A new Route to control the Enhancement of Structural and Anisotropy Ordering in Two-dimensional Particle Arrays

A. Regtmeier[*], F. Wittbracht[*], I. Dück[*], T. Rempel[*], A. Weddemann[**] and A. Hütten[*]

[*]Bielefeld University, Department of Physics, Thin films and Nanostructures
PB 100131, 33615 Bielefeld, Germany,
anna.regtmeier@physik.uni-bielefeld.de
[**]Massachusetts Institute of Technology, MA, USA

ABSTRACT

Two-dimensional arrays of magnetic nanoparticles were prepared by exposing 9 nm Co-particles to an external homogeneous magnetic field rotating around the axis perpendicular to the field direction. Due to dipolar interactions, the magnetic nanoparticles organize into highly ordered two-dimensional hexagonal particle arrays. These arrays are analyzed according to their structural properties for different rotation frequencies of the magnetic field. In a second step, the influence of plasma treatment on such particle arrays was studied. Monolayers of 13 nm Co-nanoparticles have been treated by hydrogen plasma which results in the reduction of the oxygen within the nanoparticles and a consequent increase of the magnetic moment. Further investigations showed a change of the hysteretic behavior of the nanoparticles leading to an increase of the coercivity for in-plane and out-of-plane measurements. For a better understanding of this effect, experimental data were compared to numerical simulations.

Keywords: magnetocrystalline anisotropy, plasma, magnetic nanoparticles, highly-ordered particle assembly, micromagnetic simulations

1 INTRODUCTION

Due to their wide range of applications in various scientific fields, magnetic nanoparticles have attracted a lot of attention and were thoroughly studied in the past decades. Among the many topics, the manufacturing of highly-ordered suprastructures of magnetic nanocrystals is an important step towards the design of novel nanostructured spintronic devices [1] such as granular magnetoresistance sensors [2] or data storage devices [3]. In particular for the realization of the latter application, two fundamtental requirements are necessary to guarantee good functionality of the device: a) particles need to be arranged within a sizeable, two-dimensional monolayer of high spatial ordering, and b) magnetic states need to maintain stability against thermal perturbations which can be realized by a high magnetocrystalline anisotropy [3].

In this work, we present novel possibilities to enhance both, the structural ordering during sample preparation and the anisotropy subsequent to spatial deposition. Our experimental observations are in agreement with simulations of two-dimensional arrays of interacting dipolar particles.

2 DESIGNING TWO-DIMENSIONAL HIGHLY ORDERED PARTICLE ARRAYS

The self-organization of magnetic nanoparticles along a surface is governed by a complex interplay between interparticle interactions and external forces which is still not fully understood. For the assembly of nanoparticles into mono- and multilayers on a substrate, various methods have been established. Common examples are the dropcasting under the influence of a magnetic field or spin-coating techniques. In particular the latter ones offer a controlled preparation of sizeable assemblies of high spatial order [4,5]. However, the spin-coating process does not allow to control the degree of magnetic and structural order of the nanoparticle assemblies. Since highly ordered assemblies form the prerequisite for many applications, studies on the improvement of the corresponding properties have been the scope of many recent works [6-9].

2.1 Field induced assembly of highly ordered bead arrays

Recently, a method for the realization of two-dimensional self-assembled monolayers of micron-sized superparamagnetic particles was presented. Studies on suspensions of magnetic multi-core beads revealed that the employment of a rotating homogeneous magnetic field allows for the creation of highly ordered two-dimensional particle arrays of hexagonal spatial symmetry (Figure 1) [10]. The degree of ordering manifests itself in the corresponding Fourier transform (Figure 1(a)). By comparison of the experimental observations to numerical data obtained from the solution of the Landau-Lifshitz equation for a set of discrete magnetic moments, various structural properties of the resulting assemblies could be related to their inner magnetic state. Figure 1(b) shows the magnetic equilibrium configuration. Associated simulations were performed on a 13x13 hexagonal particle grid, to ex-

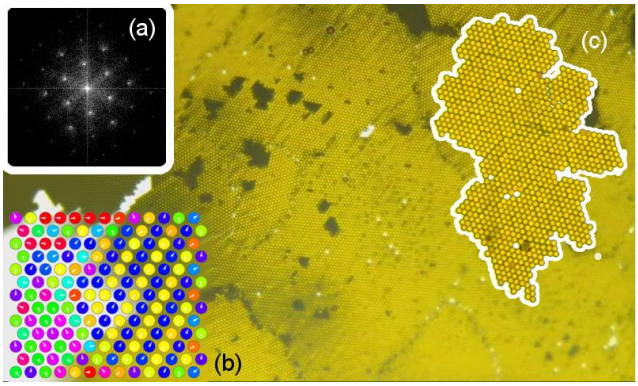

Figure 1: Magnetic microbeads assembled in highly-ordered hexagonal structures; (a) corresponding Fourier transform. (b) Magnetic moments form antiparallel domains. (c) Example of particle cluster. [10]

plain the grain-like structure of the particle assemblies. A typical solution is shown in figure 1, lower right, the color code indicates the direction of each magnetic moment in the plane of the particle assembly [10].

On the basis of these simulations, the appearance of such grains could be attributed to the interplay of the surface tension and the inner magnetic structure of the particle clusters. The formation of spatial domains with antiparallel alignment of magnetic moments entails a weak coupling energy between adjacent particle stripes of antiparallel magnetization configuration. Consequently, the assembly breaks along these lines under external stress as it was demonstrated for the case of evaporation induced forces. For the case of microbeads, the frequency was not found to have an influence on the cluster size, but on the defect concentration within a cluster.

2.2 Transition to the nanoscale

On the nanoscale, the predominant physical driving forces vary in comparison to microscale systems. Thermal Brownian motion and van der Waals attractions strongly influence the particle dynamics and, therefore, it cannot be immediately decided whether a transfer of the approach described above to the nanoscale is possible or not.

In order to obtain an experimental verification, 9.06 nm Co-nanoparticles with a standard deviation of 2.34 nm are employed (Figure 2). These particles are crystallized in the ε-Co phase. The particles are stabilized with an mixture of oleic acid and oleylamine (1:4) and dissolved in 1,2-dichlorobenzene (ODCB) at different concentrations and placed on a silicon wafer which is situated in a homogeneous magnetic field via a dropping procedure. The field direction is parallel to the substrate plane and rotates at a defined frequency f. For the creation of the rotating field, a commercial magnetic stirrer (RCT basic IKAMAG safety control) is employed. A scanning electron microscope (Leo *1530*) was used to analyze the structural properties of the monolayer-growth by imaging the evaporated droplets.

A typical example of a particle assembly is shown in Figure 2. Nanoparticles form a closed monolayer. Similar to the observations on the microscale, a high local ordering in a hexagonal lattice within a grain substructure is found. Individual grains are separated by vacancies or lattice distortions. In comparison to the microscale, a higher number of such distortions is present which can be attributed to the broader size distribution of the nanoparticles. Furthermore, lattice impurities also result from chemical remainders, caused by the selection of the disposed solvent, which induce shear stresses along the particle sheet. A more detailed explanation of the origination of dislocations can be found in [10].

In order to analyze the cluster size in dependency on the frequency of the applied field, several droplets are subsequently spotted after the evaporation of the liquid. The results are presented in Figure 3: the ratio of particles per cluster size class is shown for different frequencies between 0 and 750 rpm. Figure 3(a) shows the tendency of a decreasing cluster size with an increasing rotation frequency. The employment of a higher particle concentration results in the data presented in Figure 3(b): the cluster size increases with increasing field frequencies. This can be regarded as an experimental proof that even on the nanoscale, the magnetic interactions form a key contribution to the particle dynamics. In contrast to the observations on the microscale [10], we find indications that the frequency of the applied field can be adjusted to obtain different size distributions of clusters. A more detailed analysis will be presented in [11].

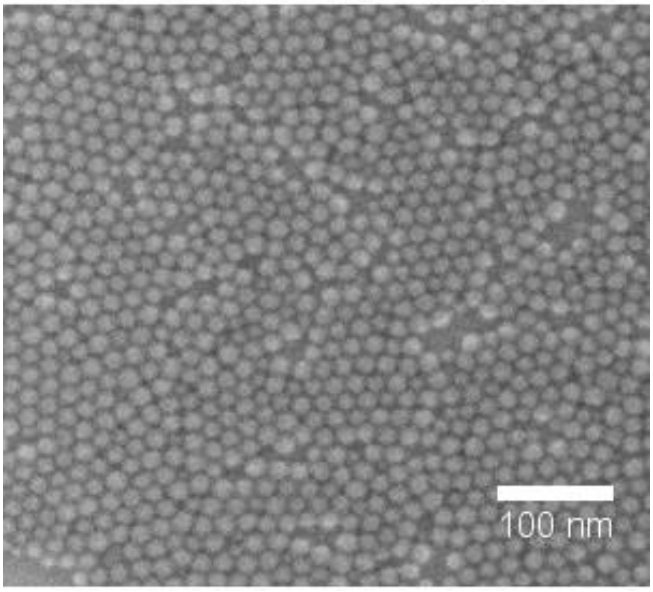

Figure 2: Scanning electron microscopy image of highly ordered Co-nanoparticles, which are crystallized in the ε-Co phase.

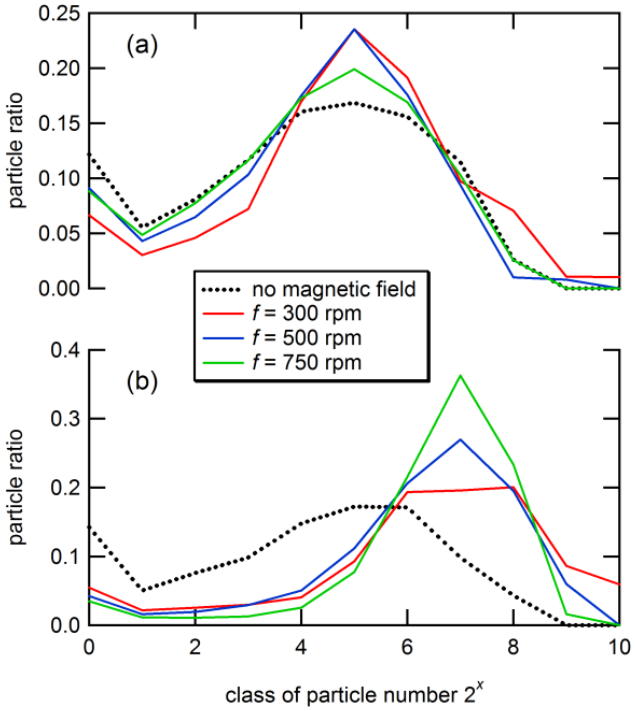

Figure 3: Ratio of particles per cluster size class in dependency on the applied field frequency for the frequencies 0, 300, 500 and 750 rpm. (a) and (b) represent suspensions of low and high particle concentration, respectively. [11]

3 ENHANCEMENT OF ANISOTROPY ORDERING IN TWO-DIMENSIONAL PARTICLE ARRAYS

The possibility to arrange magnetic nanoparticles in highly-ordered two-dimensional assemblies makes these magnetic components promising candidates for new data storage devices. Such applications require high thermal stability of the magnetic state which can be realized by particles with a high magnetocrystalline anisotropy as e.g. particles that consist of face-centered tetragonal $L1_0$ FePt alloy [12].

3.1 Experimental observations

In order to increase the degree of anisotropy ordering in the nanoparticular Co-system, we propose an annealing-type procedure. The Co-nanoparticles used in this experiment have an average diameter of 13 nm and a standard deviation of 2 nm. They are prepared by the procedure of Puntes et al. [13], using 1,2-dichlorbenzene (ODCB) as a solvent and oleylamine as a ligand. For the preparation of the two-dimensional particle assemblies a silicon wafer with a 500 nm SiO_2-layer is dipped into the particle suspension under an angel of 45°. Subsequently, the remaining liquid evaporates. Via exposure of these two-

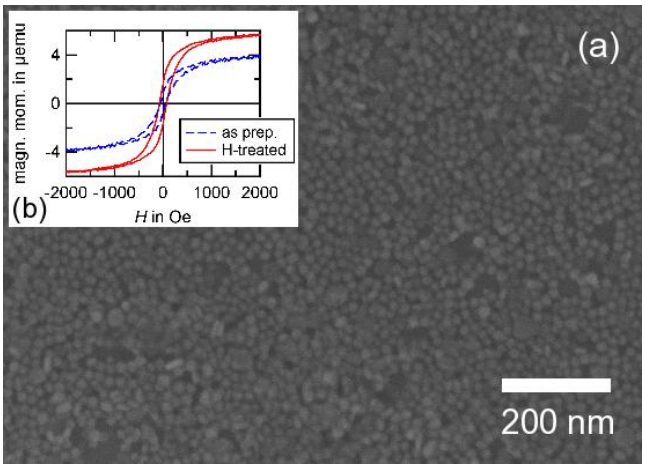

Figure 4: (a) Scanning electron microscopy image of two-dimensional particle assembly of 13 nm oleylamine-stabilized Co-particles. (b) AGM measurements before and after hydrogen treatment. [15]

dimensional arrays of 13 nm Co- nanoparticles (Figure 4(a)) to a hydrogen plasma, a multi step process is initiated: The treatment entails the reduction of the Co-particles and, hence, increases their magnetic moments (Figure 4(b)) [14].

Upon saturation, a change of the shape of the hysteresis can be observed (Figure 5). With increasing treatment duration, the coercivity for in-plane measurements (Figure 5(a)) increases as well as the field values necessary to achieve an out-of-plane alignment (Figure 5(b)) [15].

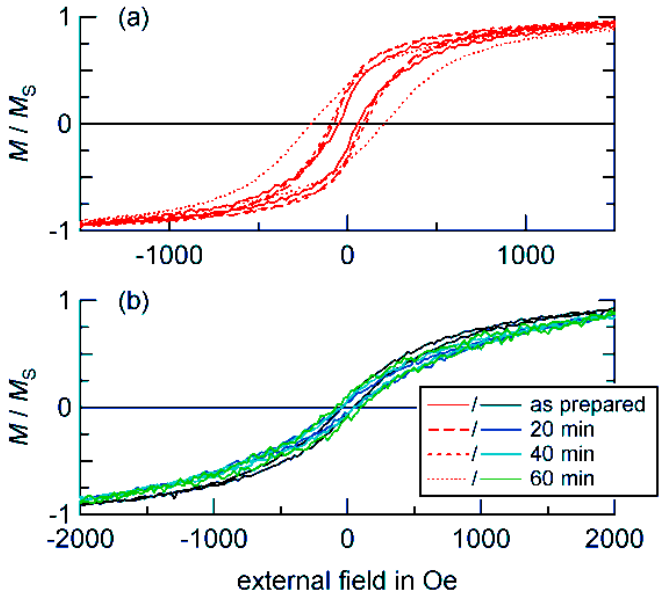

Figure 5: (a) in-plane and (b) out-of-plane AGM measurements of 13nm Co-nanoparticles. Depending on the treatment duration, the hysteretic behaviour changes. [15]

3.2 Simulations of the hysteretic behavior of the two-dimensional particle arrays

To obtain a qualitative understanding of the microscopic origins of the experimental findings, simulations of the two-dimensional particle arrays are carried out [15]. As a model system, we consider a two-dimensional particle 10×10 lattice of hexagonal symmetry with a lattice constant of 16 nm. We assume 12 nm particles of a saturation magnetization M_S = 900 kA/m. Additionally, a uniaxial anisotropy with an anisotropy constant $K_1 = 10^5$ J/m³ is chosen. For particles at the edges of the lattice, periodic boundary conditions are employed.

The distribution of the anisotropy vectors $\boldsymbol{k_i}$ is chosen in three different ways: 1) equally random on the unit sphere in three dimensions, 2) equally random on the section of the unit sphere that include an angle α with the *x*-*y*-plane between -45° < α < 45° and 3) equally random on the two-dimensional unit sphere in the *x*-*y*-plane. To analyze the hysteretic behaviour an alternating external field $\boldsymbol{H}_{ext}$ in *x*- and *z*-direction is considered. The results of the numerical calculations are shown in Figure 6.

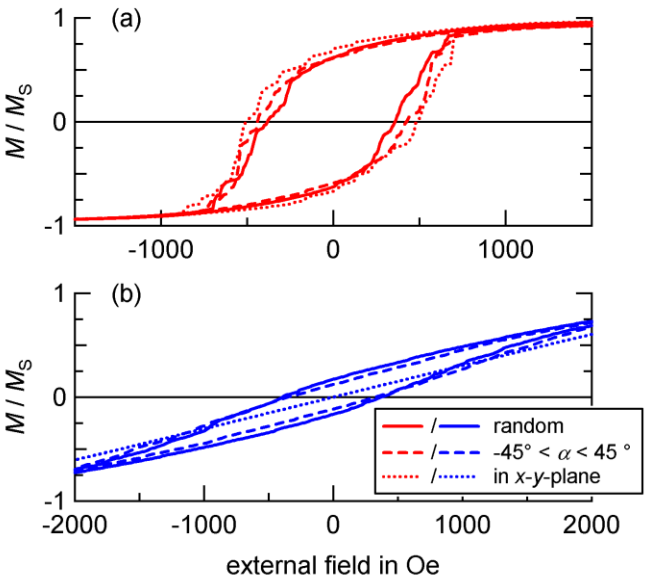

Figure 6: Calculated hysteresis loops for different anisotropy settings and different measuring fields. (a) shows the calculated in-plane and (b) the out-of-plane loop. [15]

With the easy axis vectors aligning their orientations with the particle plane, the coercive field H_c increases in case of the in-plane measurements. For perpendicular external fields instead, we find a higher magnetic field necessary to reach magnetic saturation. Thus, we were able to qualitatively show the experimentally observed changes in the magnetic response functions can be attributed to a plasma induced ordering of the magnetocrystalline easy axes along the particle assemblies (Figure 6).

In comparison to other findings [16], this method allows for ordering at mild temperatures with a decreased probability of phase transitions.

4 CONCLUSION AND OUTLOOK

In conclusion, we were able to prepare highly-ordered two-dimensional particle arrays via employment of a rotating magnetic field, by transferring the approach of Weddemann et al. to the nanoscale. The structural properties can be controlled by the field frequency and the concentration of nanoparticles in the suspension.

In order to tailor the properties of such two-dimensional particle arrays to their applicability as new data storage devices, we introduced an annealing-type procedure which allows for the enhanced magnetic order at mild temperatures. Numerical simulations of two-dimensional particle arrays showed that this enhancement is due to the migration of the magnetocrystalline easy axes into the plane of the assembly itself.

The authors would like to thank A. Dreyer, M. Peters and C. Waltenberg for synthesizing the nanoparticles and helpful discussions, the SFB 613 for financial support in the framework of the project K3, as well as the FOR 945 for financial support in the framework of the project 3. Alexander Weddemann gratefully acknowlegdes financial support of the Alexander von Humboldt foundation.

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