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MAGNETISM AND ANISOTROPY IN CORE-SHELL NANOPARTICLES

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The subject of magnetic anisotropy in nanostructured materials is of considerable interest from both experimental and theoretical points of view. Systems that consist of either isolated or interacting nanoparticles are shown to exhibit different magnetic properties of the nanoparticle surface than those of the bulk. This altering of magnetic behavior is mainly related to surface spins structure correlated with finite size effects, providing that the nanoparticles are sufficiently small so that the surface-to-volume atomic ratio would be high enough. This work reports on both the simulation and experimental approach on the magnetic behavior of ferromagnetic nanoparticles. We investigate the competition between surface and bulk magnetocrystalline anisotropy in small magnetic particles. The experimentally obtained magnetic data for ferromagnetic core-shell-type AgCo nanoparticles are interpreted consistently with the results of Monte Carlo simulation of the magnetic behavior of single domain nanoparticles.

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1. Introduction

Increased interest have been devoted recently to the experimental and theoretical study of magnetic nanoparticles due to their outstanding properties arising from the nanometric scale that gives rise to high surface-to-volume atomic ratio and strongly modified magnetic properties comparing to the bulk. Both fundamental and applicative milestones can be achieved using such mesoscopic systems [1]. It should be noticed that magnetic nanoparticles are presently active component of ferrofluids, recording tape and flexible disk recording media. Increased range of applications has been developed also in the field of biomedical materials and catalysts. This altering of the magnetic properties may be related to the occurrence of new phenomena that are of interest for technological applications. Moreover, the magnetic nanostructures can be used as model systems for studying fundamental aspects arising from nanoscopic scaling of different magnetic features. Both surface and finite size effects have been previously hold responsible for the anomalous magnetic behavior of nanomaterials. In the case of Fe nanoparticles [2], surface spins are shown to be noncollinear and ferromagnetically coupled to the core. The magnetic behavior of ferrites and metallic oxides nanoparticles has been explained in terms of finite size effects and surface spin disorder [3-5] and the influence of surface spins on the overall magnetic behavior has been modeled [6] considering enhanced surface anisotropy due to broken exchange bonds at the surface.

The paper is mainly structured in two parts. Magnetic data of core-shell bimetallic AgCo nanoparticles are presented and discussed in the first part. The second is devoted to a Monte Carlo simulation study of low temperature spin ordering with emphasis on the influence of surface anisotropy on the overall magnetic behavior of isolated nanoparticles.

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2. Experimental

The AgCo nanoparticles have been prepared using a colloidal chemistry technique, details about preparation being given elsewhere [7]. The final product consists of a colloidal solution of bimetallic AgCo nanoparticles in toluene as carrier. Moreover, up to 30 drops of the solution containing the AgCo nanoparticles are dried onto a Si substrate. The nanoparticles self-organize onto the substrate by forming quasi-regular arrays of nanoparticles with narrow size distribution as proven by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The exact composition has been proven by energy electron loss spectroscopy (EELS) to be $Ag_{30}Co_{70}$ and their structure is shown to be fcc for Ag and hcp for Co with a peculiar morphology, the Co forming incomplete shells around the Ag core. The magnetic behavior has been investigated using a vibrating sample magnetometer (VSM) with an applied field up to 1.5 T. The Monte Carlo simulation of low temperature spin ordering has been done using a parallel computational facility, considering a system of spins corresponding to a ferromagnetic isolated nanoparticle with a radius of $R = 6a$ (a being the interatomic distance) and a number $N = 905$ spins in a cubic symmetry. The spins are interacting with each other (in a first-nearest-neighborhood approximation) following a Heisenberg-type hamiltonian including exchange coupling and anisotropy terms. The surface anisotropy is considered radially oriented on the surface while the bulk magnetocrystalline anisotropy is considered uniaxial on *Oy* axis. The spin configuration energy is then minimized following a Metropolis algorithm. Macroscopic quantities such as specific heat, susceptibility or magnetization for the whole system can be derived and correlated with experimentally obtained data.

3. Experimental results and discussion

The major hysteresis loops and also field dependence of magnetization M(H) recorded at room temperature (RT) in applied field up to 1 T and parallel to the sample plane, are shown in Fig. 1.

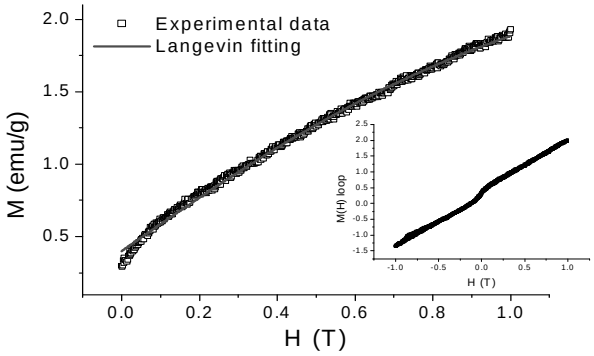

Fig. 1. Initial magnetization vs. applied field for $Ag_{30}Co_{70}$ nanoparticles. Inset: the hysteresis loop at RT.

The measurements show that the AgCo nanoparticles exhibit very weak coercivity (H_c = 145 Oe) and remanence (M_r = 0.048 emu/g) at RT (Inset of Fig. 1). The magnetization vs. applied field curve (full squares in Fig. 1) exhibits no saturation up to 1 Tesla. This anomalous magnetic behavior is similar to previously reported investigations on CoRh nanoparticles [8] and could be attributed both to the unusual multiphase polycrystalline structure of nanoparticles favouring noncollinear arrangements of magnetic moments and to the highly disordered magnetic surface layers. If the sample is regarded as an assembly of superparamagnetic nanoparticles, the field dependence of magnetization obeys a Langevin-type law:

$$M(B) = M_s \quad L \ \frac{\mu B}{kT} \ + M^{s}_{fm} \tag{1}$$

where $L(x) = cth(x) \ \ 1/x$ is the Langevin function, $M(B)$ is the magnetization vs. field, M_s the extrapolated saturation magnetization and M^{s}_{fm} corresponds to the volume fraction of nanoparticles which are already magnetically saturated at very small applied field. The magnetization vs. applied field was successfully fitted to eq.(1) (line in Fig. 1) and one may conclude that the AgCo samples act at RT as assemblies of superparamagnetic (SPM) nanoparticles and this behavior can be related to finite size effects and surface spin disorder.

4. Monte Carlo simulation

The theoretical isolated ferromagnetic nanoparticle we investigate is made of spins with S = 1 and exchange coupling between them J = 1000 (in arbitrary units).

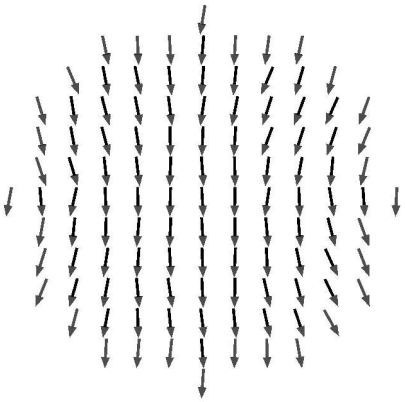

Fig. 2. The equilibrium "throttled" spin configuration of the central plane of R = 6*a* nanoparticle.

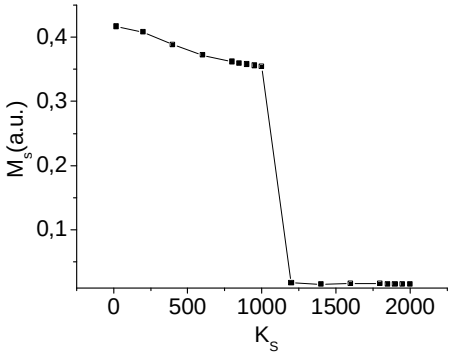

Fig. 3. The saturation magnetization of R = 6*a* nanoparticle for different surface anisotropy constants K_S. The values shows two configurational transitions.

Magnetocrystalline anisotropy is $K_V = 20$ while the surface anisotropy was ranged between $K_s = 0.2 \div 2000$. After minimization of the energy the spin configuration is shown to be strongly dependent upon the surface anisotropy, giving rise to a so-called throttled spin configuration (Fig. 2) which arises as a result of competition between uniaxial bulk anisotropy and radial surface anisotropy. This particular spin configuration is responsible for the non-saturation of the magnetization of nanoparticles even at high applied fields [7,8]. As the surface anisotropy is increasing, the spin system undergoes two configurational transitions: collinear-to-throttled and throttled-to-hedgehog (a spin state which gives no net magnetization). These transitions are visible while plotting the saturation magnetization vs. surface anisotropy constant K_S (Fig. 3).

5. Conclusions

The magnetic AgCo nanoparticles obtained as ferrofluids, shows peculiar magnetic behavior, i.e. lack of saturation even at high applied fields. This may be due to surface spin disorder imposed by broken symmetry at the surface and also reduced coordination. Finite size effects may also be responsible. In order to prove these assumptions, a theoretical system of spins, approximating the quasi-isolated nanoparticles, has been considered and their equilibrium magnetic configuration has been obtained via Monte Carlo simulation and shown to be sensitive to the surface anisotropy. For

given intermediate K_S values the so-obtained throttled spin configuration looks as the state responsible for the experimentally observed lack of saturation in the case of AgCo nanoparticles.

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