacteria;[5] it is an important mineral in many planetary science studies;[6] and there are still open questions about the well known Verwey Transition.[7,8] As is common with many materials, fabrication of magnetite in thin film form, which will be required for spintronics device applications, leads to material properties that differ from the bulk material. The most notable difference is a relative inability to saturate the sample without 10s of kOe-level applied fields (a "technical" saturation is achievable at 100s of Oe). The presence of antiphase boundaries (APBs) is often implicated as the origin of this saturation issue,[9] which is further corroborated by observations of strong pinning of magnetic domains under applied external magnetic fields.[10] However, recent evidence suggests buffer layers can reduce the density of APBs,[11] likely through strain relief.[12]

In this work, we study the temperature dependence of epitaxial magnetite films using a combination of superconducting quantum interference device (SQUID) magnetometry and magnetic force microscopy (MFM). Dark-field transmission electron microscopy (TEM) and off-axis electron holography experiments suggest that APBs with antiferromagnetic coupling give rise to sizeable out-of-plane moments,[13] which makes MFM a good candidate for studying microscopic magnetic behavior in magnetite films. While prior MFM studies have been performed on magnetite films at room temperature,[10,14–16] our relatively unique ability to perform MFM as a function of temperature allows us to observe the magnetic structure as the material goes through the Verwey transition.

The sample used in this study was a 300 nm magnetite film grown onto MgO (001) from an Fe target by reactive sputtering at 200 W dc, 300 °C, in a total pressure of 10 mTorr with Ar and O_2 flow rates fixed at 20 SCCM (SCCM denotes cubic centimeter per minute at STP) and 0.75 SCCM, respectively. The films were capped with a 3 nm Cr layer to limit oxidation. The samples were rotated at 40 rpm during growth to obtain uniform film thicknesses. SQUID magnetometry and MFM were performed on different pieces cleaved from one MgO substrate. Structural characterization was performed on a Philips X'Pert diffractometer using Cu K_α radiation. The in-plane structure is revealed by ϕ scans of the (113) diffraction peaks [Fig. 1(a)], which were performed with the sample normal tilted from the momentum transfer direction by ψ=25.21°, and with 2θ=35.2° for magnetite and 2θ=74.5° for MgO. Together with the (001) peaks observed in the standard θ-2θ scan [Fig. 1(b)], the (113) peaks' relative separation of 90° with a 45° shift from the principle axes allows us to conclude that, as usual, the film grows epitaxially on the substrate with

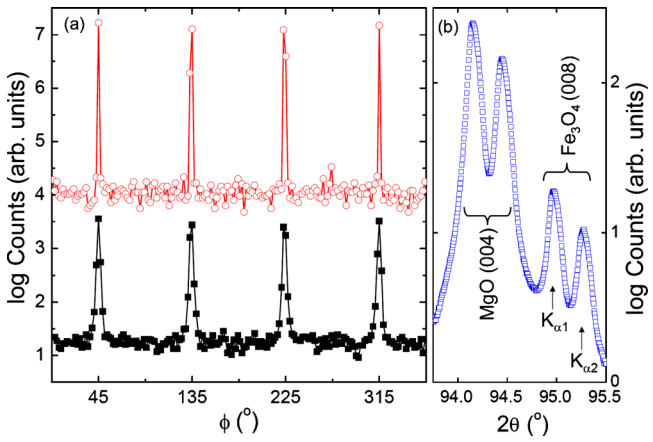

FIG. 1. (Color online) (a) Intensities of the (113) diffraction peaks as a function of rotation angle ϕ about the surface normal of the Fe_3O_4 thin film (black, solid) and the MgO substrate on which it was grown (red, open). (b) The close lattice matching along the growth direction is resolved when inspecting the MgO (004) and Fe_3O_4 (008) diffraction peaks.

a)Electronic mail: cmilleratphysics@gmail.com.

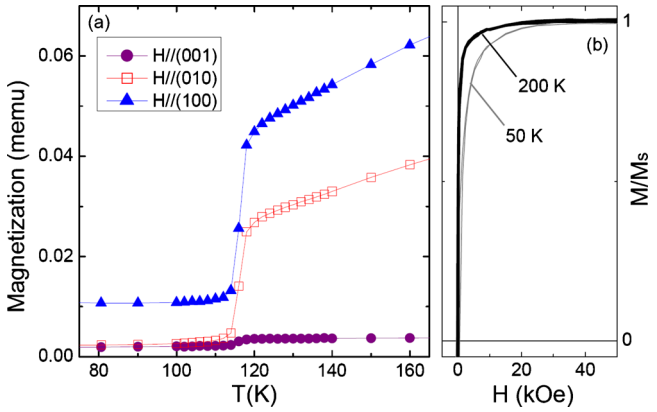

FIG. 2. (Color online) (a) Temperature dependence of magnetization of an epitaxial 300 nm Fe_3O_4 film measured along the three principle axes of the MgO substrate [growth direction is (001); (100) and (010) are in the sample plane]. A T_V of 114–118 K indicates nearly stoichiometric Fe_3O_4. (b) The lack of saturation until fields exceeding 20 kOe indicates the presence of APBs.

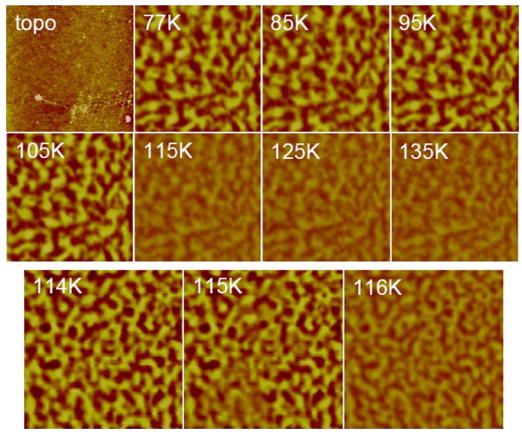

FIG. 3. (Color online) Topographical and MFM frequency shift images. The upper set of images were acquired at one location at the indicated temperatures; the image areas are 4×4 μm^2. The lower group shows a second location; the areas are 5×5 μm^2. The topographic image has undergone a second-order planefit correction, and its color scale covers 10 nm. The MFM images were average subtracted, and the color scale covers 40 and 30 Hz for the upper and lower groups, respectively.

$Fe_3O_4\{100\}\|MgO\{100\}$; small strain relative to the substrate exists.[12]

SQUID magnetometry was performed with the following measurement protocol: saturate the sample with an in-plane 30 kOe field applied along the (100) direction at 300 K; zero-field-cool the sample to 10 K; the magnetization was measured at discrete temperatures, increasing from 10 to 300 K using a small measurement field of 10 Oe. With the exception that only one saturation step was performed, the measurement protocol was repeated with the sample rotated in order to measure the magnetization along the three principle axes of the substrate. As shown in Fig. 2(a), the Verwey Transition is easily observed for all three orientations. The transition temperature, T_V, lies in the range 114–118 K, indicating the oxygen stoichiometry of the film is quite good,[17] namely, $Fe_{3-\delta}O_4$ with δ bounded above by $\sim3\times10^{-3}$. The different magnetization values along the three axes indicate that the sample's net magnetization vector lies primarily in the plane of the sample and at an angle of about 32° from (100). In films, shape anisotropy holds the magnetization in the plane, making the (110) direction the nominally preferred orientation. The relatively small in-plane anisotropy[18] may have enabled the net magnetization to rotate away from (110) after the saturating field was applied along (100). Figure 2(b) shows that the saturation field is in excess of 20 kOe, providing evidence that APBs exist in the sample.

MFM images were acquired using a custom built scanning force microscope[19] and stock MFM tips from Budget Sensors. A commercial NanoScope IIIa controller with an EXTENDER MODULE was used to obtain topographic and resonant frequency shift (MFM) images. The custom microscope is able to acquire images at a particular location across a wide range of temperatures. Registration of the scanning window is performed roughly by visually matching features in the topographical images (not shown) at the time of acquisition. Figure 3 includes a representative topographical (atomic force microscopy) image of the sample surface at 120 K, as well as subsets of two sequences of MFM images taken at various temperatures. The two sets of MFM images were acquired at two independent locations on the sample during two separate temperature sweeps through the Verwey transition with different MFM tips. The upper set was taken first using large temperature steps in the range of 77–135 K; the lower set was taken with finer temperature steps near T_V. The domain structure is similar in both series, giving us confidence that these images are representative of the sample. The only correction done to the MFM data presented here is a zero-order planefit correction (uniform average subtraction) in order to center the color scale. Bright and dark contrast can be interpreted as regions of repulsive and attractive interactions, respectively,[20] which can be used to estimate the magnetic domain size. Here, the lateral extent of the magnetic domains is on the order of 300 nm. From the persistence of the features at all temperatures within each series, it is apparent that the magnetic domains are pinned across the Verwey transition. Since misfit dislocations and local stoichiometric variations have negligible impact on pinning, APBs are the most likely defect underlying these observations.[10]

The Verwey transition is clearly evident in the MFM images. The contrast features reproduce the basic feature of the magnetization data, with the strong contrast enhancement for $T<T_V$ suggesting the magnetization tips out of plane, closer to the (001) direction. Interestingly, the image taken at 115 K in the fine T-step images shows a region with both the high and low contrast, which indicates this area of the film is in the process of undergoing the phase transition. We can conclude from these images that the transition occurs locally within a very narrow temperature window, conservatively bounded above by 2 K. The discrepancy between this temperature width and that inferred from magnetometry is due to global variations over the entire sample; the SQUID averages over the full area of the sample, while MFM is intrinsically limited to micrometer-sized fields of view. The MFM images demonstrate this point well: the contrast of images acquired just below T_V is indistinguishable from the other images taken at $T<T_V$; the images with $T>T_V$ are equally similar to one another.

The quality of the features suggests that out-of-plane moments dominate the images. These images are consistent with the shapes and sizes of the APBs shown in TEM images of thinner films.[21] The abrupt change between high and low magnetization states can be seen more clearly in Fig. 4(a) which plots the rms values for each MFM image in the two

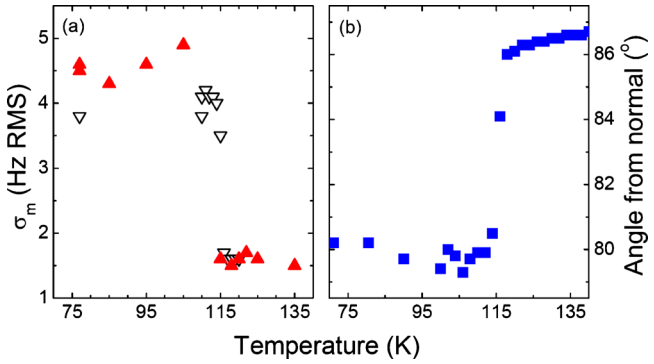

FIG. 4. (Color online) (a) rms values of the MFM images (σ_m) of the temperature series shown in Fig. 3 with coarse (red, up-triangles) and fine (black, down-triangles) temperature steps. The two data series were taken at different locations with different MFM tips, so the values cannot be directly compared between the two curves. (b) Temperature dependence of the angle between the total magnetization vector and the surface normal.

complete MFM series as a function of temperature. The magnetic component of the frequency shift is roughly proportional to the second derivative of the sample's stray field in the direction perpendicular to the sample plane, so the contrast is related to the out of plane component of the total magnetization. The increase in contrast for $T<T_V$ therefore indicates that the magnetization is tilting out of the sample plane. This interpretation is verified by using the three orthogonal magnetization measurements to calculate the angle, θ between the total magnetization vector and the surface normal as $\theta=\arccos(M_{001}/|M_{\text{total}}|)$. As shown in Fig. 4(b), the magnetization vector tips out of plane precisely at the Verwey temperature, leading to the enhanced MFM contrast. This temperature-dependent orientation may have a negative impact on magnetite-based spintronic phenomena [e.g., tunneling magnetoresistance (TMR) (Ref. 22)] whose figure of merit depends explicitly on the relative orientation of two materials' magnetization vectors. Corrections for this issue would increase the spin polarization inferred from TMR measurements and the simplistic Julliere formula.[23]

In summary, we have used MFM to probe the temperature dependent nanoscale magnetic domain structure of epitaxial thin film magnetite through the Verwey transition. On the local scale probed by MFM, the Verwey transition happens over a temperature range less than 2 K. The observed domain structure persists through the transition, presumably pinned by APBs. MFM images acquire strong magnetic contrast below T_V, indicating that the low-temperature magnetization has rotated out of the sample plane relative to the high-temperature state. This point is further verified by SQUID magnetometry measurements of the magnetization along the three principle axes of the sample.

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