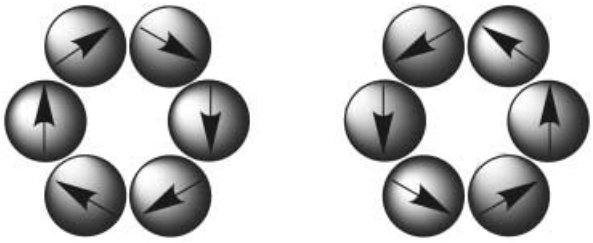


Figure 1. Flux-closure domains produced by cyclic ensembles of magnetic dipoles, in clockwise and counterclockwise configurations.

Magnetic Effects in Nanomaterials

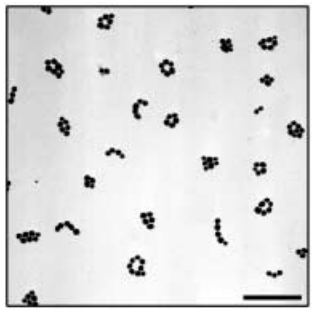
Flux Closure in Self-Assembled Cobalt Nanoparticle Rings**

*Steven L. Tripp, Rafal E. Dunin-Borkowski, and Alexander Wei**

The drive toward ultradense information storage has stimulated considerable interest in magnetic nanostructures, particularly those with bistable domains and minimal crosstalk between elements.[1] Magnetic rings are appealing candidates for such applications because their magnetostatic fields can be entrained into chiral domains commonly referred to as flux-closure (FC) states (see Figure 1). Here magnetic dipoles are aligned into a closed circuit and produce a net moment of zero, which minimizes both the magnetic energy and the field outside of the ring. Bistable FC states have been used extensively in early data-storage applications involving ferrite cores, which served as bits in electronically addressable magnetic memory devices.[2] More recently, magnetic rings have been proposed as elements in novel device architectures for magnetoresistive random-access memory (MRAM), with subsequent studies directed at the FC states of Co microrings fabricated by lithography.[3–5] However, these structures are far from the physical size limit of flux closure, which ultimately depends on the magnetic remanence of the host material.

In this Communication, we demonstrate that single-walled Co nanoparticle rings can support stable FC states at room temperature, using off-axis electron holography to visualize magnetic flux with nanometer spatial resolution.[6] These bracelet-like rings are created by dipole-directed self-assembly, with dimensions well below the limits of conventional lithography: A ring of six 27-nm Co particles (the average size used in this study) is less than 100 nm in diameter.[7,8] Self-assembled nanorings also have intriguing possibilities for integration with nanopatterned surfaces, with application toward spin-polarized electronic devices.[3]

Co nanoparticles encapsulated in a 3–4 nm CoO shell (27 ± 4 nm, 10^{12}–10^{13} particles mL^{-1}) were dispersed in toluene with varying amounts of *C*-undecylcalix[4]resorcinarene (**1**) as a surfactant (1–100 μM) as previously described, then deposited onto carbon-coated copper grids and dried in air using a standardized procedure.[7] These dispersion conditions produce a variety of self-assembled nanostructures as imaged by transmission electron microscopy (TEM) including five- and six-particle rings, short chains, and close-packed aggregates containing three or more particles (see Figure 2). A statistical analysis suggests that the relative yield of dipole-



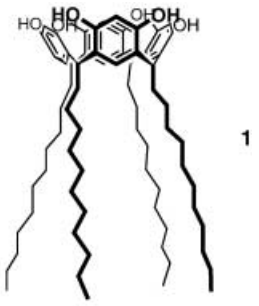


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Figure 2. TEM image (Philips EM-400, 80 kV) showing nanoparticle rings and chains formed by dipole-directed self-assembly. Co nanoparticles (27 ± 4 nm, 10^{12} particles mL^{-1}) were dispersed in toluene with resorcinarene **1** (10^{-6} M), then deposited as a thin wetting layer onto a carbon-coated Cu grid and dried in air. Scale bar = 250 nm.

[*] Prof. A. Wei, Dr. S. L. Tripp
Department of Chemistry, Purdue University
West Lafayette, IN 47907 (USA)
Fax: (+1) 765-494-0239
E-mail: alexwei@purdue.edu
Dr. R. E. Dunin-Borkowski
Department of Materials Science
University of Cambridge, Pembroke Street
Cambridge CB2 3QZ (UK)

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directed aggregates (rings and chains) is optimal at an initial concentration of 10^{12} particles mL^{-1} and surfactant concentrations of 10 μM or more (see Figure 3). The latter parameter is important for increasing the viscosity of the residual wetting layer, which stabilizes the rings against van der Waals "collapse" during the drying stage.[7] However, higher levels of **1** correlate with a greater percentage of nanoparticles in open chains, which indicates that ring formation is most favored at intermediate surfactant concentrations. The self-assembled rings and chains captured in the TEM images do not necessarily represent an equilibrium distribution: While these nanostructures are likely to equilibrate in solution at zero field, additional shear forces during surface adsorption and drying may affect the final distribution of immobilized species.

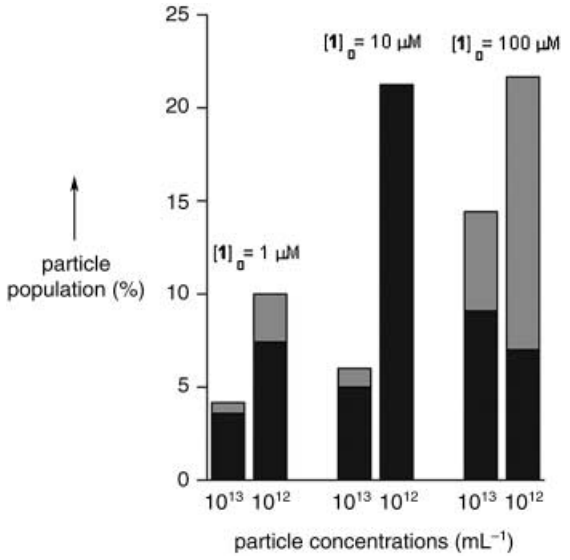

Figure 3. Distribution of Co nanoparticles observed in dipole-directed assemblies, as a function of initial particle and surfactant concentrations. Particle populations in self-assembled rings and chains are plotted as dark and light grey areas, respectively. Particle counts were taken over areas of at least 8 μm^2.

Remanent magnetic FC states in individual nanoparticle rings were recorded at room temperature under zero-field conditions by electron holography (see Figure 4). Continuous magnetic flux lines revealed the in-plane induction to be confined within each ring ensemble, despite irregularities in particle shape and deviations from radial symmetry in the self-assembled nanostructures. Magnetic force microscopy did not indicate any out-of-plane magnetization, which signified the absence of magnetic vortex cores such as those observed in planar magnetic disks.[9–11] These observations are consistent with a magnetostatic description of FC states in cyclic ensembles of single-domain particles.[12]

Electron holography records additional phase information which reveals the handedness of the magnetic domains within the Co nanoparticle rings (see Figure 4, bottom row). A statistical sampling of FC states indicates an approximately 50:50 (racemic) mixture of clockwise and counterclockwise ground-state configurations, to which the rings relaxed after exposure to a 2 T out-of-plane magnetic field. The chiral FC states are stable at room temperature and persist in low magnetic fields. This coercivity implies cooperativity in magnetic coupling, and suggests that FC states may be achieved at room temperature using even smaller nanoparticles.[13] This is in stark contrast to vortex states in thin magnetic disks of similar material, which are stable only for diameters of 100 nm or more.[14]

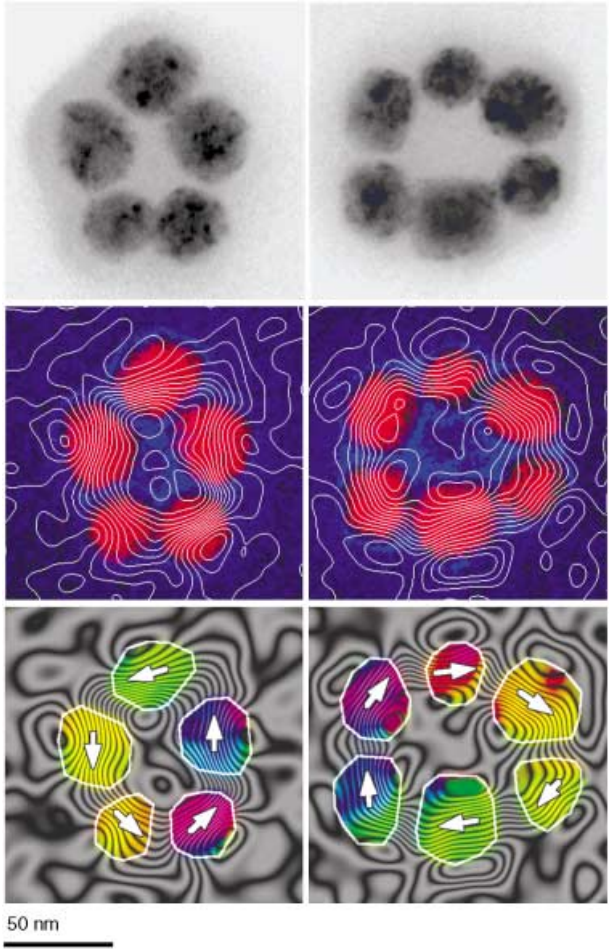

Figure 4. TEM and electron holography images of self-assembled Co nanoparticle rings, taken with a Philips CM-300 equipped with a Lorentz lens (300 kV). Samples were briefly subjected to plasma cleaning prior to TEM analysis. Top: bright-field images of nanoparticle rings; middle: magnetic FC states imaged in zero-field conditions using off-axis electron holography and displayed in the form of contours, superimposed on elemental maps obtained by energy-filtered TEM analysis (red = Co, blue = C). The magnetic flux enclosed between adjacent contours is $h/128e$; bottom: direction of the magnetic flux indicated using arrows and colors (red = right, yellow = down, green = left, blue = up). The magnetic contribution to the measured holographic phase shift was separated from the mean inner potential contribution by taking the difference between phase images recorded with the sample turned over in the electron microscope.

The Co nanoparticle rings presented here offer at least two unique opportunities for studying magnetism on the nanoscale. First, the FC states comprise discrete single domains, whose magnetization behaviors and reversals can be modeled precisely by micromagnetic simulations.[12]

Second, the chirality of the FC states can be switched by out-of-plane or circularly polarized magnetic fields generated by electrical currents, as demonstrated recently with a submicron magnetic cylinder.[15] Explorations in this direction would require integrating magnetic nanorings with electrically conductive nanowires. Self-assembly may prove to be pivotal in the construction of such hybrid nanomaterials.

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