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Numerical study of the structure and the magnetic properties of Co clusters on Au surfaces

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We model the growth process and the evolution of the magnetic behavior of Co clusters on Au surfaces in the case of low temperature co-deposition of Co and Au atoms and in the case of room temperature deposition of Co atoms on reconstructed Au(111) surfaces. The magnetic structure is obtained in either case by a Monte Carlo simulation, which includes exchange and magnetostatic (dipolar) intercluster interactions and perpendicular anisotropy for each Co cluster. Our simulations show an enhancement of the magnetization remanence that in the case of co-deposition is correlated with the annealing conditions and in the case of the deposition on the Au surface with the amount of deposited Co. The numerical results interpret experimental findings on these systems. An important finding of the experimental work confirmed by the numerical modeling is that these Co/Au structures show the way to control magnetic properties of clusters deposits over a large range of values.

1 Introduction

Finite-size effects occurring in nanoparticles and ultrathin films with reduced dimensionality have been the subject of intense study in the last decade [1, 2]. The physical properties of these materials as a function of their size is of fundamental interest as well as of technological importance, and related directly to the issue of the fundamental limits of data storage. In order to get a deeper insight into the relationship between nanoscale structures and magnetism, a new approach, based on self-organization of Co clusters on Au surfaces has been developed. More specifically the low-temperature co-deposition on Co and Au clusters was studied [3], which is a system with strong tendency to segregation [4] and a paramagnetic to ferromagnetic behavior is demonstrated due to phase separation in the deposited film which is temperature driven. Also in the room-temperature deposition of Co atoms on reconstructed Au(111) surfaces [5–7], a transition from superparamagnetic to ferromagnetic behavior is obtained and is attributed to the formation of a percolating network of Co clusters. These results open the way to spin engineering of cobalt films on Au surfaces.

In this work we model the growth process and the evolution of the magnetic behavior of Co clusters on Au surfaces in the case of low temperature co-deposition of Co and Au atoms and in the case of room temperature deposition of Co clusters on reconstructed Au(111) surfaces. The evolution of the sample morphology and the magnetic structure is obtained in both cases by a Monte Carlo simulation. Our numerical results have been used to interpret experimental findings on these systems.

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2 The numerical model

We have performed Monte Carlo simulations on the phase separation of a binary alloy, in the case of low temperature Co/Au co-deposition, in order to get a better insight into the segregation mechanism. In our model we consider a binary alloy A_xB_y with a certain concentration of vacancies ($c_V = 1 - x - y$) [8] on a two-dimensional triangular lattice and allow for repulsive pair interactions between nearest neighbour AB pairs. The Hamiltonian of the alloy is:

$$H = \sum_{\langle i,j \rangle} \left(C_i^{\mathrm{A}} C_j^{\mathrm{A}} \phi^{\mathrm{AA}} + C_i^{\mathrm{A}} C_j^{\mathrm{B}} \phi^{\mathrm{AB}} + C_i^{\mathrm{B}} C_j^{\mathrm{B}} \phi^{\mathrm{BB}} \right) \tag{1}$$

where $C_i^{\mathrm{X}} = 1$ or 0 in the case that an atom-X exists or does not exist in site-i respectively. $\phi^{\mathrm{XX}'}$ is the pair potential between atoms X and X′ in nearest neighbour sites. The Hamiltonian of the binary alloy with vacancies can be transformed to an Ising Hamiltonian with spin $S = 1$

$$H = -J_a \sum_{\langle i,j \rangle} S_i S_j + H_0 \tag{2}$$

where $J_a = \frac{1}{2}\left\{ \phi^{\mathrm{AB}} - \frac{1}{2}\left(\phi^{\mathrm{AA}} + \phi^{\mathrm{BB}} \right) \right\}$ and H_0 is a constant. The three possible values of the spin $S_i = +1, 0, -1$ correspond to the site-i being occupied by an atom A, a vacancy or an atom B, respectively. The dynamics associated to this model assumes a vacancy mechanism with different jump rates (Γ_{A}, Γ_{B}) for the atoms A and B.

For the room temperature deposition of Co atoms on (111) reconstructed Au surfaces we have developed a model, which is similar to the one used in Ref. [5]. Namely, an initial coverage of 1 ML exists on the substrate that consists of 1-D rows of coupled, bilayer clusters. Further Co deposition causes (a) nucleation of new clusters at random positions between the rows and (b) increase of the volume of existing clusters. To fulfill these requirements we consider Co clusters with a hexagonal prism shape located on the sites of a triangular lattice $L \times L$. The clusters are characterized by their volume (V_i), their basis area (A_i) and their height (H_i). These are related by $V_i = A_i\ H_i$. All sites on the odd-numbered rows of the triangular lattice are occupied by bilayer clusters ($H_i = 2$) with basis area $A_i = N_w$. The condition of maximum basal area ($A_i = N_w$) is the prerequisite for exchange coupling between nearest neighbor clusters. A cluster at site i is visited at random and the local volume V_i (or "mass") is increased by a constant amount $\mathrm{d}V = 1$. We assume that clusters grow in a layer mode and every new monolayer of a growing cluster is completed after N_w visits to the same site. The deposition procedure continues until a total amount of p monolayers is deposited. In our model 1 ML is equivalent to $L^2 N_w$ visits to the lattice sites.

The magnetic properties of the samples in both cases are modelled by a classical Heisenberg Hamiltonian with nearest neighbour exchange interactions (J_{ij}), long-range dipolar interactions (g_{ij}) and perpendicular anisotropy (k_i) [9]. The magnetic Hamiltonian is

$$H = -\sum_{\langle i,j \rangle} J_{ij} \hat{S}_i \hat{S}_j + \sum_{i,j} g_{ij} \frac{\hat{S}_i \hat{S}_j - 3\left(\hat{S}_i \hat{r}_{ij} \right)\left(\hat{S}_j \hat{r}_{ij} \right)}{r_{ij}^3} - \sum_i k_i S_{iz}^2 - h \sum_i S_{iz} \tag{3}$$

where $\langle \ldots \rangle$ indicate nearest neighbours and the hats indicate unit vectors. The last term on the right hand side of Eq. (4) is the Zeeman energy due to the applied field (h). Typical runs consisted of 10^4 Monte Carlo steps per spin and 10^3 initial steps were used for thermalization, while averages over 10 different samples were taken.

3 Results and discussion

3.1 Low temperature co-deposition

We have performed simulations on a 50 × 50 triangular lattice with periodic boundaries. For the alloy parameters we have taken $\phi^{\mathrm{CoCo}} = -0.0837$ eV/atom, $\phi^{\mathrm{AuAu}} = -0.0212$ eV/atom and $\phi^{\mathrm{CoAu}} = -0.0276$ eV/atom as obtained from simple calculations [10]. The low-temperature deposition

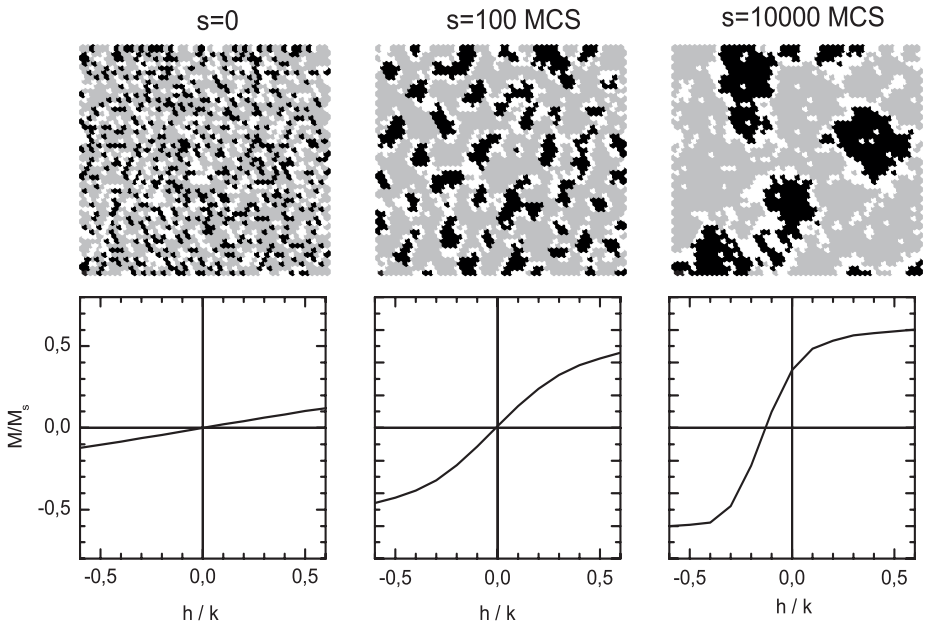

Fig. 1 (a) Segregation of a $Co_{70}Au_{30}$ cluster film with 25% vacancies at 150 K at different annealing times, measured in Monte Carlo Steps. Dark sites correspond to Co atoms, grey sites to Au atoms and white sites to vacancies. (b) Corresponding time evolution of the hysteresis loop of a $Co_{70}Au_{30}$ film.

(T_{dep} = 30 K) ensures that the two immiscible metals (Co and Au) form a homogeneous alloy. The segregation begins by annealing the alloy at T = 150 K. Therefore, our simulation was performed at T = 150 K and initiated from a homogeneous alloy $Co_{70}Au_{30}$ containing an approximate vacancy concentration $c_v \sim 25\%$ as obtained from the experiment [3]. The final results, however, do not depend critically on the vacancy concentration.

Snapshots of the evolution of the domains in a typical sample are shown in Fig. 1, where the growth of the Co domains with annealing "time" (measured in Monte Carlo steps per spin) is demonstrated. The vacancies tend to aggregate in the interface between Co-rich and Au-rich regions, thus reducing the average size of the Co islands. We note that introduction of different jump rates between Co and Au, assumed proportional to their atomic masses ($\Gamma_{Au}/\Gamma_{Co} \sim 0.5$), slows down only slightly the phase separation and it does not introduce any qualitative differences in the final morphology of the system. We have therefore considered $\Gamma_A = \Gamma_B$.

To proceed with the magnetic properties, the value of the exchange energy is estimated from the wall energy as J = 300 K [11] while the dipolar energy between nearest neighbors is calculated to be of the order of g = 1.5 K. Finally, the anisotropy energy is taken to be k = 90 K so that the as-deposited Co clusters are superparamagnetic at the temperature of the simulation, in accordance with the magnetic measurements at the early stages of the annealing process.

The evolution of the hysteresis loop during annealing is also presented in Fig. 1, where a transition from a superparamagnetic sample, exhibiting no hysteresis, to a ferromagnetic film with an almost square loop is demonstrated. In Fig. 2, we have plotted the simulated evolution of the remanence of the $Co_{70}Au_{30}$ film together with the experimental findings of Ref. [3] for comparison. The qualitative features of the experimental measurements are satisfactorily reproduced. Namely, the remanence assumes very small values at the early stages of the annealing process, as the small Co clusters are superparamagnetic. As soon as the size of the Co domains exceed the superparamagnetic limit, which in our model is proportional to the domain area, a rapid increase of the magnetization appears that is characteristic of the ferromagnetic behaviour.

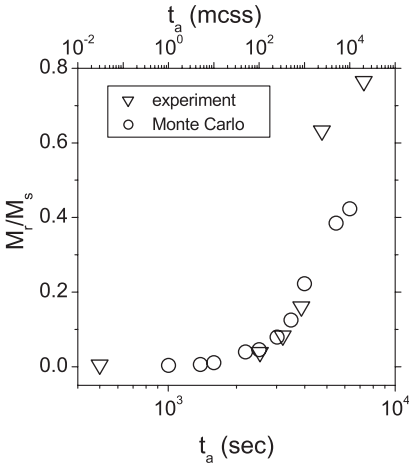

Fig. 2 Time evolution of the remanence of a $Co_{70}Au_{30}$ film with 25% vacancies annealed at 150 K. Stars: experimental data, circles: simulation data. Different time axes are used for the experimental (top) and simulated (bottom) data.

3.2 Room temperature deposition on the reconstructed (111) Au surface

We consider all the Co clusters with a perpendicular easy axis and anisotropy energy $k_i = K_1 V_i = K_0(V_i/V_0)$ and $K_0 = 2000$ K. Only clusters with height at least 2 ML (i.e. $V_i \geq 2N_w$) are exchanged coupled to their nearest neighbors. Since exchange coupling occurs only between the surface atoms of neighboring clusters, the intercluster coupling strength scales as $J_{ij} = J_0 (V_i/V_0)^{\alpha} (V_j/V_0)^{\alpha}$, where $J_0 = 200$ K and $\alpha \sim \frac{1}{2} - \frac{2}{3}$. The magnetostatic energy scales with the cluster volume and therefore we write $g_{ij} = (V_i/V_0)\ (V_j/V_0) g_0$ and $g_0 = M_s^2 V_0^2/a^3 \sim 5$ K. Any intermediate value $0 \leq V_i \leq V_0$ of the cluster volume is allowed and not just $V_i = 0$ and $V_i = V_0$ (maximum value) as in a previous model described in ref [5]. In our model, N_w is the only parameter, not taken from experiments and it leads to a complicated relation between the coverage of the substrate (i.e. the fraction of occupied by Co sites) and the amount of deposited material in monolayers, $p = N/(L^2 N_w)$. The simulated data for the coverage are compared to the experimental data in Fig. 3. Despite the simplicity of our model for the film morphology, the agreement with the experiment is quite satisfactory, justifying our assumptions that existing Co clusters on the surface both expand in area ($N_w = 2$, provided the best fitting) and increase in height. The evolution of film magnetization as a function of surface coverage is shown in Fig. 4. We observe that the onset of magnetization occurs close to $p \sim 1.5$ ML that corresponds to a coverage of $c \sim 75\%$. Given that the first monolayer of Co atoms deposited on Au forms rows of closely packed clusters [5], this value is close to the percolation threshold, where it is naturally expected that ferromagnetism would occur. Furthermore, the overall evolution of the magnetization with coverage is good agreement with the experiment.

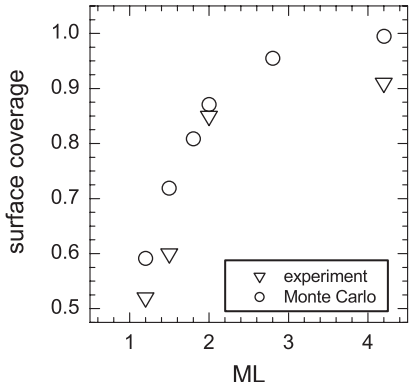

Fig. 3 Surface coverage as a function of the deposited Co monolayers (ML) on Au(111). The cluster area is equal to $N_w = 2$.

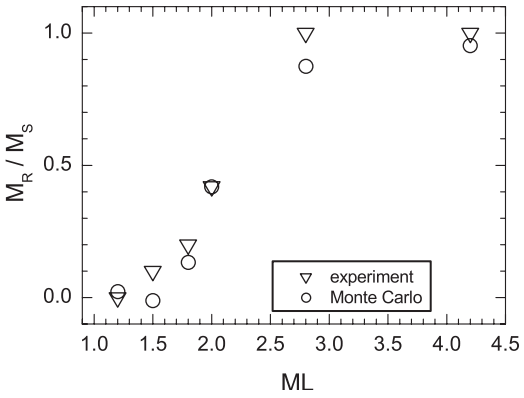

Fig. 4 Evolution of magnetisation remanence at $T = 300$ K with the amount of deposited Co on Au(111).

4 Conclusions

Modelling of the evolution of film morphology and the corresponding magnetization has been performed for Co deposited on Au surfaces under different conditions and compared with experimental measurements. Thermal annealing of films grown by low-T co-deposition of Co and Au atoms shows a paramagnetic to ferromagnetic transition as a result of a thermally driven segregation process characterized abrupt rise of the magnetization with annealing time. Deposition of Co atoms on Au(111) reconstructed surface shows a superparamagnetic to ferromagnetic behaviour as initially formed Co clusters expand and coalesce, with a characteristic abrupt increase of the magnetization above the percolation threshold.

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