Field-enhanced magnetic moment in ellipsoidal nano-hematite

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Received 24 February 2014
Accepted for publication 7 March 2014
Published 16 June 2014

Materials Research Express 1 (2014) 026114
doi:10.1088/2053-1591/1/2/026114

Abstract
Bulk hematite is a canted antiferromagnet at room temperature and displays weak magnetic coercivity above the Morin transition temperature $T_M \sim 262$ K. Below $T_M$, hematite displays traditional antiferromagnetic behavior, with no net magnetic moment or magnetic hysteresis. Here, we report that ellipsoidal nanocrystals of hematite (ENH) display a significant field-enhanced magnetic moment (FEMM) upon being poled by a magnetic field. This poled moment displays a giant coercive field of nearly 6000 Oe at low temperature. Atomic resolution transmission electron microscopy indicates that the nanocrystals are single crystalline, and that the surfaces are bulk-terminated. The apical terminations include the <001> sets of planes, which are implicated in possible formation of FM-arrangements near the surface. We tentatively suggest that FEMM in ENH could also arise from uncompensated surface spins or a shell of ordered spins oriented and pinned near the surface by a magnetic field. The gradual loss of magnetic moment with increasing temperature could arise as a result of competition between surface pinning energy, and $kT$. The large coercive field points toward possible applications for ENH in digital magnetic recording.

Keywords: magnetism, nanocrystals, hematitite, coercive field, core-shell nanocrystals, surface pinning, antiferromagnetism
1. Introduction

Nanoparticles of magnetic materials display unique colloidal, optical, physical and chemical properties not found in their bulk counterparts [1, 2]. These properties enable applications in solid state devices [3], biology [4, 5], imaging [6], medicine [6–8], and DNA separation [9, 10]. Oxides of iron, especially at the nano scale, are of further interest due to unusual crystal lattice terminations in nanocrystal surfaces, leading to unusual magnetic states condensed at or near the surface. Novel properties at the surface can enable potential applications in photocatalysis, drug delivery, water processing, and other fields [11–17].

Bulk single crystal hematite (\(\alpha\)-Fe\(_2\)O\(_3\)) is a canted antiferromagnet (c-AFM) below its Néel transition temperature, \(T_N \approx 950\) K. Spin canting away from the basal plane produces a weak spontaneous magnetic moment, a small magnetic hysteresis and a coercive field of 0.33 T at room temperature. Below the Morin transition \(T_M \approx 262\) K, this weak moment becomes fully suppressed due to a transition from canted antiferromagnetic (c-AFM) order at high temperature to traditional antiferromagnetic order (AFM) at low temperature. At 4 K, well below \(T_M\), hematite displays no net moment, together with zero coercive field and an absence of magnetic hysteresis. Previous studies of nano-sized hematite reveal that the Morin transition becomes suppressed with decreasing particle size [18]. The coercive field in hematite (both bulk and nano) decreases to zero below \(T_M\), revealing no magnetic hysteresis at low temperature. In this paper, we report that a spontaneous field-enhanced magnetic moment (FEMM) and a giant magnetic hysteresis can develop in ellipsoidal nanocrystals of hematite (ENH) upon exposure to an external magnetic field. We further find that the coercive field increases to large values with decreasing temperature. High resolution electron microscopy studies reveal several unusual crystal surface terminations which could be implicated in the formation of unusual magnetic ground states and structures at or near the surface of ellipsoidal nano-hematite.

2. Materials and methods

Samples of ENH were synthesized by a ‘forced hydrolysis’ method in which the selective binding of phosphate ions along the [2-1-4] crystal planes leads to the formation of ellipsoidal nanoparticles from a solution of iron chloride [19, 20]. A solution was made by vigorously shaking 4.8 mM (1.3 g) of iron chloride hexahydrate (FeCl\(_3\).6H\(_2\)O, Aldrich) and 0.1 mM (12 mg) of sodium dihydrogen phosphate (NaH\(_2\)PO\(_4\), Aldrich) in 1 liter of de-ionized water (MilliQ plant with 0.22 micron filter yielding 18.2 M-\(\Omega\)-cm conductivity). The solution was placed in a preheated oven for 120 h at 98 °C and subsequently furnace-cooled to room temperature. The resulting colloidal suspension, containing nanocrystals of hematite, was washed by repeated centrifugation at 10 000 rpm and re-dispersion in deionized water using an ultrasonic bath. This process was repeated four times, yielding sediments of hematite nanocrystals of ellipsoidal shape.

Powder x-ray diffraction (XRD) was performed on a Scintag XDS 2000 diffractometer. Rietveld refinement was performed using the graphical user interface EXPGUI [21]. Nanocrystal size and morphology were investigated using a Hitachi-H9000NAR transmission electron microscope (TEM) operating at 300 keV. Magnetic properties were studied by varying temperature (2–300 K) and magnetic field (0–9 T) in a physical properties measurement system (PPMS) by Quantum Design, Inc. For the magnetic measurements reported here, the powder
sample was fixed in an epoxy resin (Bisphenol A diglycidyl ether resin, ITW-Devcon) in order to minimize the physical movement of the nanoparticles while performing magnetic measurements in field. The magnetic measurements reported in this letter are from one sample placed within the PPMS cryostat; however, the results are reproducible over a number of batches of samples. For the sample reported here, 11 mg of nanocrystals were evenly mixed using a non-magnetic pick in 27 mg of epoxy. The resin added a minor diamagnetic component to our magnetic property measurements.

3. Results and analysis

XRD shown in figure 1 confirms that our sample is high purity hematite ($\alpha$-Fe$_2$O$_3$). A careful search was performed, along with Rietveld refinement, to eliminate possible signs of the known oxides and oxi-hydroxides of iron (magnetite, maghemite, goethite, akaganite, lepidocrocite and feroxyhite). No evidence of secondary phases was found in our samples. Lattice parameters derived from Rietveld refinement yield crystal parameters $a = b = 5.03042(15)$, and $c = 13.7931(6)$, along with Wyckoff positions Fe at $(0, 0, 0.35417)$ and O at $(0.30739, 0, 0.25)$ [21]. These are very close to values reported for bulk hematite of $a = 5.038$ and $c = 13.772$, Fe at $(0, 0, 0.3553)$ and O at $(0.3059, 0, 0.25)$ [22], and $a = 5.0346$ and $c = 13.7473$, Fe at $(0, 0, 0.35564)$ and O at $(0.3056, 0, 0.25)$ [23], with the most notable discrepancy being an elongation of the $c$ axis.

Results from bright field TEM and high resolution (HRTEM) are shown in figure 2. Images were filtered with an aperture of radius 9.1 nm$^{-1}$ in order to remove noise beyond the lattice resolution of the microscope. Amplitude-contrast bright-field images indicate that the nanocrystals have a uniform distribution of shape and size (figure 2(a)). The crystals are ellipsoidal, with a length of $70 \pm 11$ nm and a width of $40 \pm 5$ nm. Note the presence of at least two facets at each end; these are further analyzed from high-resolution transmission electron microscopy (HR-TEM), and discussed in the following section.
Figures 3 and 4 show data from magnetization measurements in variable temperature and magnetic field. In figure 3(b) (inset, top left), we observe a weak coercive field of \( \sim 40 \) Oe in the magnetic hysteresis (M versus H loop) measured at 300 K, consistent with the fact that hematite is a canted antiferromagnet at this temperature. However, the hysteresis loop at 4 K performed upon zero-field cooling (ZFC) from 300 K shows a remarkably high coercive field (coercivity) of \( \sim 6000 \) Oe. The same figure shows that coercive field measured in ZFC samples increases with decreasing temperature. It is also evident in figure 3(c) (inset, lower right) that the coercivity increases rapidly with increasing maximum field reached during a magnetic hysteresis measurement.

Figure 4 shows temperature dependence of magnetization of our ENH sample with differing history of applied magnetic field. Lines 1, 2, 3 and 4 are plots of magnetization as a function of temperature during warming in a field of 1000 Oe (arrows indicate warming or cooling). As shown by the arrow, line 5 was measured during cooling in a field of 5 T. It is clear from line 1 that the sample displays a Morin transition upon cooling in zero field. The moment at low temperature is zero within measurable limits, indicating a transition from c-AFM to AFM. The transition is broadened due to particle size effects, consistent with previously reported results for small particles of hematite [24]. As shown in line 2, the Morin transition is suppressed when the sample is cooled in a low field of 1000 Oe. Remarkably, line 3 shows a rise of magnetic moment with decreasing temperature when the sample is cooled in zero field but exposed to a poling field of 5 T at 4 K before being measured in 1000 Oe during warming. This field-enhanced magnetic moment, or ‘FEMM’ behavior, is further enhanced when the
sample is cooled in a high magnetic field of 5 T, as shown in line 4. FEMM behavior is also observed when the sample is cooled in a high magnetic field (line 5) during measurement. However, the moments are saturated and do not show an activated behavior.

4. Discussion

Reflections from powder XRD of our ellipsoidal nano-hematite, shown in figure 1, are consistent with hematite (ICDD PDF #72-0469). Rietveld refinement and careful examination of the reflections along with known reflections from a number of possible secondary phases such as other oxides and hydroxides confirms that we have hematite of very high phase purity. The absence of both secondary phases and secondary crystal structures was carefully confirmed using XRD, TEM and magnetization data. High-resolution TEM shows that the nanocrystals are homogenous, with no formation of secondary crystal structures within the bulk or near the surface of the nanocrystal.

Figure 2(a) shows a high resolution image of the faceted end of one such nanocrystal, noise filtered for spacings smaller than the 0.11 nm lattice resolution. Detailed examination of a number of crystals at high resolution shows that the hematite lattice extends all the way to the
surfaces of individual crystals. A larger flat facet on the left side of the image is terminated by a $<104>$ type surface. This appears to be a dominant surface found near the tapered edges at the tip of nearly all of the nanocrystals, and is observable in all of our bright field images of type shown in figure 2(b). The shorter facet at the tip of the particles is terminated by the basal plane of the hexagonal structure; the long axis corresponds to the $<001>$ axis. Figure 2(c) shows a digital diffractogram confirming that each crystallite can be treated as a single crystal. This is also consistent with the uniform contrast observed in the bright field images and from the continuous lattice fringes in HRTEM. A systematic observation of images in the bright field and HRTEM convinces us that the nanocrystals have a uniform hematite crystalline structure without any additional detectable crystalline phase.

In figure 3, we note that the observed coercive field at 300 K in ellipsoidal nano-hematite is lower than the coercive field of 0.33 T measured in bulk hematite [25]. This is consistent with the observation that the coercive field is small in small particles: a $\sim$3000 Oe coercive field is observed in larger pseudocubic nanocrystals ($\sim$350 nm) of hematite [26]. The interesting result here is that the hysteresis loop at 4 K in figure 3 is larger than that at 300 K, consistent with FEMM behavior noted above and discussed below. Further, it displays a remarkably large coercive field of $\sim$6000 Oe which rises with decreasing temperature. This is not consistent with hematite, which is antiferromagnetic below the Morin transition. It is also clear from line 1 in figure 4 that our samples of ellipsoidal nano-hematite undergo a Morin transition as expected for small particles of hematite and thus ought to show no net magnetic moment, and zero coercive field, at low temperature. Both figures 3 and 4 are consistent with a field enhanced

![Figure 4. Magnetization ($M$) as a function of temperature ($T$) in ellipsoidal nano-hematite crystals. Arrows indicate the direction of change of temperature during measurement [1]: zero field cooled and measured in a field of 1000 Oe [2]; cooled and measured in a field of 1000 Oe [3]; zero field cooled, ‘poled’ at 4 K with a 5 T field, and measured in a field of 1000 Oe [4]; cooled in a field of 5 T and measured in a field of 1000 Oe [5]; ‘poled’ at 300 K with a 5 T field, then cooled and measured in a field of 5 T. The Morin transition is broadened due to particle size effects. Field-cooling in increasingly higher fields displays an increase in magnetic moment.](image-url)
magnetic moment, or FEMM, in which a net magnetic moment in ENH remains pinned upon being exposed to high magnetic field. In our hysteresis loops in figure 3, our ENH sample becomes exposed to high magnetic field before sweeping back through zero. This is consistent with figure 4, in which the sample develops a net spontaneous magnetic moment upon exposure to high magnetic field. The moment is enhanced at lower temperature and is also better ‘pinned’, as evidenced by increasing coercive field with decreasing temperature.

Magnetic properties of the many oxides of iron have been extensively characterized in the bulk and, to some extent, in nanoparticulate form [25–29]. For crystal sizes below 100 nm, iron oxides of different size and shape display unexpected and fascinating magnetic and structural characteristics. Such behavior has been examined from several different viewpoints, mostly classified as ‘particle size’ effects. Theoretical studies, for the most part, have examined size effects on the relative free energy of the surface of a nanocrystal [30]. In addition, phase transitions in critical phenomena requiring long-range order (leading to ferromagnetic or antiferromagnetic ground states) become compromised when the lattice size is smaller than a critical length scale (or an order parameter) and is unable to sustain long-range order [31]. Magnetic properties of nano-materials have also been examined based on another broad class of effects, sometimes referred to as ‘core–shell’ type behavior. In its most widely studied form, core–shell structure implies a variance in crystal structure or chemical phase between the bulk and the surface of the nanocrystal; this may or may not be intended during the growth of the nanocrystal. Core–shell type behavior can also exist when the crystal lattice of the nanocrystal extends uniformly from its bulk to its surface. Theoretical investigations indicate that unusual magnetic order can nucleate near the surface of the nanocrystal due to constraints of size and shape in the nano-lattice. This can yield unusual magnetic properties due to a ‘magnetic core–shell’ structure [32]. Finally, unusual magnetic behavior can arise from purely ‘surface’ effects, or lattice terminations revealed on the surfaces of nanocrystals which are not usually found in bulk crystals.

We now briefly discuss possible mechanisms for the observed FEMM behavior in our samples of ellipsoidal nano hematite. First-principles density functional calculations indicate that stable local spin configurations of Fe2O3 (0001) are dependent upon the number of Fe bilayers near the hetero-interface [33]. A local ferromagnetic (FM) up-up spin structure is found to be energetically favorable for a single bilayer, whereas an up-up, down-down AFM structure is favorable in the case of four bilayers. FM behavior of magnetic spins near the surface of Fe2O3, especially in view of the observations of several <001> sets of planes exposed near the apex of the ellipsoid, would explain the observations in figures 3 and 4. Wang et al indicate that O3-terminated (0001) terminated Fe2O3 surface yields an unusual electronic structure with noticeable presence of states from the subsurface Fe layer [34]. Spin states such as these could either remain pinned at specific surface terminations, or exist in a core–shell type magnetic structure with FM-like order near the surface and AFM-like order in the bulk of the nanocrystal [35]. FEMM behavior, and a large coercive field, could arise from a core–shell type arrangement of the magnetic lattice in which a possible bias between the surface shell and the bulk can be induced and poled by external magnetic field. We therefore conjecture that the field-enhanced magnetic moment behavior, reminiscent of ferromagnetism, could arise from surface spins oriented upon exposure to a magnetic field and pinned at or near the surface of ellipsoidal Fe2O3 nanocrystals. The coercive field observed in magnetic hysteresis is very high, opening up the potential for the application of ellipsoidal nano-hematite in digital magnetic recording.
5. Conclusion

We report field-enhanced magnetic moment (FEMM) in ellipsoidal nano-hematite (ENH) below the Morin transition. This moment increases with decreasing temperature, correlated with an increase of coercive field to nearly 6000 Oe. Although the observation of a net magnetic moment, and a giant coercive field, is counter-intuitive in an antiferromagnetic material, our observations possibly arise from uncompensated spins pinned at the surface of ENH samples. A giant coercive field observed in our magnetic hysteresis measurements provides a basis for potential applications of ellipsoidal nano-hematite in digital magnetic recording technologies.

Acknowledgements

The authors gratefully acknowledge partial support from AFOSR-MURI to PG, Swiss NSF PBFRP2-134284 to VM, US NSF-0449969 to PG and -0952643 to MS, DE-FG02-06ER46328 to MGJ, and the UWM-RGI to PG, MGJ and MS. We thank Donald Robertson of the UWM HRTEM lab, and Steve Hardcastle of UWM-AAF of their support. The authors would like to thank Chantal Rufer for her valuable suggestions regarding the synthesis of nanoparticles. S Sen and V Malik contributed equally to this paper.

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