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Magnetoresistive telegraph noise in Langmuir-Blodgett films of colloidal magnetite nanocrystals as seen via scanning tunneling microscopy

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Temperature-dependent fluctuations in the local current passing through close-packed magnetite nanocrystal (NC) films were probed by scanning tunneling microscopy. This phenomenon, which peaked near the blocking temperature (T_b), reflects spin-polarized tunneling fluctuations due to NC magnetization switching events. The current exhibited telegraph noise patterns, switching between low and high states. Above T_b both states occurred with equal probability while below it the high current state dominated, which is consistent with a superferromagnetic ground state where the NC moments are aligned.

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I. INTRODUCTION

Assemblies of single domain magnetic nanocrystals (NCs) are an important test bed for studies of strongly interacting dipolar systems.[1,2] Their temperature-dependent magnetization switching dynamics[3,4] has been related to the microscopic details of spin-glass transitions,[5–8] and their large interaction domains have been ascribed to dipolar ferromagnetism.[9] The collective magnetic properties are usually studied on macroscopic scales using magnetometry[3,4,10,11] and other ensemble averaging techniques.[5,7,12,13] Single-particle measurements have been made on isolated particles deposited randomly onto a micro-superconducting quantum interference device (micro-SQUID).[14] Spin-polarized scanning tunneling microscopy (SP-STM) has been applied to ferromagnetic metal islands deposited in ultrahigh vacuum on nonmagnetic metals[15,16] and even used to study magnetization switching dynamics in such islands.[17] Typically, such islands are only weakly interacting and their magnetization is primarily influenced by the individual magnetic dot anisotropy properties. Collective magnetic behavior has been imaged by magnetic force microscopy,[18] electron holography,[19] and x-ray photoemission electron microscopy,[2] which showed magnetic domains extending over multiple NCs in the assembly. Here we describe how the local collective dynamics of NC assemblies are revealed by the noise in the tunneling current measured using STM.

Magnetite (Fe_3O_4) is a half metal, with a high degree of spin polarization at its Fermi level, as confirmed by magnetotransport experiments on colloidal Fe_3O_4 NC assemblies.[20,21] In that work magnetoresistance (MR) values up to 10–25 % were obtained around the blocking temperature (~200 K) at moderate magnetic fields and were attributed primarily to interparticle tunneling MR due to the dependence of MR on temperature and bias voltage. The bulk form of magnetite has been studied by SP-STM in the pioneering work of Wiesendanger *et al.*[22] Interestingly, several studies of bulk magnetite surfaces reported on the insulating properties of these surfaces.[23–25] However, the work on our magnetite NCs, both on scanning tunneling spectroscopy of single NCs (Ref. 26) and on multiple NC arrays[20] consistently showed that the tunneling density of states of these NCs is high around zero bias (the Fermi level) and that an insulating gap opens only below the Verwey transition, which occurred at ~100 K for these NCs.[26] In the present work we probed the local fluctuations in current passing through a close-packed Fe_3O_4 NC film using a nonmagnetic STM tip.

The basic experimental concept is illustrated in Fig. 1(a). When tunneling current is measured between a metal tip and a bare gold substrate, the current noise is influenced by shot noise, junction instabilities, and instrumental noise, but is relatively low and sets the baseline noise of this experiment [part 1 of Fig. 1(a)]. When current noise is measured over a magnetic particle in a monolayer thick film over a conductive nonmagnetic substrate the current noise is expected to be similar to the baseline STM junction noise [part 2 of Fig. 1(a)]. In this case, the nonmagnetic tip emits unpolarized electrons and the single magnetic particle acts as a spin filter, but since the original distribution of electron spins is isotropic, to a first approximation, the passing fraction of polarized electrons would be constant irrespective of the magnetization orientation of the NC. However, when the tunneling current passes through at least two Fe_3O_4 NCs, acting as two individual spin filters, it is sensitive to the relative magnetization orientations of the two (or more) NCs. The tunneling conductance is roughly proportional to the square of the spin-polarization level at the Fermi energy of the neighboring magnetic NCs and to the cosine of the angle between their magnetic moments.[23] When the temperature is tuned to a magnetization-switching rate measurable by the STM electronics, near T_b, then a modulation in the tunneling current passing through ≥2 particles may be detected, as shown in part 3 of Fig. 1(a), providing that the interparticle resistance is not negligible compared to the tip-sample gap resistance. The characteristic amplitude and rate of this modulation depend on the temperature, the particle size, the local, time-varying magnetostatic interaction fields, and the interparticle resistances (relative to particle-tip and particle-substrate resistances).

II. EXPERIMENT

Details of the Fe_3O_4 NC film preparation method are given in Ref. 21. In brief, magnetite NCs were synthesized

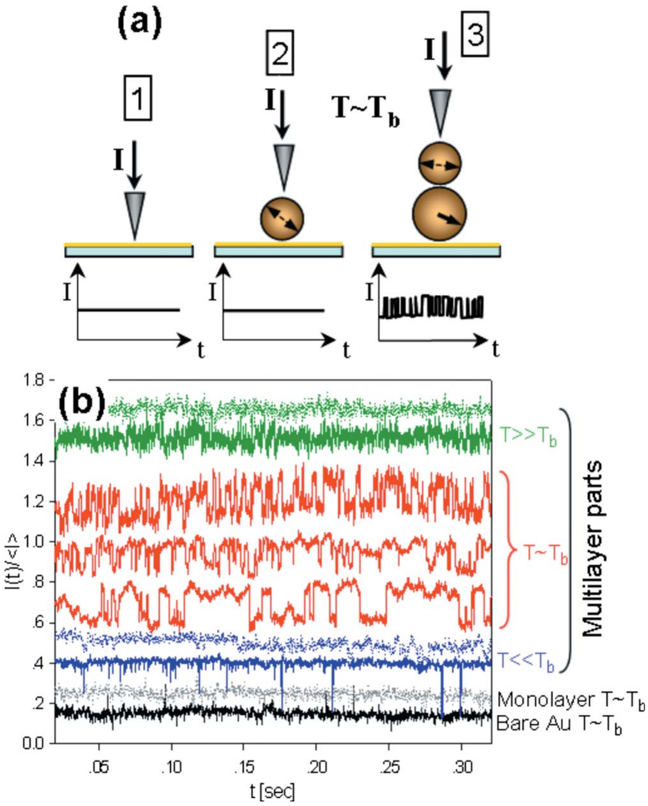

FIG. 1. (Color online) (a) Scheme of the experimental measurement configurations and expected $I(t)$ curves around T_b. Measurement over a bare gold substrate (1) and a magnetite NC monolayer (2) are not expected to produce noise in the tunneling current, while measurements over multiple particle paths (3) should produce magnetization-dependent current fluctuations. (b) $I(t)$ measurements, at several temperatures, over different parts of the samples, normalized to the average current and shifted for clarity. The two lower curves are control experiments performed over bare Au film and a NC monolayer area. The rest of the curves were measured over multilayer areas.

using a simple aqueous coprecipitation process and subsequently coated with oleic acid and dissolved in hexane. The excess oleic acid was removed from solution by several precipitation dissolution cycles. Langmuir-Blodgett (LB) films were prepared by depositing the coated NC heptane solution on an ethylene glycol subphase. All preparation steps were performed under a nitrogen atmosphere in glove boxes to avoid oxidation of Fe_3O_4 to γ-Fe_2O_3. The close-packed NC LB films were deposited on a smooth mica/gold(111) surface for STM measurements as well as carbon coated transmission electron microscopy (TEM) grids, and polycarbonate plastic sheets for magnetometry, and annealed in ultrahigh vacuum at 470 K to evaporate excess oleic acid and increase the interparticle electron tunneling rate. Two samples were prepared from similar batches of Fe_3O_4 NCs with different deposition and annealing conditions, which resulted in slightly different average interparticle separations, and therefore different array resistance and dipolar interaction strength.

The samples were first characterized by (TEM, Tecnai F20, FEI) and their temperature dependent ac magnetic susceptibility was measured using a Quantum Design MPMS-XL5 SQUID magnetometer. The STM experiments were performed using an ultrahigh vacuum, variable temperature system (Omicron Nanotechnology GmbH) using a Pt/Ir tip. The tunneling current as a function of time was measured over individual NCs at various temperatures. The sample temperature was controlled by a liquid-nitrogen-cooled flow cryostat to an accuracy of about ± 5 K. In a typical topography scan the overall tip-substrate resistance was ~ 1 GΩ (tip bias of 0.2 V and current set point of 0.2 nA), but for the $I(t)$ measurements the tip was brought close to a specific NC by setting the current to 100 nA, dropping the junction resistance to ~ 2 MΩ, which is on the order of the tunneling resistance through interparticle junctions.[21] This was required in order to make the interparticle resistance a major part of the overall tip-sample resistance. After the tip approach, the feedback loop was turned off and 2048 current readings were recorded at 160 μs time intervals. $I(t)$ curves were measured 5 times on each selected NC, under a small bias voltage (~ 20 mV). It was previously shown that the magnetite nanocrystals used here have a high conductivity[26] as well as maximal MR (Ref. 21) at low bias conditions. The $I(t)$ values were typically limited to ~ 10 nA, to minimize potential heating of the NCs at the measurement point. During these measurements the tip-sample drift was <1 nm. Vertical drift during the measurement was minimized by using a 0.1 s stabilization delay before turning feedback loop off. Reference curves were collected on bare gold areas at various temperatures. It should be noted that the $I(t)$ data presented here were collected while scanning the topography and without a noticeable tip deterioration after each $I(t)$ measurement.

III. RESULTS AND DISCUSSION

The average diameter of the NCs estimated from the TEM images [as in Fig. 2(b)] was 8.0 ± 2.3 nm and interparticle separation in the range of 0.5–1.5 nm. A TEM image of the film [Fig. 2(a)] and the STM topography image of a Fe_3O_4 NC film [Fig. 2(b)] indicated that the samples were 0–3 particles thick. The height profiles as the one shown in Fig. 2(c) were used to determine which are the multilayer thick parts of the sample (marked as 2 and 3 in the profile). For comparison, a bare gold area on the same substrate was imaged [inset of Fig. 2(b)] and the current noise over that area was probed at several temperatures.

The difference in interparticle dipolar interaction strength between the two samples resulted in different magnetization freezing transition temperatures (T_b), ~ 210 K for sample I and ~ 150 K for sample II, taken from the peak temperature of the imaginary component of the ac susceptibility.[27]

Figure 1(b) shows some typical current traces measured on selected Fe_3O_4 NC locations. Current fluctuations appeared only over multilayer regions and were not observed for a bare gold substrate or over monolayer areas of the films. These fluctuations were strongest around T_b and have often appeared as two-state telegraphic-noise patterns for both samples, significantly diminishing at higher and lower temperatures. Below T_b the occurrences of low-current states

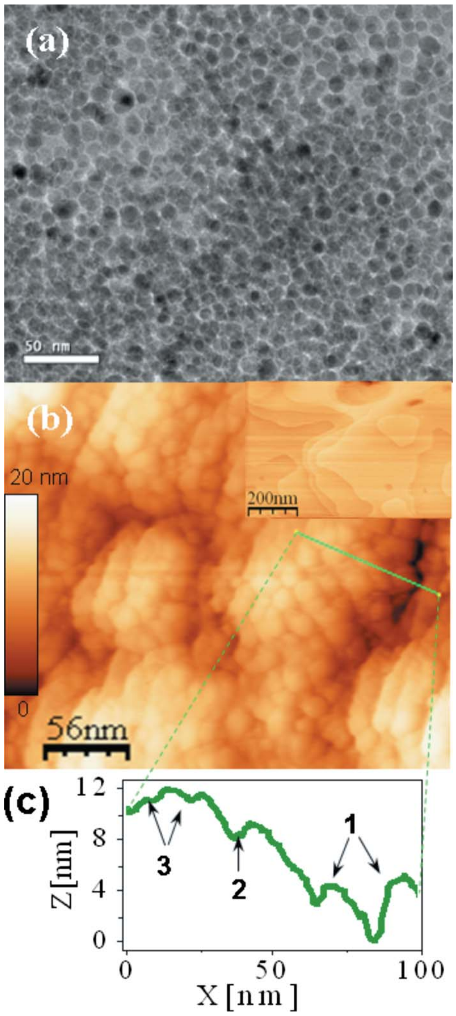

FIG. 2. (Color online) (a) A TEM image of magnetite NC film 1–3 particles thick. The minority of the film area was one monolayer thick (darker particles in STM image) and the majority of the area was 2–3 particles thick. (b) STM topography image with a STM topography image of a bare gold area domain of the same sample (inset). (c) A line profile of the STM topography image. The numbered arrows mark the thickness in terms of nanoparticle layers.

became less frequent than the high-current states (the lower curve corresponding to $T \ll T_b$, for example).

Noise-power spectral-density curves were obtained from the Fourier transforms of the current-time traces. Figure 3(a) exhibits the noise-power spectral density of current traces measured at several temperatures for sample I and on a bare gold substrate. Each curve in Fig. 3(a) is an average of ten traces. There are significant differences between the spectra measured on bare gold and on multilayer areas around T_b in the two samples and between spectra measured at different temperatures over multilayer areas. The lowest noise levels were obtained on bare gold and on the NC multilayer areas at temperatures far from the T_b (154 and 300 K for sample I or 96 and 197 K for sample II). The current fluctuations in those cases had nearly $1/f$ noise characteristics up to about 100 Hz. The highest noise powers obtained were over a multilayer around T_b for both samples. The major difference

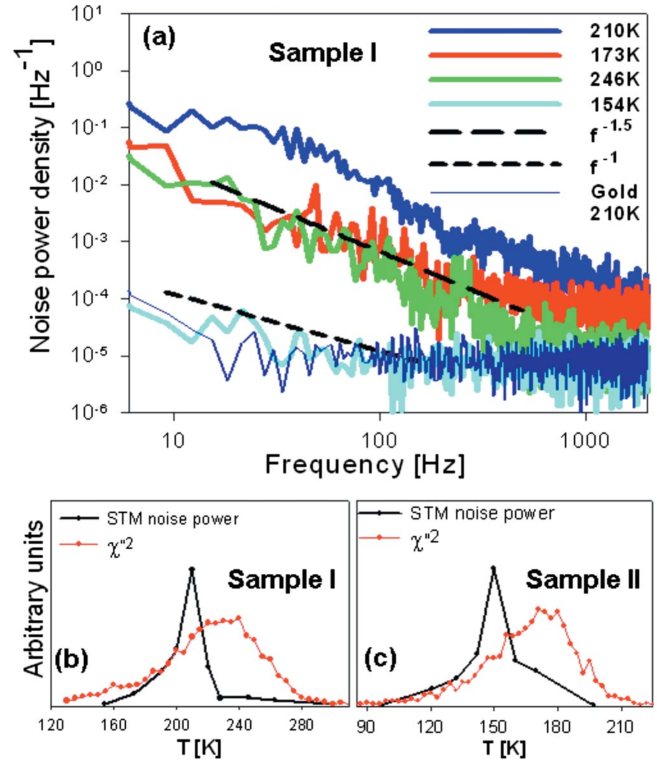

FIG. 3. (Color online) (a) Noise-power spectral density of current traces measured on sample I at several temperatures and on a bare gold substrate. (b), (c) A comparison between the square of the ac magnetic susceptibility data (lower broad peaks) to the power-noise spectral density at 100 Hz (higher sharp peaks) plotted as a function of temperature for the two samples.

occurred around 10 Hz, where the current noise power over multilayer parts was about three orders of magnitude larger than over the bare gold substrate, and diminished toward 1000 Hz. Similar noise variations were previously observed for current noise in lithographically defined magnetic tunnel junctions when studied as a function of magnetic field.[28]

The observed spectral power distributions may be the result of fluctuations with multiple time constants, probably contributed by particles of different sizes or at different local dipolar fields along the conduction path. Similar curves were observed over many multilayer positions at the films, with slight variations in the power amplitude. The plots of the noise-power spectra over the multilayers around T_b roughly fitted a $1/f^{1.5}$ law in the 30–1000 Hz frequency range. This frequency dependence was predicted for Barkhausen noise dominated by long-range dipolar interactions[29] and observed in noise measurements of magnetic tunnel junctions.[28,30] Co NC arrays with weaker dipolar interactions exhibited magnetic noise of the form $1/f^{\alpha}$ with $\alpha \leq 1$,[31] which was measured with a 17.8 μm^2 scanning micro-SQUID detector. Telegraph noise was not observed there because of averaging over the large area of the device, and because the arrays were considerably thicker, 5–10 layers of particles.

Figures 3(b) and 3(c) compare the temperature dependence of the imaginary component of the ac magnetic susceptibility and the STM current noise-power density at 100 Hz for both samples. The susceptibility signal is squared because of the expected roughly M^2 dependence of the interparticle spin-polarized tunneling probability.[32] Nevertheless, the M^2 dependence is postulated for noninteracting magnetic particles (or electrodes) and with the strong interparticle dipolar interaction, the power of 2 might be reduced due to collective magnetization switching events. The current noise-power peaks at a slightly lower temperature than the magnetic susceptibility and the peaks are much sharper. While the magnetic-susceptibility measurement is dominated by the larger particles, the current noise is equally sensitive to the smaller particles in the distribution. The smaller particles, which contribute to the low-temperature tail of the $\chi''(T)$ curve freeze at slightly lower temperatures, and could be responsible for the lower peak temperature observed for the current noise.

The correlation between current fluctuations and magnetic susceptibility shows that spin-polarized tunneling plays a crucial role in the electron tunneling through the films. The connection between the magnetic susceptibility and magnetic noise is provided by fluctuation-dissipation theory[33] but its applicability to the present case is questionable due to the strong nonequilibrium nature of the system at T_b and below. The high-current states presumably correspond to more or less parallel alignment of two particle moments, assuming that all the particles have the same sign of the spin polarization. When one of the NCs switches, the current drops to a characteristic value, for a given position.

To further study the distribution of these states, the telegraph noise was analyzed in hundreds (>500) of $I(t)$ curves measured on various positions in sample II at each temperature. Generally, parts of the noise patterns were complicated, switching between multiple current levels, but part of them clearly switched between two current states, probably reflecting situations where the MR was dominated by a single-particle switching. Segments with two clearly discernible current levels were isolated and analyzed by manually setting thresholds [as illustrated in Fig. 4(a)] for the low- and high-current states. The data were converted into binary form, and then the overall time spent at high- and low-current states was counted. The results are shown in Fig. 4(b) (for sample II). Above T_b(~150 K) the high- and low-current states occur with roughly equal probabilities, which is consistent with a superparamagneticlike state where the interparticle interactions are insignificant. Below T_b, as the magnetization switching slows down and interparticle interactions become dominant, the two states deviate significantly in occurrence, where the high current, parallel configuration state increases to ~65% of the time. Sample I was thoroughly analyzed at only three temperatures which showed a similar trend. At 210 K (~T_b) the up state occurred 71±7% of the time, while at higher temperatures (228 and 263 K) the up state occurred with 48±8% and 51±8% probabilities, respectively. Dense nanoparticle assemblies were suggested to have a superferromagnetic ground state with parallel moments.[1,2,9] In addition, the superparamagnetic to superferromagnetic transition was predicted to have an associated resistance drop due to the alignment of magnetic moments.[34]

The MR measured as a function of temperature on similar arrays also peaked around T_b.[21] In the treatment of the particle junctions exhibiting a two-state switching behavior we define a spin-polarized tunneling resistance ratio analogous to MR as

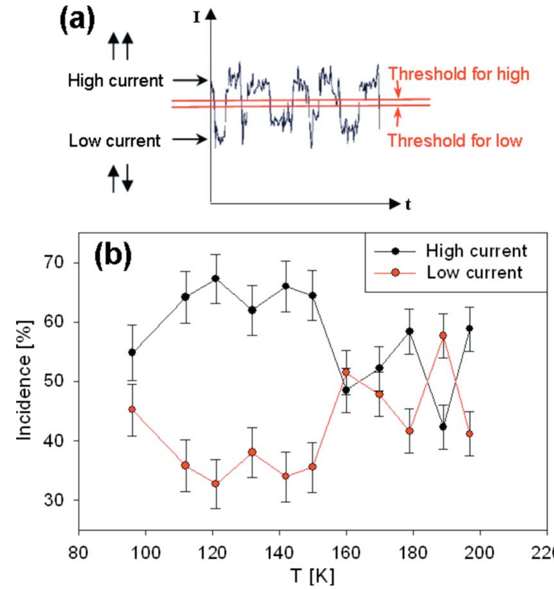

FIG. 4. (Color online) (a) A sample of an $I(t)$ curve exhibiting telegraph noise with thresholds set for data binarization. (b) The temperature dependent relative incidence of high- and low-currant states measured on sample II. Each data point is the average of hundreds of curves.

$$\frac{\Delta R}{R_{\max}} = \frac{R_{\uparrow\uparrow} - R_{\uparrow\downarrow}}{R_{\uparrow\downarrow}} = \frac{I_L - I_H}{I_H} \approx -\frac{2P^2}{1+P^2},$$

where $R_{\uparrow\uparrow}$ and $R_{\uparrow\downarrow}$ are the resistances of the array in the "parallel" and "antiparallel" states and I_H and I_L are the respective high- and low-current states. The resulting values of $\Delta R/R_{\max} \sim -30\%$ near T_b are higher than those reported for the tunnel MR in Ref. 21. The expression for MR using P, the material-dependent spin polarization, is derived from Julliere's model for magnetic tunnel junctions.[35] In addition, $\Delta R/R_{\max}$ is proportional to the resistance ratio between the interparticle junction resistance and the total tip-sample resistance, which is difficult to estimate. Assuming that the interparticle junctions dominate the tip-sample resistance P should be ≥42% at 150 K, otherwise P should be larger. Given the random crystallographic orientations of the NCs, 100% spin polarization would not be expected.

IV. CONCLUSION

In conclusion, we have demonstrated a STM-based technique that uses spin-dependent tunneling within thin magnetic NC assemblies to measure the temperature-dependent dynamics of magnetization fluctuations. The current fluctuations near the magnetization freezing transition (T_b) closely follow the temperature dependence of the magnetic susceptibility and are governed by magnetization switching within the magnetic nanoparticle arrays. These current fluctuations are the result of interparticle variations in the rate of spin-polarized tunneling due to switching in the magnetic moment configurations of the NCs.

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