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Reversal of Flux Closure States in Cobalt Nanoparticle Rings With Coaxial Magnetic Pulses**

By Takeshi Kasama, Rafal E. Dunin-Borkowski, Michael R. Scheinfein, Steven L. Tripp, Jie Liu, and Alexander Wei*

Soft magnetic rings are candidate materials for nonvolatile random-access memory (NVRAM) devices, owing to their capacity to support bistable flux closure (FC) domains.^[1,2] These chiral states have zero magnetostatic energy, and can be closely packed with minimal coupling for ultradense information storage. FC states have been studied in micrometer- and sub-micrometer-sized magnetic rings, and can be switched by coaxial currents^[3] or in-plane magnetic fields ($H_{x,y}$).^[2,4-7] The fundamental rate limit in FC switching has been determined to be in the low-picosecond range, orders of magnitude faster than the switching speeds in present-day microprocessors.^[8] However, magnetic rings are most commonly prepared by top-down lithographic methods, which face some serious challenges to produce nanostructures with lateral dimensions below 100 nm.^[9,10]

We have been investigating the self-assembly and collective magnetic behavior of Co nanoparticle rings as an alternative to lithographically fabricated nanorings.^[11] The Co nanoparticle rings can be produced by dipole-directed assembly with diameters well below 100 nm, yet support stable FC states at room temperature.^[12] The Co nanoparticle rings have been examined under zero-field conditions by off-axis electron holography, a transmission electron microscopy (TEM)

technique for imaging in-plane magnetization,^[13] which showed the remanent FC states to be consistent with a magnetostatic description of a cyclic ensemble of magnetic dipoles.^[14]

Here we show that the polarization of individual FC states can be switched reversibly by applying coaxial magnetic pulses (H_z) in alternating directions (Fig. 1). The changes in FC polarization were recorded by electron holography at zero field in between H_z pulses. The H_z -induced switching was also simulated by micromagnetics calculations, which suggested the existence of novel metastable states at intermediate H_z prior to FC reformation. To our knowledge, such H_z -induced FC switching has not been reported at either the macroscopic or microscopic level, and may represent a phenomenon unique to magnetism on the nanoscale.

Weakly ferromagnetic Co nanoparticles (25–30 nm) with a thin CoO shell (ca. 3 nm) were prepared as previously described and dispersed in a toluene solution with a macrocyclic surfactant (C11 resorcinarene), then deposited at room temperature onto a Cu grid coated with a holey carbon film. A significant fraction of Co nanoparticles were deposited as rings, assembled via magnetic dipolar interactions.^[11,12] Individual rings comprising 5–11 particles were examined by electron holography, which revealed well-defined FC states at 298 K as a mixture of clockwise (CW) and counterclockwise (CCW) polarizations (Fig. 2). In each case the magnetic induction was essentially confined within the annular ensemble, despite the fact that many of the nanoparticles were irregularly shaped, and the rings themselves were not fully symmetrical. The as-prepared Co nanoparticle rings were remarkably stable against oxidation, and could support FC states even after 3 years of storage under ambient conditions.

Electron holography was also used to record changes in FC polarization following exposure to H_z pulses of varying strengths.^[13,15] The direction of the H_z pulses was defined relative to an initial exposure of the Co nanoparticle rings to a strong coaxial magnetic field ($H_z = +2$ T), prior to their analysis under zero-field conditions. In this study, the duration of the magnetic “pulse” was on the order of seconds, produced by manually changing the current in the TEM objective lens. However, pulses of much shorter duration can be expected to have similar effects on the FC domains (see below).

Co nanoparticle rings were first subjected to magnetic pulses of up to 2 T in the $+z$ direction, then re-examined at zero field by electron holography. Remarkably, no scrambling of FC

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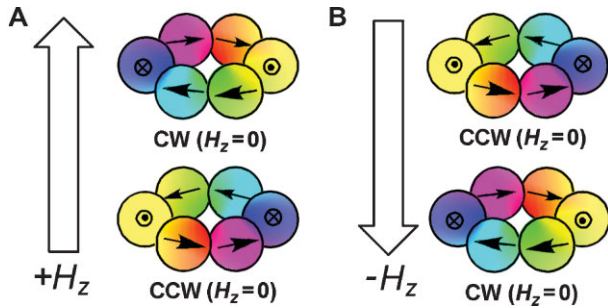


Figure 1. H_z -induced FC reversal in individual Co nanoparticle rings. A) A mixture of FC states (clockwise (CW) and counterclockwise (CCW)) is observed under zero-field conditions, following exposure to a field of 2 T within the electron microscope column. B) Applying an H_z pulse in the opposite direction switches the polarization of the initial FC states.

states was observed: the initial polarization was restored in every nanoparticle ring, regardless of the strength of applied H_z (Supporting Information). The rings were also exposed to 2 T pulses with a significant in-plane component by introducing a 15° tilt in the sample stage, but again no changes in FC polarization were observed.

In contrast, the FC states can be switched by applying a coaxial magnetic pulse in the $-z$ direction. The threshold H_z values which define the coercivities for FC switching are determined in part by the collective magnetization of the nanoparticles. Rings assembled from polycrystalline Co nanoparticles experience FC reversal at H_z values between 1600 and 2500 Oe (Fig. 2; $1 \text{ Oe} = 10^3/4\pi \text{ A m}^{-1}$), whereas rings assembled from Co nanocrystals with face-centered cubic (fcc) structure exhibit significantly higher thresholds for H_z -induced FC reversals, up to 4000 Oe (Fig. 3). These measurements indicate that the coercivity of the Co nanoparticle rings is more strongly influenced by magnetocrystalline anisotropy and the strength of interparticle coupling than by ring size or other geometric factors.

Coaxial field-induced FC switching appears to be a fully reversible process. Subsequent application of an H_z pulse in the $+z$ direction results in a second FC reversal, and reapplying H_z in the $-z$ direction produces a third reversal (Fig. 4). We

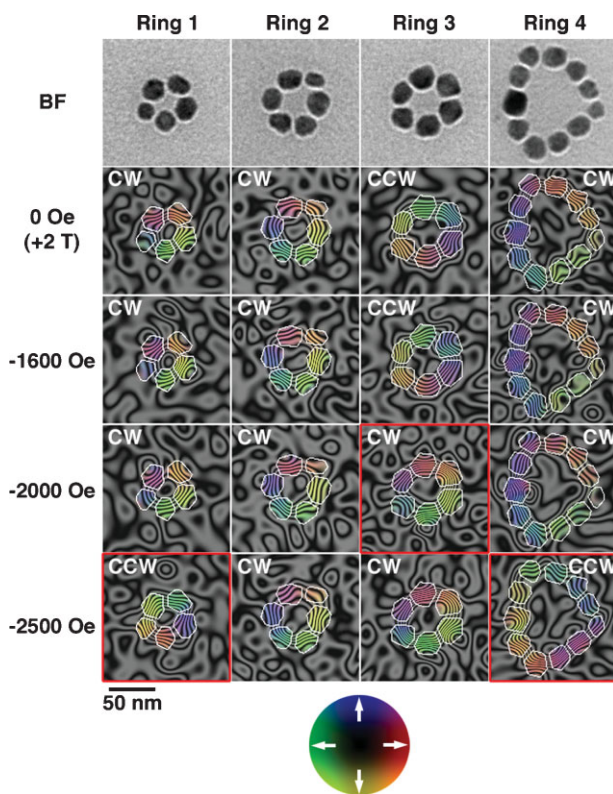


Figure 2. FC polarizations and magnetic induction maps of polycrystalline Co nanoparticle rings measured by electron holography, following exposure to a coaxial magnetic pulse (H_z). Top row: bright-field TEM images; 2nd row: initial FC states, with prior exposure to a coaxial magnetic field ($H_z = +2 \text{ T}$); 3rd row, after exposure to $H_z = -1600 \text{ Oe}$: no changes in FC states; 4th row, after exposure to $H_z = -2000 \text{ Oe}$: FC reversal in Ring 3; 5th row, after exposure to $H_z = -2500 \text{ Oe}$: FC reversals in Rings 1 and 4. FC polarization is portrayed using a color wheel (red = right; blue = up; green = left; yellow = down). The contour spacing is 0.065 rad, and correlates inversely with projected in-plane magnetic flux.

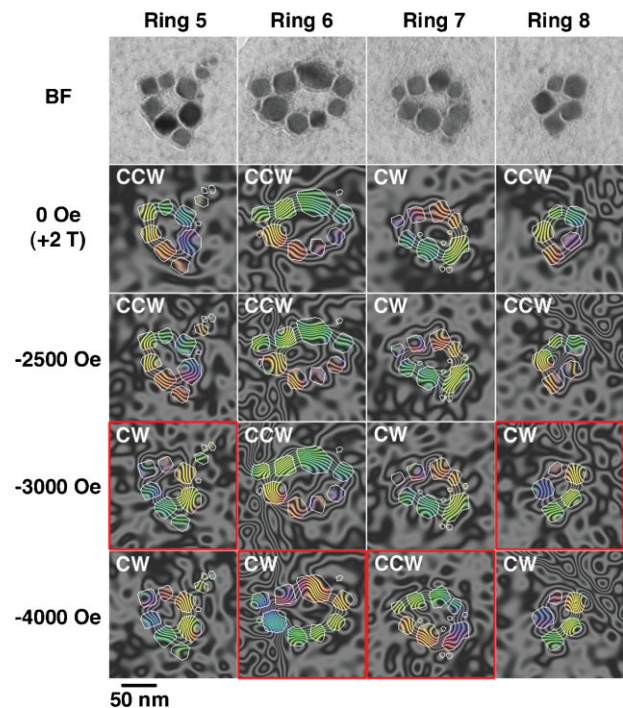


Figure 3. FC polarizations and magnetic induction maps of fcc Co nanoparticle rings, following exposure to H_z pulses. Top row: bright-field TEM images; 2nd row: initial FC states, with prior exposure to a coaxial magnetic field ($H_z = +2 \text{ T}$); 3rd row, after exposure to $H_z = -2500 \text{ Oe}$: no changes in FC states; 4th row, after exposure to $H_z = -3000 \text{ Oe}$: FC reversals in Rings 5 and 8; 5th row, after exposure to $H_z = -4000 \text{ Oe}$: FC reversal in Rings 6 and 7 (no switching observed after exposure to $H_z = -3500 \text{ Oe}$). FC polarization is portrayed using a color wheel; contour spacing is 0.196 rad.

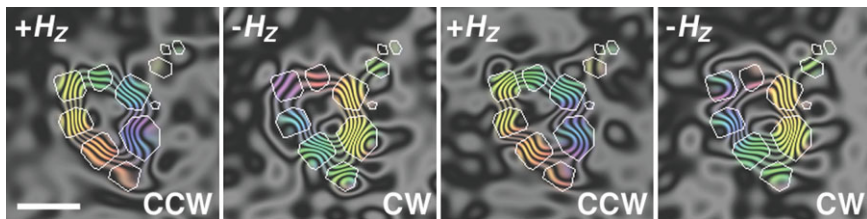


Figure 4. Multiple FC reversals of a 7-membered Co nanoparticle ring (Ring 5), switched by alternating $+H_z$ and $-H_z$ pulses. Bar = 50 nm.

note that the FC switching conditions are not universal: in the polycrystalline Co nanoparticle sample, some rings experienced an FC reversal with H_z fields as low as several hundred Oe, and in at least one case no switching was observed (Ring 2, Fig. 2). Nonetheless, FC switching can be expected in most Co nanoparticle rings, and the reversals are correlated strongly with the history of prior coaxial magnetizations.

The H_z -induced reversals in FC polarization were simulated using magnetodynamic calculations based on the Landau–Lifshitz–Gilbert equations (LLG Micromagnetics). These simulations reveal the effect of coaxial fields on the magnetic induction of nanoparticle rings in three dimensions and at variable H_z . In contrast, electron holography describes in-plane induction measured from phase shifts projected in the z -direction at zero field. A construct based on a seven-membered Co nanoparticle ring (height = 25 nm) was used to model the magnetic induction (Fig. 5). Local magnetic moments within the nanoparticle ring were calculated as discrete cubic elements (3.5 nm) with a time step of 0.2 ps,

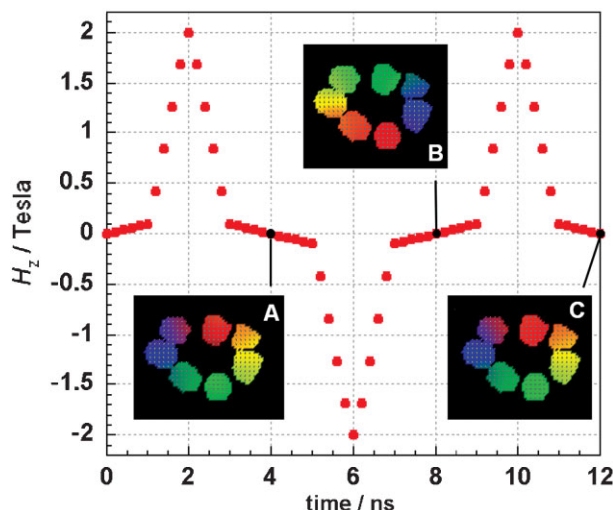


Figure 5. Magnetodynamic simulation of FC switching in Co nanoparticle rings, following exposure to alternating H_z pulses. A) Initial FC state (CW) at zero bias after a +2 T pulse; B) FC reversal to CCW after a -2 T pulse; C) Second FC reversal to CW after another +2 T pulse. Local magnetic moments were calculated as discretized cubes (3.5 nm) with a time step of 0.2 ps, using a gyromagnetic frequency of 17.6 MHz Oe $^{-1}$ and a phenomenological damping constant of 1.0.

which was sufficient to equilibrate the net magnetization energy in between steps.

The nanoparticle ring construct was subjected to three consecutive magnetic pulses alternating in the positive and negative direction (± 2 T). Fully restored FC states were observed at zero field: the FC polarization following the first (positive) H_z pulse was found to be CW (Fig. 5A), and served as the initial FC state in accord with the electron holography studies. Applying a second pulse in the

$-z$ direction produced a FC reversal to CCW (Fig. 5B), and applying a third pulse in the $+z$ direction switched the FC polarization back to CW (Fig. 5C). These simulations reproduce the multiple FC reversals recorded in Figure 4, lending further support to a magnetodynamic correlation between FC states and the direction of the coaxial magnetic pulse.

Examination of the ring magnetization prior to FC reformation reveals a novel intermediate state. The magnetization evolves from a coherent, coaxially aligned domain with $+z$ orientation (Fig. 6A and D) to a stacked “double vortex” bidomain, such that the in-plane induction in the upper and lower halves of the ring is polarized in opposite directions (Fig. 6C and E). A similar bidomain has been postulated to exist in soft magnetic nanotubes at low H_z , also based on micromagnetics simulations.^[16] This metastable bidomain persists until H_z drops below +800 Oe, which results in the annihilation of the double vortex and a restoration to an FC-like state (Fig. 6C and F).

The existence of a double vortex in the nanoparticle ring precludes the use of a simple Ising model to describe the magnetodynamics leading to FC reversal.^[17] However, it may be instructive to consider the in-plane magnetizations of the upper and lower regions of each particle as distinct subdomains. At +1000 Oe, the top and bottom halves are aligned antiferromagnetically within each particle, and collectively form the double vortex (Fig. 7A). As H_z decreases, local magnetic singularities arise and destabilize the relationship between particle subdomains (Fig. 7B), which quickly reorganize into single domains while simultaneously relaxing into the thermodynamically favored FC state (Fig. 7C and D).

A careful inspection of the simulated magnetization within the nanoparticle ring at $H_z = 0$ reveals that while the total magnetostatic energy is nearly zero, a small net moment in the z direction remains (ca. 10^{-4} G). This remanent magnetization (M_z) is aligned by prior H_z exposure, and may provide the basis for correlating FC reversals with coaxial magnetic pulses. While the magnetodynamic correlation of M_z with FC polarization in H_z -induced FC reversals remains to be confirmed, its putative role may be uniquely relevant to the case of magnetic nanoparticle rings, as simulations of other types of nanostructures do not reveal comparable memory effects (unpublished work). It is worth mentioning that magnetodynamic exchanges between M_z and in-plane FC

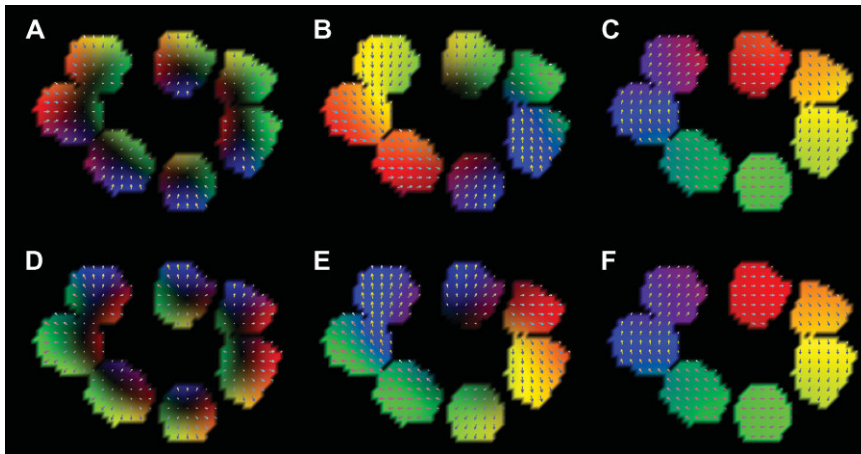


Figure 6. Micromagnetics simulations of 7-membered Co nanoparticle ring in coaxial magnetic fields, with top (A,B,C) and bottom (D,E,F) cross sections viewed along the +z axis. A) and D) Nanoparticle ring exposed to $H_z = +2$ T; regions dominated by coaxial magnetization appear dark. B) and E) Nanoparticle ring exposed to $H_z = +1000$ Oe supporting a “double vortex” bidomain; the polarizations of the top and bottom halves of the ring are CCW and CW, respectively. C) and F) Nanoparticle ring exposed to $H_z = +800$ Oe, with reformed FC (CW) state.

states can be decoupled by applying coaxial ac magnetic pulses, which have been shown recently to reverse the direction of vortex cores in magnetic disks independently of FC polarization.^[18]

In summary, the bistable FC states in self-assembled Co nanoparticle rings can be switched by coaxial magnetic pulses, with threshold H_z values ranging from 1600 to 4000 Oe. Additional FC reversals can be induced by switching the direction of H_z , offering a unique mechanism for inverting magnetic data. The FC switching can be reproduced by magnetodynamics calculations, which further suggest a remanent M_z component embedded within the FC states not observable by electron holography, and the existence of a transient double-vortex state immediately following the H_z pulse. The intriguing behavior of Co nanoparticle rings

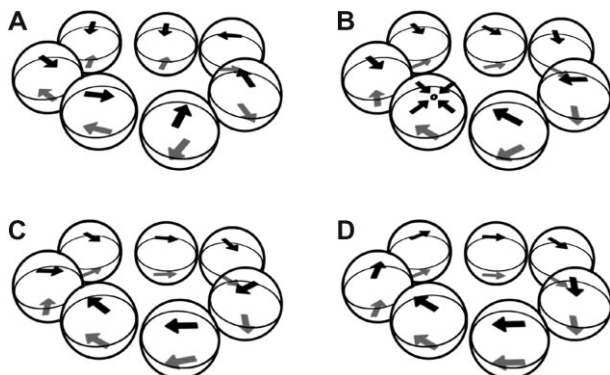


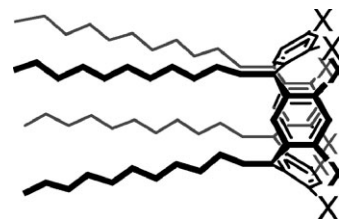
Figure 7. Evolution of in-plane magnetization in upper and lower halves of Co nanoparticle rings, based on magnetodynamic simulations between $H_z = +1000$ and $+800$ Oe. Antiferromagnetically aligned bidomains in individual nanoparticles collectively form the double vortex state (A), but are destabilized by the onset of local singularities (B), resulting in the restoration of single domains (C) and their reorganization into a coherent FC state (D).

and their relevance to novel NVRAM concepts warrant further study.

Experimental

Synthesis and Self-Assembly of Polycrystalline and fcc-Co Nanoparticle Rings: Polycrystalline Co nanoparticles were prepared by the thermolysis of $\text{Co}_2(\text{CO})_8$ in toluene in the presence of a macrocyclic surfactant, C11 resorcinarene tetraphosphinite (**1**), followed by magnetically induced precipitation to obtain weakly ferromagnetic nanoparticles with an average particle size of 27 nm [11]. Co nanocrystals with fcc structure were prepared by thermolysis of $\text{Co}_2(\text{CO})_8$ in the presence of C11 resorcinarene **2** (without **1**), followed by magnetically induced precipitation. The Co nanoparticles were redispersed in a toluene solution (ca. 10^{12} particles mL^{-1}) containing surfactant **2** at millimolar concentration, and deposited onto a Cu grid coated with a holey carbon film. The self-assembly of Co nanoparticle rings can be attributed to

magnetic dipolar interactions, as previously established [11,12].



1: X, X = -P(Ph)
2: X = OH

Off-Axis Electron Holography [13,15]: Images were obtained with a Philips CM-300 field-emission gun TEM (300 kV) equipped with a Lorentz lens, a rotatable electron biprism (200 V) located in the selected-area aperture plane, and a Gatan multiscan CCD camera (1024 × 1024 pixels). The holographic interference fringe spacing is 3 nm with a contrast of 25%. Samples were briefly subjected to plasma cleaning prior to TEM analysis. 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. The divergent magnetic contours beyond the Co nanoparticle rings (grey areas) are due to statistical noise and/or imperfect subtraction of the mean inner potential contribution of the carbon support film.

It may be noted that the spacing between the phase contours (in radians) is significantly different in Figures 2 and 3. The increased spacings and coercivities of the nanoparticle rings in Figure 3 may be attributed to larger particle size, lower surface oxidation, higher magnetocrystalline anisotropy, or a combination of the above.

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