Dipolar ferromagnetic phase transition in Fe_3O_4 nanoparticle arrays observed by Lorentz microscopy and electron holography

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Dipolar ferromagnetism formed in Fe_3O_4 nanoparticle arrays is revealed by Fresnel Lorentz microscopy and electron holography. Dipolar domain walls do not lie preferentially along macrograin boundaries but depend on the overall shape of the assembly, meaning magnetostatic energy dominates. The domain structures are imaged at different temperatures for both monolayer and bilayer arrays. The domain wall contrast in the monolayer region is visible until 575 °C, and the magnetic order parameter steeply drops toward the temperature. In the bilayer region, finer and more complicated domains are formed. © 2011 American Institute of Physics. [doi:10.1063/1.3556562]

Dipolar ferromagnetism was theoretically predicted by Luttinger and Tisza,¹ who showed that a face-centered-cubic lattice of point dipoles has a ferromagnetic ground state. Dipolar ferromagnetism is distinguished from the common ferromagnetic order due to exchange interactions. Experimental evidence for this state was first obtained in rare-earth salts, with a dipolar Curie temperature $T_{c,dip}$ of ~ 0.1 K.² Later calculations^{3,4} suggested the feasibility of the dipolar ferromagnetic state at higher temperatures for dense assemblies of monodomain magnetic nanoparticles. Magnetic force microscopy⁵ and x-ray photoemission electron microscopy⁶ have provided experimental evidence of dipolar ferromagnetic ordering in nanoparticle assemblies. Electron holography^{7,8} (EH) revealed the existence of vortexlike magnetic domains in monolayers of 8 nm ϵ -Co nanoparticles with a 4.2 nm edge-to-edge separation. The domains were stable over at least 1 h at 108 K. However, questions remain about the nature of the magnetic ordered state. In this paper we use transmission electron microscopy (TEM) to image the structural arrangement of Fe_3O_4 nanoparticles, and Fresnel Lorentz microscopy (FLM) and EH to image their magnetization patterns at different temperatures. We show that the overall shape of the assembly, rather than the macrograin boundaries of the nanoparticle arrays, dominates the magnetization pattern. Temperature-dependent magnetic imaging from 24 to 605 °C shows the evolution of these magnetostatic domains and provides direct evidence of a dipolar ferromagnetic phase transition.

Magnetic nanoparticles of Fe_3O_4 were synthesized by decomposition of iron acetylacetonate in oleic acid and oleylamine surfactants.⁹ The nanoparticles of 13.4 ± 1.5 nm diameter were used to form a Langmuir layer on immiscible liquid using a minitrough. After allowing the oleic acid to evaporate, the nanoparticles were compressed to obtain close-packed monolayers, and then transferred to carbon-coated TEM grids by the Langmuir-Schaefer method. Fig-

ures 1(a) and 1(b) show the low magnification TEM image of the array and the higher magnification image in the array region, respectively.¹⁰ Small black dots in the array in Fig. 1(a) were areas with particle agglomerates. The particles were separated by the surfactant, with an edge-to-edge separation of 1.6 ± 0.6 nm, and had random crystallographic orientations. The arrays have hexagonal ordering, with some

FIG. 1. (Color) Monolayer array of surfactant-coated Fe_3O_4 nanoparticles. (a) Low magnification TEM image near the array film edge. (b) Higher magnification image to see the structural arrangement of nanoparticles. The insets show the FT of regions within a single macrograin. (c) Color map of the macrograin orientations. Different colors are used to indicate the rotation angle α . (d) An over-focused FLM image (72 μm defocus) of the same region as Fig. 1(a), showing the magnetic domain walls. The arrows indicate the direction of collectively ordered magnetization. The error in determining the wall positions was 0.15 μm . The positions are superimposed on the structural macrograins as dashed lines in Fig. 1(c). Circles indicate where black and white domain walls appear to converge near a structural grain boundary.

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FIG. 2. FLM images of domain walls for a region containing both ML and BL arrays, as a function of temperature, (a) 24 °C, (b) 400 °C, (c) 500 °C, (d) 530 °C, (e) 550 °C, (f) 605 °C. The lightest regions indicate a carbon supporting film without nanoparticles. The medium contrast regions are ML, and the darker regions are the BL.

5-(red) or 7-(blue) fold packing along macrograin boundaries, as shown by the black line in Fig. 1(b). The relative orientations of the macrograins are quantified from Fourier transformation (FT) images of each grain. The insets of Fig. 1(b) show hexagonal patterns with a relative rotation angle $\alpha=23^\circ$, where we define α as illustrated in Fig. 1(c). We used this method to map the macrograins and determine their relative orientations as shown in Fig. 1(c), where the orientations are distinguished by different colors. The grain sizes ranged from 0.3–2.0 μm .

When an intermediate lens of the TEM¹⁰ was defocused to take FLM image in the same region, dipolar ferromagnetic domains were observed; domain walls appear as white and black lines in Fig. 1(d). The domain wall contrast reversed when the defocus direction was changed from the over-focus to under-focus. More complicated and smaller domains were also observed in some regions. The positions of the main domain walls are drawn as dotted lines in Fig. 1(c). While the magnetic domains and structural macrograins are not greatly different in size for this sample, earlier work⁸ on monolayers with structural order only a few nanoparticles across also showed micron-sized magnetically ordered regions. Magnetization measurements indicated much lower coercivity than in dilute dispersions, due to magnetocrystalline anisotropy (K) averaging. For particles with relatively low K, magnetostatic interactions are believed to dominate the domain structure. The magnetic domain walls do not lie along the macrograin boundaries, as might be expected.¹¹ Larger gaps, such as the V-shaped tear in the sample of Fig. 1(a), lead to domain walls that are predominantly parallel or perpendicular to the edges. The black and white domain walls often terminate together at a macrograin boundary where there are defects, vacancies and a large change in the orientation angle α , as has been seen in soft magnetic materials with $\Delta\alpha>20^\circ$.¹²

Figures 2(a)–2(f) show FLM images taken at different temperatures. The area had monolayer (ML) and bilayer (BL) regions, which have two close-packed layers of nanoparticles and are formed during the self-assembly process.¹³ A region containing both ML and BL regions is shown in the higher magnification TEM image inset in Fig. 2(a). In the BL region, smaller and more complicated domains were formed.

FIG. 3. (Color) Temperature dependence of magnetic induction maps determined from the reconstructed phase images of the same region as that shown in Fig. 1(a), (a) 24 °C, (b) 400 °C, (c) 500 °C, (d) 550 °C, (e) 575 °C, and (f) 605 °C.

Note that the domain wall positions in the ML often continue into the BL region, as indicated by arrows in Fig. 2(a). Between 24 and 400 °C there were reductions in the contrast of the domain walls, as expected with a reduced magnetic order parameter (OP) (Ref. 14) but the wall positions were unchanged. As the sample was heated to 500 °C, the walls surrounding smaller domains fluctuated in both the ML and BL regions, and some were absorbed into larger domains [Figs. 2(b) and 2(c)]. Between 530 [Fig. 2(d)] and 550 °C [Fig. 2(e)], almost all the domain walls in the BL region disappeared. In the ML region between 550 and 580 °C, the domain walls fluctuated rapidly, and then disappeared by 605 °C, as shown in Fig. 2(f). This means that the dipolar ferromagnetic interaction in the BL region is weaker than that in the ML region. When the temperature was decreased to 24 °C, domain structures similar to those in Fig. 2(a) were reconstructed. When the arrays were re-imaged at higher magnification after cooling, the structural order of the nanoparticles was unchanged, even though the surfactant molecules had decomposed. Electron beam irradiation stabilizes the positions of the particles, and some remnants of the surfactant remain as a glassy carbon matrix.¹⁵

To quantitatively evaluate the dipolar ferromagnetic field, EH was performed in the ML region of Fig. 1(a) after the heating experiment described above. Figures 3(a)–3(f) show the temperature dependence of the magnetic flux distribution obtained by EH.¹⁰ Here the black lines in the domains correspond to magnetic flux lines, and 2.0×10^{-16} Wb of flux flows between a pair of lines. The color is used to show the in-plane magnetization direction.¹⁶ The red and green regions indicate stripe domains with magnetization directed downward and upward, respectively. The brighter colors indicate larger flux density. Strong color contrast near the array film edge is an artifact that arises from spatial frequency filtering during the EH reconstruction processes.¹⁷ The spatial resolution was 0.24 μm which determined from the fringe spacing in the holograms. Micron-sized stripe domains (indicated by “A–D”), similar in pattern to those of Fig. 1(d), were observed in the right region at 24 °C in Fig. 3(a), however, more complicated and smaller domains were formed in the left region. As the sample temperature increased, the smaller domains disappeared by 500 °C and then the main domains gradually collapsed from the left side.

The magnetic OP is the ratio of the experimental flux density to the theoretical value with complete alignment of

FIG. 4. (Color online) Magnetic OP as a function of temperature obtained from EH images in Fig. 3.

the dipoles.^{8,10} When the dipoles fluctuate in plane as illustrated in Fig. 4, the OP is less than 1.0. We measured the OP in the main domains “A–D” at each temperature,¹⁰ and plotted the average values as a function of temperature (Fig. 4). The error bars indicate the standard deviation of the OP values. The curve has a similar trend to that in the plot Denisov *et al.*¹⁴ calculated for 3 nm Co particle ensembles. In their report, stronger dipole interaction brings higher $T_{c,dip}$. This is consistent with the EH results [Figs. 3(a)–3(f)] that the $T_{c,dip}$ in the large domains (about 580 °C) were higher than that in the small domains (less than 500 °C). The OP values less than 200 °C show 0.26–0.44, indicates that the dipoles fluctuate with high angles: 64°–75° in each domain,¹⁰ as in illustration of Fig. 4. In 8 nm ϵ -Co nanoparticle arrays, the OP values were 0.4–0.6 at –165 °C (108 K).⁸ Therefore, this dipole fluctuation with high angle is one of the typical features of dipolar ferromagnetism, which is different from “ripple” with small angle (a few degrees) in exchange-based ferromagnetism.

Our results demonstrate the existence of dipolar ferromagnetic 180° domains in well-ordered arrays of 13.5 nm Fe_3O_4 nanoparticles using FLM and EH. The domain walls do not lie preferentially along the macrograin boundaries but depend on the shape of the array which affects the magnetostatic energy. In the long-range dipole interacting arrays, the domain sizes and shapes remain fixed over time, up to ~500 °C. The walls surrounding the smaller domains disappeared at lower temperatures than those of the larger domains, and domains in ML were larger and more stable than

those in BL. Moreover, the large magnetic domains in ML region were visible at temperatures as high as 575 °C, close to the T_c of bulk Fe_3O_4 (585 °C). This supports the existence of a true phase transition, with spontaneous development of long-range magnetic order. While the OP was well under 1.0 even at 24 °C, this might be improved if there were crystallographic alignment of the nanoparticles. Dipolar ferromagnets are not merely of fundamental interest; they provide an interesting alternative to exchange-based ferromagnets. Because this phase transition can be well above room temperature, dipolar ferromagnets made with high moment metallic particles in an insulating matrix could have high permeability without large eddy current losses. Such nanocomposites could someday replace the ferrites now used in phase shifters, isolators, circulators, and filters in microwave communications and radar applications.

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