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Magnetic properties of nickel nanoparticles embedded in amorphous Al₂O₃ matrix

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Abstract. Multilayer thin films consisting of 10 bilayers of (Al₂O₃+Ni)/Al₂O₃ were deposited by magnetron sputtering onto Si(100) substrate. Nickel nanoparticles are formed inside amorphous alumina matrix by self-assembly growth process. It was determined by GISAXS measurements that nickel particles are spheroidal with diameter < 3 nm and that they form paracrystal-like body-centered tetragonal lattice. Magnetic properties of the prepared thin films were studied. Due to the nanometer size of nickel particles, their magnetic structure is single domain and they show superparamagnetic behaviour. Anisotropy of magnetic properties was observed when magnetic field is applied parallel or perpendicular to the thin film surface and it was attributed to dipole-dipole interactions between particles. This was confirmed using simulations of the $M(H)$ curve of the 2D superlattice of the identical superparamagnetic particles, which was performed using Monte Carlo method and Metropolis algorithm.

1. Introduction

Nanosized magnetic particles have been extensively investigated in the last few decades due to the variety of their potential application, such as biomedical applications (enhancing quality of magnetic resonance imaging (MRI), hyperthermic treatment of tumor cells, drug delivery) [1,2], data storage [3] etc. Magnetic structure of nanosized magnetic particles is single-domain [4] and they can be characterised by their magnetic moment. Single domain particles exhibit superparamagnetic behaviour at high temperatures and blocking of magnetic moment due to the anisotropy barrier at low temperatures, which results in a slow relaxation of the magnetization of the system. The temperature, at which transition between blocked and superparamagnetic regime occurs, is strongly dependent on the parameters of the system, applied magnetic field and the time scale of the experiment. Besides individual properties of the particles (size, shape, crystalline structure etc.), their mutual interaction also affects magnetic behaviour of the system. This is especially important for the systems with high concentration of magnetic particles as dipole-dipole interaction between particles can lead to appearance of a collective state at low temperatures, such as super spin glass state or even long-range ferromagnetic ordering [5]. Understanding magnetic behaviour of assembly of single-domain particles is important for their possible applications, as well as for better fundamental knowledge of magnetic phenomena in nanosized structures.



Magnetron sputtering deposition is a relatively simple and efficient method for preparation of well-ordered 3D lattice of nanosized nickel particles embedded in amorphous alumina matrix. Size, shape and separation between particles can be easily tuned by changing the deposition parameters, which also allows tailoring magnetic properties of the thin film.

2. Experimental

Thin films consisting of 10 alternating Al₂O₃ and Al₂O₃+Ni bilayers were prepared by magnetron sputtering deposition (KJLC CMS-18 System) on Si(111) substrate. Pure Ni (99.995%) and Al₂O₃ (99.995%) were used as targets in the DC (50 W) and RF (300 W) magnetrons, respectively. The substrate was held at 300°C and the pressure of the process gas (Ar) was 0.4 Pa. The deposition time for each mixed layer was 30 s, and deposition time of the Al₂O₃ layer was varied from 10 to 75 s in order to obtain samples with different separation between layers containing nickel particles. Magnetic properties of the thin films were investigated using Quantum Design PPMS with VSM option and magnetic measurements were performed in temperature range 2-300 K in applied magnetic field up to 9 T.

3. Results and discussion

Structural properties

Nanosized nickel particles are formed inside amorphous Al₂O₃ matrix during the deposition of Ni+Al₂O₃ layer by the self-assembly growth process combined with the surface morphology effects. A similar effect was previously observed for nickel particles in alumina matrix with single Ni+Al₂O₃ multilayer [6], as well as for Ge particles formed in amorphous silica and alumina matrices [7,8]. Size, shape and spatial arrangement of nickel particles in the sample with larger separation between nickel containing layers were investigated using Grazing Incidence Small Angle X-ray Scattering (GISAXS) technique¹. Numerical analysis of the measured GISAXS map was performed according to a model described in [9] which revealed spheroidal shape of the nickel particles with radius 1.4 ± 0.1 nm. Also, it was determined that nickel particles are arranged in paracrystal-like body-centered tetragonal lattice with lattice [9] parameters $a = 5.8 \pm 0.2$ nm and $c = 3.7 \pm 0.1$ nm.

Magnetic properties

In Fig. 1 zero field cooled (ZFC) and field cooled (FC) magnetization curves measured in different magnetic fields applied parallel to the thin film surface are shown. For all measuring fields ZFC magnetization increases with the increasing temperature, obtains maximum at temperature T_{max} and decreases with further increase in temperature, whereas FC magnetization decreases with increasing temperature. ZFC and FC branch of magnetization curve separate at temperature T_{irr} which is slightly higher than T_{max} . Observed behaviour of the ZFC and FC magnetization curves is in accordance with the model of superparamagnetic particles which are blocked in non-equilibrium state due to the anisotropy barrier at low temperatures and with a rather narrow distribution of sizes which causes small deviation of T_{irr} from T_{max} . But with closer inspection of the ZFC and FC curves in Fig. 1 it is found that T_{max} (and T_{irr}) remain practically constant with increasing magnetic field up to 0.1 T, which contradicts the model of noninteracting single domain particles where applied magnetic field lowers the barrier so that magnetic moments become thermally unblocked at lower temperature with expected magnetic field dependence $T_{max} \sim (1 - H/H_0)^2$ [10]. The deviation of experimental results from theoretical predictions suggests that the model of noninteracting single domain particles cannot be applied for the studied system. In samples with rather high concentrations of magnetic particles, dipole-dipole magnetic interaction between particles needs to be taken into consideration. Several

¹ GISAXS measurements were performed at Synchrotron Elettra in Trieste. Detailed results and analysis will be published elsewhere.

models have been proposed to describe effects of the dipole-dipole interaction [11]. Although they agree with some experimental observations, they cannot fully explain magnetic behaviour of dense magnetic nanoparticle systems. It should be noted that due to the large number of parameters (size, shape, distribution of sizes of the particles, surface effects, crystalline structure, interactions) it is extremely difficult to model magnetic nanoparticle systems and some approximations must be used. A modified superparamagnetic model is often used for systems with moderate concentration of particles in which particles retain typical superparamagnetic behaviour but with barriers modified by interactions. With increasing concentration of the particles, their mutual dipole-dipole interaction becomes dominant and the system is no longer described as assembly of individual particles, as experimental results point to collective behaviour. In order to estimate the influence of dipole-dipole interactions on the macroscopic magnetic properties of our thin films, we prepared samples with smaller separation between the layers of the nickel particles. Preliminary measurements of ZFC and FC curves (not shown) indicate possible occurrence of a collective super spin glass state: in addition to splitting of ZFC and FC curves and distinct maximum of the ZFC curve, FC magnetization curve does not increase upon cooling and obtains small minimum in low temperature region, which is an indication of the super spin glass state. It seems that dipole-dipole interactions are significant in the studied systems and that they can lead to a collective state with the reduction of the separation between particles.

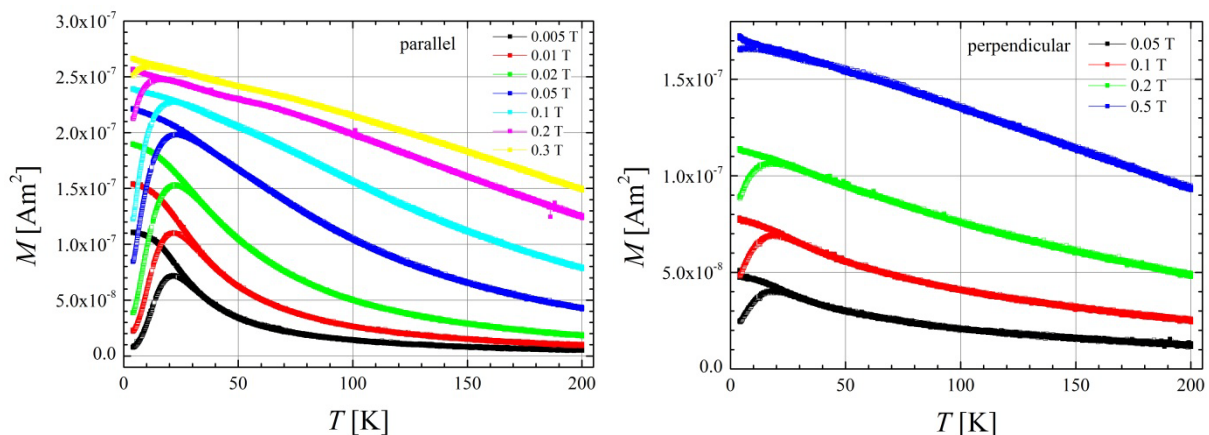


Figure 1. ZFC (open symbols) and FC (full symbols) $M(T)$ curves measured in applied field parallel to the thin film surface.

As our system is essentially 2-dimensional i.e. spatial arrangement of the particles is infinite in the thin film plane (xy -plane) with only 10 layers of particles in direction perpendicular to the thin film (z -direction), measurements were also performed with magnetic field applied perpendicular to the thin film to investigate possible anisotropy of the magnetic properties (Fig. 2). Comparing $M(T)$ ZFC and FC measurements with parallel and perpendicular applied field orientation (Figs. 1 and 2) striking anisotropy is observed: magnetic moment of the sample is approximately one order of magnitude smaller when measured in perpendicular orientation of the applied field with respect to the parallel one. Possible reason for the observed anisotropy of the magnetic properties are dipole-dipole interactions, as it will be discussed in the following paragraphs.

Measurements of the field dependence of magnetization of the sample for parallel and perpendicular orientation of the applied field at various constant temperatures were also performed. At temperatures ≤ 20 K $M(H)$ loops show a hysteresis which is a consequence of the slow relaxation of the magnetization at low temperatures (in Fig. 3 measurement at 2 K is shown). At high temperatures thermal energy is high enough so that magnetization of the system achieves equilibrium value during the measurement of one point and $M(H)$ loops are reversible (Fig. 4 shows measurement at 300 K). $M(H)$ curves are consistent with the $M(T)$ curves and also show anisotropy. Namely, $M(H)$ loops for

magnetic field applied perpendicular to the thin film are less steep and reach saturation at higher field. This anisotropy is more pronounced at low temperature (2 K), but can also be noticed even at high temperature (300 K).

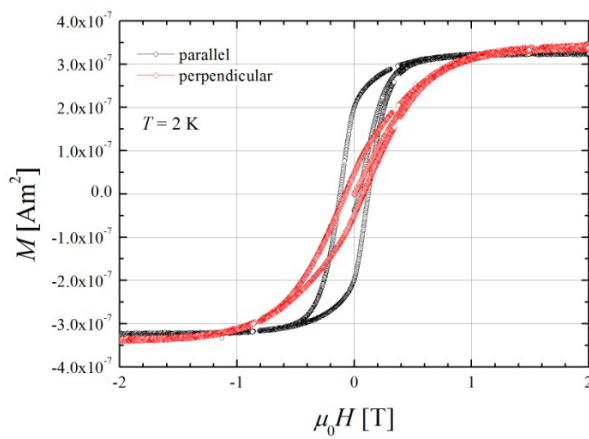


Figure 3. $M(H)$ curves for applied field in parallel and perpendicular direction at 2 K.

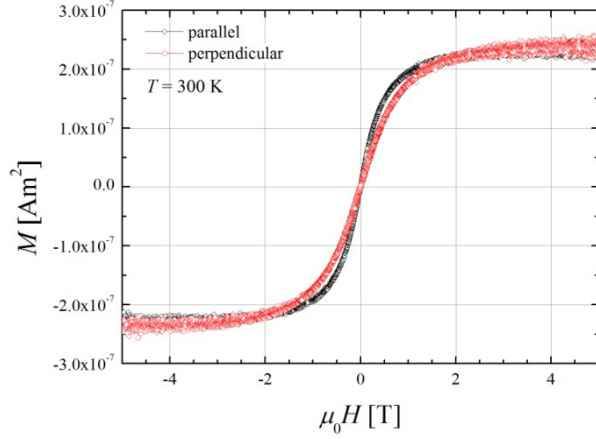


Figure 4. $M(H)$ curves for applied field in parallel and perpendicular direction at 300 K.

Both $M(T)$ and $M(H)$ measurements for both orientations of thin film with respect to the applied field suggest that particles' magnetic moments tend to lie in the thin film plane, which makes it harder to magnetize the system when magnetic field is applied perpendicular to the thin film. If we assume that anisotropy axes are oriented randomly, only the dipole-dipole magnetic interaction, which is anisotropic in its nature, can account for the observed anisotropy. To verify this assumption Monte Carlo simulations of the $M(H)$ curves were performed for the magnetic field applied in both parallel and perpendicular direction. The energy of the assembly of single domain particles is given by:

$$E = -K \sum_i \left(\frac{\vec{\mu}_i \cdot \hat{n}}{\mu_i} \right)^2 + \frac{\mu_0}{4\pi} \frac{1}{2} \sum_{i,j} \frac{1}{r_{ij}^3} \left(\vec{\mu}_i \cdot \vec{\mu}_j - 3 \frac{(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij})}{r_{ij}^2} \right) - \mu_0 \sum_i \vec{H} \cdot \vec{\mu}_i, \quad (1)$$

where K is the anisotropy constant, μ_i is the magnetic moment of the particle i , \hat{n} is the unit vector of the anisotropy axis of the particle i , r_{ij} is the separation between particles i and j , H is the applied magnetic field and other symbols have their usual meaning. For convenience equation (1) was transformed to:

$$E' = -\sum_i (\hat{\mu}_i \cdot \hat{n})^2 + \frac{\mu_0 \mu^2}{4\pi K V a^3} \frac{1}{2} \sum_{i,j} \frac{a^3}{r_{ij}^3} \left(\hat{\mu}_i \cdot \hat{\mu}_j - 3 \frac{(\hat{\mu}_i \cdot \vec{r}_{ij})(\hat{\mu}_j \cdot \vec{r}_{ij})}{r_{ij}^2} \right) - \frac{\mu_0 \mu}{K V} \sum_i \vec{H} \cdot \hat{\mu}_i, \quad (2)$$

where a is the lattice constant. We assumed that the particles are identical and that the anisotropy axes are oriented randomly. In the simulation constant $\mu_0 \mu^2 / 8\pi K V a^3$ was set to 0.15 and the values of other parameters were typical for superparamagnetic systems. Simulation was performed for 100 particles arranged in 10x10 quadratic array in xy plane and the periodic boundary conditions were used for the calculation of the dipole-dipole energy. Monte Carlo simulation of the $M(H)$ curve was performed at constant temperature $T = 10$ K according to the standard Metropolis algorithm [12]. Results of the simulation are shown in Fig. 5. They confirm that for a regular 2D array of superparamagnetic particles the anisotropy of the macroscopic magnetic properties is a consequence of the dipole-dipole interactions between particles. In addition, coercive field of the simulated $M(H)$ curves is lower for the perpendicular case, which is also in accordance with the experimental results. Exact values of the saturation magnetization and coercive field of the simulated curves are different than the experimental ones due to the different choice of the parameters of the system. Main aim of the simulation was to demonstrate that dipole-dipole interactions between particles lead to anisotropic magnetic behaviour of the 2D superlattice of single domain particles.

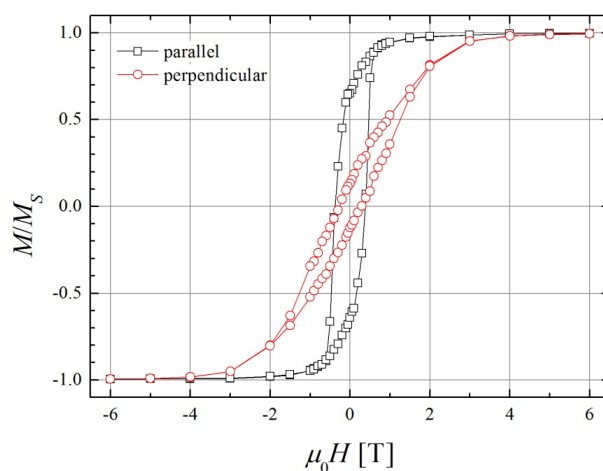


Figure 5. Simulated $M(H)$ curves for parallel and perpendicular orientation of magnetic field.

4. Conclusion

Thin films of nanosized nickel particles embedded in amorphous alumina matrix were prepared by magnetron sputtering deposition and magnetic properties of the prepared samples were investigated. The nickel particles are single domain and they show blocking of magnetic moment at low temperatures. The dipole-dipole magnetic interaction between the particles influences the dynamics of the system and can lead to collective behaviour. Simulations performed using Monte Carlo method are in accordance with experimental results confirming that the used model is appropriate.

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