The Verwey transition observed by spin-resolved photoemission electron microscopy

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ABSTRACT

We have imaged the magnetic domains on magnetite (001) through the Verwey transition by means of spin-resolved photoemission electron microscopy. A He laboratory source is used for illumination. The magnetic domains walls above the Verwey transition are aligned with (110) in-plane directions. Below the Verwey transition, the domain structure is interpreted as arising from a distribution of areas with different monoclinic c-axis, with linear 180° domain walls within each area and ragged edges when the magnetic domain boundaries coincide with structural domain walls. The domains evolve above the Verwey transition, while they are static below.

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1. Introduction

Magnetite is the archetypal magnetic material [1]. Somewhat surprisingly, the number of studies directly observing the spatial distribution of its magnetic domains is not too large. This can be attributed to the limitations of the techniques that allow imaging the magnetic domains with nanometer resolution. Magnetic force microscopy (MFM) has been used [2–5] but MFM maps the stray field probed by a magnetic tip some nanometers above the surface and furthermore the low coercive field of magnetite complicates the imaging. Another technique is Lorenz microscopy, which has been used for small crystals [6–8]. By using low-energy electrons to enhance the surface sensitivity, magnetic domains can be imaged using different physical phenomena. First, an spin-polarized electron beam can be used as illumination, and the diffracted electrons can be detected, in the so-called spin-polarized low-energy electron microscopy (SPEEM) [9]. In such mode, magnetic contrast is detected due to the scattering between the incoming electron beam and the near surface region of the sample. It requires a crystalline sample to provide information on a high intensity of backscattered electrons. Its advantage is that it provides the spin and energy dependent electron reflectivity, giving a glimpse into the spin-dependent density of states of the sample. From a practical point of view, the particular spin-direction of the illuminating beam can be reversed in milliseconds, so difference images can be obtained quite rapidly. By means of a spin-manipulator the spin-direction can be made to point in any desired direction, opening the possibility of acquiring the spatially resolved 3D magnetization-vector spatial distribution with nanometer resolution [10]. Another option is to use a circularly polarized X-ray beam for illumination, to detect the surface magnetization by the different photo-absorption cross-section in a photoemission electron microscope (PEEM). This is the method used in X-ray Magnetic Circular Dichroism (XMCD) in PEEM, or XMCD-PEEM [11]. In this mode, the photon energy is tuned to a core level of a specific magnetic element, and the secondary electrons are taken as a measure of the X-ray absorption intensity. As in SPEEM, difference images, this time between opposite circular polarizations, are used to image the magnetic domains with nanometer resolution. An advantage of the technique is that it allows to do element specific magnetic imaging, and to estimate the spin and orbital components of the magnetization. To have enough intensity, a synchrotron source is required, and switching the light polarization usually takes minutes so the technique is often slower than SPEEM.

Both SPEEM [12,13] and XMCD-PEEM [14,15] have been previously applied to magnetite (001). In this work, we describe our observations of the magnetic domains on the (001) surface of magnetite with a different technique: spin-resolved PEEM, i.e., the spin-analysis of the electrons photoexcited upon illuminating by a non-polarized light source. Spin-analysis has been hampered by the lack of imaging spin-analyzers until recently [16]. Their recent development opens a new way to do magnetism research at

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http://dx.doi.org/10.1016/j.apsusc.2016.05.140
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surfaces: in its spin-resolved PEEM application they already provide for imaging magnetic domains in a laboratory environment with a non-scanning technique, even on the non-crystalline samples required by SPLEEM. But this is just the start: the ability to analyze the spatial distribution of electrons from a surface in real and reciprocal space with spin analysis at low energies opens the way for a new level of understanding spin behavior near surfaces.

2. Experimental methods

The sample is a crystal of natural origin [17] cut to an optimal hat shape 10 mm in diameter to provide a uniform potential surface in front of the objective lens. This facilitates variable temperature experiments as well as exploring large areas of the surface with only minor tilt adjustments. Characterization of resistivity in a physical measurement system gives a Verwey transition at 114 K, below the ideal one at 122 K. Additional XRD characterization indicates the existence of some FeO within the bulk. The sample was cleaned after introduction in the PEEM system by a few cycles of consecutive steps of sputtering with Ar ions at 1 keV followed by annealing to 870 K in 10⁻⁶ Torr of O₂, each step taking typically 10 min. After four cycles the low-energy electron diffraction (LEED) pattern showed a sharp 2 × 2 pattern, whose detailed structure has recently been solved [18], and that is reproducible under ultra high vacuum conditions. The same sample has been studied with XMCD–PEEM [15] as well as SPLEEM [13], with the Verwey transition being detected at 108–112 K.

The instrument used is a PEEM microscope equipped with an energy filter and an imaging spin–filter. Both the microscope and the spin-filter have been described previously [16,19]. The microscope has an energy resolution of 12 meV and consists of an all-electrostatic tetrode objective lens and a double hemispherical analyzer. The spin-filter is an imaging spin-filter based on low-energy electron diffraction at a Au-passivated Ir(001) single crystal [16,20]. In order to switch to spin-filtered mode, the Ir(001) crystal is introduced into the electron optical beam path, with images recorded with a multi-channel plate image intensifier and a fluorescent screen.

3. Results and discussion

After several cleaning cycles, the crystal presented a well-ordered LEED pattern, shown in Fig. 1b, that corresponds to the √2 × √2R45° reconstruction [18]. Then the crystal was transferred into the microscope. In Fig. 1a a PEEM image was acquired by imaging the spatial distribution of secondary electrons at final state energy of 4.80 eV, under illumination with a Hg–Xe arc lamp (5.9 eV, acquisition time of 10 s). The energy resolution set for the PEEM and spin-resolved PEEM experiments was 80 meV. The sample, by the time it was prepared for this experiment, had already been subject to over fifty cleaning cycles. The cleaning cycles produce a distinctive topography with square “mesas”. Such mesas are protrusions, which on the surface shown in Fig. 1a and c have a typical lateral size of 2 μm. These mesas grow in size and eventually the surface is covered with them, giving rise to a rough surface. We believe that the origin of the roughness process is the presence of bulk dislocations together with the surface growth that takes place during oxidation of magnetite. While cleaning the surface argon ion sputtering preferentially removes oxygen. Annealing in vacuum thus produces a reduced surface. To obtain a stoichiometric surface, the sample is annealed in oxygen at ~10⁻⁶ mbar. But such annealing actually oxidizes magnetite to hematite, freeing iron cations that diffuse through the crystal and react with oxygen to make the magnetite surface grow [21,22]. As observed in the figure, many of the mesas are superimposed, forming lines. It is likely that some of those structures originate from polishing scratches, as they do not have any definite angle with the crystallographic directions. The crystal was mounted with the [100] axis along the image x-axis and the [010] direction along the y-axis. The crystallographic orientation is confirmed by observing the orientation of the sides of the mesas, which correspond to the in-plane compact (110) directions [23].

The distribution of magnetic domains at room temperature in the surface of magnetite (001) has been described previously [12–14]. At room temperature, the magnetocrystalline anisotropy has minima along the (111) directions [24], i.e., the (bulk) magnetic easy axes. But none of those directions is contained by the (001) surface. Thus, close to the surface there is a competition between the magnetocrystalline anisotropy and the shape anisotropy, with the latter driving the magnetization parallel to the surface. Upon cooling, the magnetocrystalline anisotropy changes, and when reaching the isotropic point, the first order magnetocrystalline anisotropy vanishes [24]. From that temperature, and down to the Verwey transition [13,25] (discussed later) the magnetocrystalline anisotropy has minima along the (100) directions. Given the contribution of the shape anisotropy, the expected surface easy axes below the isotropic point are the [100] and [010] ones.

In order to image the magnetic domains, the imaging spin-filter is introduced in the electron beam path after the double-hemispherical energy analyzer. The illumination source is, in this case, a He lamp, with a main peak energy corresponding to the He I emission line which has a photon energy of 21.2 eV. In order to obtain a pure magnetic image, the spin-analyzer is set to two different scattering energies, and the quantitative evaluation of the spin-polarization map in the whole PEEM image follows the procedure outlined in Ref. [16]. In the present case, the scattering energies used were 10.25 and 11.50 eV, which have nearly opposite
spin sensitivity (they are respectively -65% and +57% [19]). From each couple of images acquired at different scattering energies, a pixel-by-pixel asymmetry image can be used to locate the magnetic domains (see Fig. 3), or an spatially resolved map of the absolute spin-polarization can be obtained with the appropriate spin sensitivities (see Fig. 2a). In the current geometry, the spin-analyzer is sensitive to the in-plane spin polarization component along the y-axis of the figures. Areas with either no magnetization, or a zero component of the magnetization along the y-axis are imaged gray in the asymmetry image, or white in the spin-polarization one.

In Fig. 2a the spin-polarization map of secondary electrons at a final state energy of $E_f + 5.82$ eV is plotted as a color image, with red indicating positive polarization and blue indicating a negative one. As has already been employed in scanning electron microscopy with polarization analysis, the spin-polarized secondary electron emission is directly related to the magnetization direction at the point of secondary emission position [26]. Thus the spin-polarization map corresponds to the distribution of the y-component of the magnetization across the surface. The sample temperature in Fig. 2a was 114 K, which in this sample is just above the Verwey temperature but below the isotropic point. The interpretation of the image is then rather simple: magnetic domains along the y direction are detected shown as either red or blue areas (i.e., magnetization along [010] or [010]). In addition, the white areas should correspond to domains with magnetization along either [100] or [100]. Thus all the boundaries observed in the figure are either 180° magnetic domain walls, between blue and red regions, or 90° between the colored and the white areas. The magnetic domains themselves are rather large, with areas up to several tens of microns in width presenting the same magnetization. The domain wall boundaries are mostly oriented along the compact surface directions, i.e. the in-plane ⟨110⟩: ones. The cut across the spin-polarization image presented in Fig. 2c indicates that the absolute polarization from the magnetite surface at a final state energy of $E_f + 5.82$ eV is close to 10%.

Upon cooling the Verwey transition [25] is encountered. When the Verwey temperature is crossed, several properties of magnetite change [27,28]. First, and historically the most important, there is an increase of the resistivity of two orders of magnitude, i.e., magnetite undergoes a metal-insulator transition. The high-temperature cubic phase transforms into a monoclinic one [29], and the magnetic anisotropy becomes uniaxial, and increases by one order of magnitude [30]. The easy axis is then the monoclinic

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Fig. 2. (a) Spin-polarization map showing regions of the surface where the secondary electrons have positive (red) or negative (blue) spin-polarization. The sample temperature is 114 K, just above the Verwey transition for this sample. The field of view is 132 μm. The illumination is performed by a He I lamp, and the energy of the secondary electrons is $E_f + 5.82$ eV. (b) Outline of the magnetic domains shown in (a). (c) Profile of the spin-polarization along the line marked with a yellow line in (a). (d) Spin-polarization map, acquired at a temperature of 100 K, well below the Verwey transition, acquired in the same plane and conditions of image (a). (e) Outline of the magnetic domains shown in (c). (f) Profile of the spin-polarization along the line marked with a yellow line in (d). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Sequence of asymmetry images acquired while ramping the temperature from 120 K to 80 K and back to 120 K. The field of view is 132 μm. The kinetic energy of the imaged electrons is $E_f + 5.82$ eV. Each individual image corresponds to the average of 14 images couples with each scattering energy (10.25 and 11.50 eV respectively), each with an exposure time of $10$ s. The temperature ramp is performed in 2 K steps, waiting for the temperature to stabilize before acquiring the PEEM images.
c-axis. There are several orientations possible for the lower symmetry monoclinic phase relative to the high-temperature cubic phase, as discussed by Kasama et al. [6]. The monoclinic distortion is such that the c-monoclinic axis points within ~0.2° along one of the cubic [100] axis. Thus, the crystal becomes twinned, with regions with different c-axes in each one. As the shape anisotropy makes it energetically unfavorable to have domains with an out-of-plane magnetization, we expect it selects monoclinic orientations along [100] and [010] orientations for the (001) surface. An additional detail is that monoclinic twins with opposite c-axes are often generated when crossing the Verwey transition, as observed by low-energy electron microscopy [23]. All taken together, below the Verwey transition we expect to find on the (001) surface structural domains which correspond to areas with the monoclinic axis along [100] or [010] or [010]. In the first case, no magnetic contrast is expected in our experimental configuration which is sensitive only to domains along the y-axis, as the easy axis is also along [100]. In the second case, domains should be observed given our current experimental configuration. Fig. 2d corresponds to the same area that was imaged above the Verwey transition in Fig. 2a. The large scale domain distribution has changed drastically. This indicates that the influence of the particular magnetic domain orientation (above the Verwey transition) in the nucleation of a given monoclinic orientation is limited, despite the substantial magnetostriiction of magnetite. The shape of the observed magnetic domains tends to be elongated along the y-axis. The 180° domain walls between them tend to be along the x or y-axis. The edges between the colored domains and the white areas are ragged, and do not show a preferred orientation. As the easy axis of the monoclinic phase of magnetite is along the monoclinic c-axis, in the white areas the monoclinic c-axis (and thus the magnetization) must be along the x-axis, as indicated in the schematic of Fig. 2e. Then the boundaries between the imaged y-axis magnetic domains and the x-axis ones should correspond to domain walls pinned at structural domain walls between monoclinic regions with different c-axis. The absolute spin-polarization is the same (close to 10%) to the one observed above the Verwey transition, as shown in the profile presented in Fig. 2f.

In addition to crystals with different c-axis, in monoclinic magnetite microtwinning has been observed by transmission electron microscopy [6,7]. The microtwinning does not affect the 180° magnetic domain walls in the sense that the easy axes are shared between the microtwins, and the magnetic domain walls are at right angle of the microtwin domain walls. At the present observation scale the microtwinning is not resolved, but we have previously detected it by low-energy electron microscopy on this same sample.

In Fig. 3 we present the evolution of the domains through the Verwey transition: from 120 K, in which the sample is in the cubic phase, down to 80 K, and back to 120 K. The domains evolve smoothly between 120 and 110 K. But keeping the sample at 108 K the domains evolve so the averaged image shown in Fig. 3 appears blurred. This is taken as the occurrence of the Verwey transition. Below the Verwey transition, from 106 K to 100 K and back to 108 K, the magnetic domain distribution remains static. When increasing the temperature, the domains appear blurred at a slightly higher temperature, about 110 K. Then the same style of domains that were observed before cooling is detected: large domains with mostly [110] orientation of the domain walls, and there is substantial motion of the domain walls between the Verwey transition and 120 K.

4. Summary

We have observed in real space the distribution of magnetic domains on the surface of magnetite at low temperature around the Verwey transition. In order to observe the domains, the spin-polarization of secondary electrons photoexcited upon illumination with 21.2 eV light is used. The instrument employed is a novel high resolution photoemission microscope coupled to a high-efficiency imaging spin-analyzer. For the first time on magnetite (001) the near surface real-space reorganization of the magnetic domains has been followed in detail, both upon crossing the transition when cooling and when heating. No further evolution of the magnetic domains is detected below the Verwey transition, while the magnetic domains walls in the cubic phase above the transition keep moving at every temperature step of 2 K.

Acknowledgments

This research was only possible thanks to the support and encouragement of Prof. J. Kirschner. It was partly supported by the Spanish Ministry of Economy and Competitiveness (MINECO) under Project No. MAT2012-38045-C04-01 and MAT2015-64110-C2-1-P. We thank A.K. Schmid for his help with and loan of the magnetite crystal.

References