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Magnetic properties of self-assembled Co clusters on Au(111) below the ferromagnetic phase transition

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Abstract. We report on the magnetic properties of Co clusters grown on Au(111) in the cluster-size range from 300 to 12 000 atoms. These clusters are superparamagnetic at room temperature, while at low temperatures blocking of the thermal fluctuations leads to a macroscopic remanence. The hysteresis curves measured *in situ* by means of x-ray magnetic circular dichroism show that the blocking temperature scales with cluster size, following a finite-size scaling power-law behaviour. We find that the blocking temperature of these clusters is substantially reduced by a thin silver overlayer, indicating a reduction in the perpendicular magnetic anisotropy at low coverages. With this change in anisotropy a clear change in the shift exponent λ can be observed.

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 [1–6]. The physical properties of these materials as a function of shrinking dimension are of fundamental interest as well as of technological importance, and relate directly to the issue of the fundamental limits of data storage. Modern recording media have a granular structure containing single-domain magnetic particles with a typical size of 20 nm. With existing state-of-the-art technology, a data bit is written to a region on the disc in an area which contains hundreds of particles. In order to reduce the data bit size, the magnetic particle size must be reduced to maintain sharp boundaries between the bits, but smaller grains have a volume so small that the anisotropy energy is not sufficient to prevent thermal energy from demagnetizing the medium—this is the so-called superparamagnetic limit.

Of specific interest for model studies is the morphologically well-characterized system of Co clusters grown on the $(23 \times \sqrt{3})$-reconstructed Au(111) surface. The reconstruction consists of domains ∼150 Å long, forming a herringbone pattern [7]. When Co is deposited at room temperature, it nucleates at the kinks in the zigzag pattern, growing in 2 ML high, roughly hexagonal islands, 73 Å apart in the $[1\bar{1}2]$ direction. These islands start to percolate at a coverage of ∼1 ML and become contiguous at coverages of ∼2 ML.

The easy axis of magnetization at low coverages is perpendicular to the surface [8, 9] with a transition to in-plane magnetization at a coverage of ∼4.5 ML [8]. The perpendicular

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magnetic anisotropy (PMA) at low coverages has been found to increase after the deposition of Au overlayers ($\geqslant$0.2 ML) [10]. It has been suggested that the strain induced by the 14% lattice mismatch between the Au substrate and hcp cobalt at low coverages causes the PMA, although a recent extended x-ray absorption fine-structure (EXAFS) study [11] indicated that the growth of Co on the Au substrate is, in fact, incoherent and therefore essentially strain-free.

At low coverages the Co clusters show superparamagnetic behaviour at room temperature [12, 13], which is characterized by rapid orientational fluctuations of a particle's overall magnetic moment. A transition to 2D ferromagnetism should occur at around the coverage where the clusters become contiguous. There are various claims in the literature about the precise coverage at which the transition occurs. Padovani *et al* [14] observed a sudden onset of 100% remanent magnetization at 1.6 ML coverages, while other studies report a more gradual onset of remanence at coverages of 2–3 ML [13]. These differences might be in part due to variation in sample preparation methods. Compared to a prepared Au(111) single-crystal surface, Au(111) films grown on a substrate have more defects and a higher roughness, so they can show a mixture of the herringbone and a linear reconstruction, on which the Co clusters will grow at widely varying rates [14]. Of course, another problem of comparing coverages in the literature is that the calibrations might be considerably different.

When superparamagnetic samples are cooled down, the thermal fluctuations of the particles' magnetic moment are eventually no longer able to overcome the anisotropy barrier between opposing spin directions, so the magnetization 'freezes' along an easy axis. In the presence of an applied external field, the blocking of the thermal fluctuations leads to a macroscopic remanence M_0. The blocking temperature, T_B, should not be confused with the Curie temperature, T_C, at which the spontaneous magnetization of the individual clusters disappears. In fact, T_C for nanoparticles is often higher than for the bulk material [5, 15].

In the work described here we studied the temperature dependence of the magnetization of Co clusters grown *in situ* on a Au(111) single crystal for coverages below the 2D–ferromagnetic transition. The hysteresis curves for a range of cluster sizes up to $N = 12\,000$ atoms were measured using the x-ray magnetic circular dichroism (XMCD) signal at the Co 2p edge [16,17]. At the 3d-transition-metal $L_{2,3}$ absorption edges, 2p core electrons are excited into empty 3d valence band states. Spin conservation of the excited electron together with spin–orbit interaction results in a signal which is proportional to the sample magnetization [9, 18]. The magnetic hysteresis loops monitored in this way showed no sign of remanence at room temperature, with blocking temperatures ranging from 220 K down to 50 K for the smallest clusters. The dependence of T_B on the cluster size appears to follow a finite-size scaling power law, with a clear strain-related change in the shift exponent λ after deposition of a Ag overlayer.

2. Experimental procedure

The Au(111) single-crystal surface was prepared by cycles of Ne ion bombardment and annealing to 900 K. Co was deposited at room temperature from an electron beam evaporator, with the pressure during deposition remaining below 1×10^{-10} mbar. The deposition rate was kept constant by monitoring both the emission of the evaporator and the drain current from the sample which is caused by the Co ions hitting the substrate. This allowed us to grow the desired cluster sizes within an accuracy of 20%. Ag overlayers were deposited at room temperature from a resistive heater, with typical deposition rates of $\approx$0.25 ML min^{-1}; the Ag coverage was monitored with a quartz microbalance.

Magnetic characterization of clusters grown *in situ* was performed by means of XMCD under UHV conditions at beamline ID12B of the European Synchrotron Radiation Facility in Grenoble, using 85% circularly polarized light from a helical undulator. Complete hysteresis

loops were recorded by varying the applied H field while monitoring the Co L_3 absorption edge at ∼780 eV through its fluorescence yield. The fluorescence was measured using a photodiode with an acceptance angle of 40° perpendicular to the incident light. The sample was rotated by 10° away from normal incidence towards the photodiode. Using the fluorescence yield it is possible to separate the comparatively weak signal of the Co clusters from the intense electron yield background of the Au substrate.

A field of up 7 T from a superconducting magnet could be applied to the samples, with the H-direction parallel to the incident beam. Hysteresis loops were measured for cluster sizes ranging from $N = 300$ to 12 000 atoms. Samples could be cooled down to temperatures of ∼5 K with a helium cryostat. For each cluster size a series of hysteresis loops versus temperature was recorded; this measurement was repeated after the deposition of a Ag overlayer.

3. Results and discussion

Figure 1 shows two typical sets of hysteresis loops for large clusters (12 000 atoms) and small clusters (1500 atoms) at temperatures from 300 K down to 20 K. At room temperature all clusters in the size range under investigation were superparamagnetic and well above their blocking temperatures. The average number of atoms per cluster, N, was obtained by fitting the hysteresis curves with a Langevin function

$$M(H) \propto \coth\left(\frac{mNH}{kT}\right) - \left(\frac{mNH}{kT}\right)^{-1} \tag{1}$$

where M is the sample magnetization, k is Boltzmann's constant, and m the magnetic moment per Co atom. This moment was assumed to have the bulk value of 1.7 μ_B. In principle, the XMCD signal properly normalized to the sum intensity should give the orbital and spin magnetic moments *per hole* [18]. But since the exact number of holes as a function of cluster size is not known, we had to use the well-known bulk value for the magnetic moment. This may well introduce a systematic error, as Stern–Gerlach-type magnetic deflection experiments on free Co clusters gave enhanced magnetic moments of 2.2 μ_B per atom at small cluster sizes [15, 19], while other studies found reduced magnetic moments for Co atoms in contact with a noble metal [21]. The cluster volumes determined using equation (1) are consistent with the sample drain current measured during evaporation, and all cluster volumes given in this paper were determined in this way. The Langevin functions gave consistent cluster sizes at all temperatures above T_B. Without scanning tunnelling microscopy (STM) or Auger measurements, there is no means of knowing the absolute coverages, but comparing our room temperature hysteresis data to the results of Takeshita *et al* [13] and Padovani *et al* [14] suggests that our largest clusters correspond to a coverage of ∼1.5 ML. The hysteresis loops at 60 K and 40 K in figure 1(b) show a narrowing at the waist which is due to the range of cluster sizes that are present. These loops are a mixture of the steeper Langevin function and the more open hysteresis curves of the blocked particles [20].

The onset of remanent magnetization at the blocking temperature can be seen to occur in figure 1 at ∼200 K for the $N = 12\,000$ clusters, and at ∼100 K for the 1500-atom clusters. The result of evaporating a Ag overlayer of ∼7 Å thickness on top of the $N = 1500$ clusters is shown in figure 2. Although the overall shape of the hysteresis loops remains unchanged, the blocking temperature reduces from 100 K to 80 K, with a correspondingly reduced coercivity at low temperatures (e.g., from 0.75 T at RT to 0.55 T at 20 K). This is an indication that—unlike the Au overlayers on Co/Au(111) [10]—the Ag overlayer reduces the out-of-plane anisotropy. For each cluster size, T_B was determined from the onset of the remanent magnetization, as

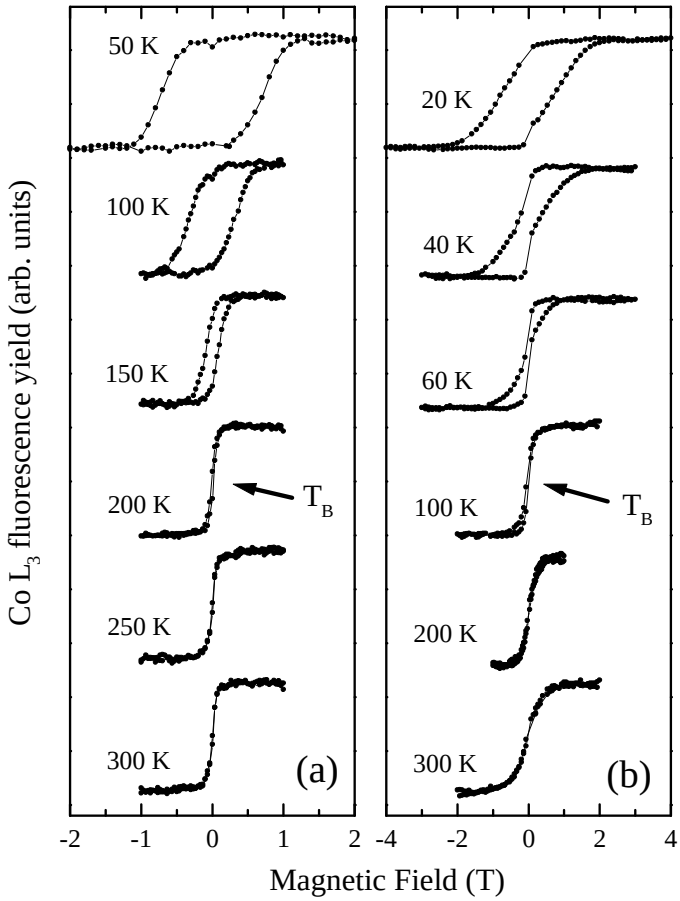

Figure 1. Hysteresis curves for (a) large ($N = 12\,000$) and (b) small ($N = 1500$) Co clusters on Au(111) measured by means of XMCD for decreasing temperatures. The hysteresis curves start to open at the blocking temperature (indicated by the arrows). Note the different magnetic field ranges for the two cluster sizes; for the smaller clusters much larger fields are required to align all the spins. The shape of the hysteresis curves at lower coverages shows the presence of a range of cluster sizes, some of which become ferromagnetic earlier than others.

shown in the inset of figure 3; for the smallest clusters ($N = 300$) the blocking temperature was as low as 50 K.

It is of fundamental interest to know whether the relation between cluster size and blocking temperature found in this experiment follows a finite-size scaling power law in the same way as the Curie temperature does for small particles [5, 6], and whether the change in anisotropy induced by the Ag overlayer will influence the scaling behaviour [22]. In the thin-film limit, the power law

$$\frac{T_c(\infty) - T_B(d)}{T_B(d)} \propto d^{-\lambda} \tag{2}$$

is normally used to cover a wider range of film thicknesses or particle sizes [23, 24]. Here, $T_c(\infty)$ is the bulk critical temperature, T_B the blocking temperature, d the particle diameter, and λ the shift exponent describing the power law. Figure 3 shows the result of plotting the reduced blocking temperature, $T_c(\infty)/T_B(d) - 1$, versus the cluster diameter (calculated

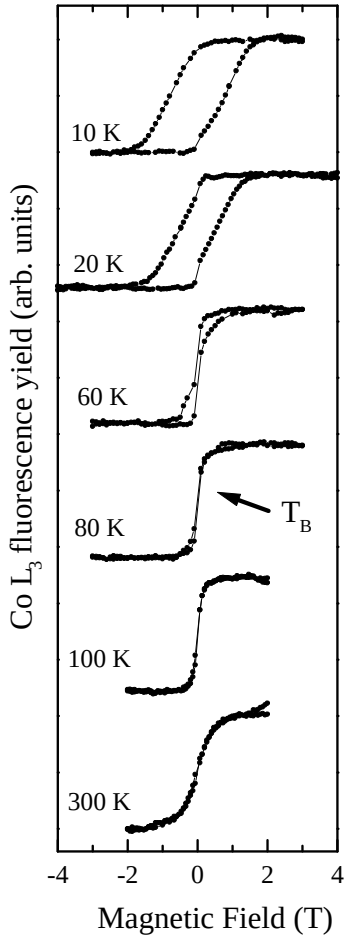

Figure 2. Hysteresis curves for Ag on Co/Au(111) at a cluster size of $N = 1500$ atoms. The blocking temperature can be seen to have dropped compared to figure 1(b).

from the cluster volume assuming circular, bilayered particles), without (•) and with (○) a Ag overlayer. The solid and dashed lines represent the best fits to a power law as given in equation (2). It is clear that on the logarithmic scale the data do indeed fall on straight lines, with shift exponents of $\lambda = 0.87 \pm 0.03$ for the bare clusters, and $\lambda = 1.18 \pm 0.03$ for the Ag-covered clusters.

This system with its perpendicular anisotropy should be described by the Ising model, which predicts shift exponents of 1.56 for three dimensions, and 1.0 for two dimensions (see Barber [25] and references therein). The shift exponents found in this work, however, clearly differ from these values. This is in agreement with previous findings that in the thin-film limit the shift exponent deviates from the predictions made by purely statistical models, and shows a dependence on the exact structure of the system, and its coordination number and exchange coupling [22, 26]. In Gd films, strain has been found to reduce the critical exponent in the thin-film limit [22], a trend that is in agreement with our own observation that λ increases upon Ag deposition. It is clear that further detailed investigations are required to link the observed shift exponents to the magnetic and structural properties of the clusters studied in this work.

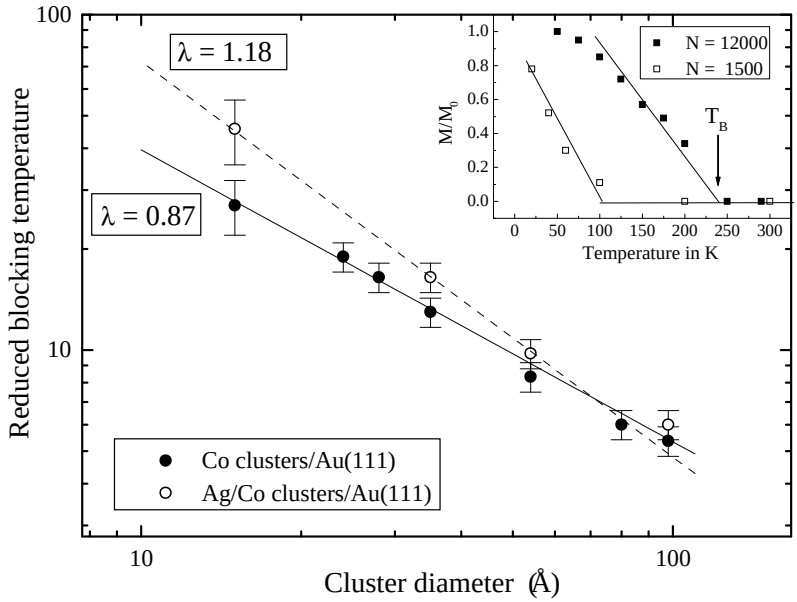

Figure 3. The reduced blocking temperature, $T_c(\infty)/T_B(d) - 1$, versus the average cluster diameter; •: Co clusters on Au(111), ○: Co clusters with a Ag overlayer. T_B was determined from the onset of the remanent magnetization, as shown in the inset. The solid and dashed lines are fits to a power law as given in equation (2). The shift parameter λ is 0.87 ± 0.03 for the Co clusters and 1.18 ± 0.03 with a Ag overlayer.

4. Conclusions

We have measured the dependence of the blocking temperature on cluster size for a wide range of superparamagnetic Co clusters on Au(111), and obtained a finite-size scaling power law relating the blocking temperature and cluster diameter, with a shift exponent of $\lambda = 0.87$. Upon evaporation of a 7 Å Ag overlayer the perpendicular magnetic anisotropy of the Co clusters is reduced, as can be observed through a strong reduction in the blocking temperature. The modified surface structure also results in a change of the finite-size scaling exponent to $\lambda = 1.18$. This finding confirms previous reports on the importance of electronic and structural properties for the critical exponents in the thin-film limit.

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References

[1] Dürr W, Taborelli M, Paul O, Germar R, Gudat W, Pescia D and Landolt M 1989 *Phys. Rev. Lett.* **62** 206
[2] Li Y and Baberschke K 1992 *Phys. Rev. Lett.* **68** 1208
[3] Schumann F O, Buckley M E and Bland J A C 1994 *Phys. Rev.* B **50** 16 424
[4] Huang F, Kief M T, Mankey G J and Willis R F 1994 *Phys. Rev.* B **49** 3962
[5] Tang Z X, Sorensen C M, Klabunde K J and Hadjipanayis G C 1991 *Phys. Rev. Lett.* **67** 3602
[6] Elmers H J, Hauschild J, Höche H, Gradmann U, Bethge H, Heuer D and Köhler U 1994 *Phys. Rev. Lett.* **73** 898
[7] Voigtländer B, Meyer G and Amer N M 1991 *Phys. Rev.* B **44** 10 354

Wollschläger J and Amer N M 1992 *Surf. Sci.* **277** 1
[8] Allenspach R, Stampanoni M and Bischof A 1990 *Phys. Rev. Lett.* **65** 3344
Speckmann M, Oepen H P and Ibach H 1995 *Phys. Rev. Lett.* **75** 2035
[9] Dürr H A, Dhesi S S, Dudzik E, Knabben D, van der Laan G, Goedkoop J B and Hillebrecht F U 1999 *Phys. Rev.* B **59** R701
[10] Ferré J, Jamet J P, Pommier J, Beauvillain P, Chappert C, Megy R and Veillet P 1997 *J. Magn. Magn. Mater.* **174** 77
[11] Marsot N, Belkhou R, Magnan H, Le Fèvre P, Guillot C and Chandesris D 1999 *Phys. Rev.* B **59** 3135
[12] Xu J, Howson M A, Hickey B J, Greig D, Kolb E, Veillet P and Wiser N 1997 *Phys. Rev.* B **55** 416
[13] Takeshita H, Suzuki Y, Akinaga H, Mizutani W, Ando K, Katayama T, Itoh A and Tanaka K 1997 *J. Magn. Magn. Mater.* **165** 38
[14] Padovani S, Chado I, Scheurer F and Bucher J P 1999 *Phys. Rev.* B **59** 11 887
[15] Bucher J P, Douglass D C and Bloomfield L A 1991 *Phys. Rev. Lett.* **66** 3052
Douglass D C, Cox A J, Bucher J P and Bloomfield L A 1993 *Phys. Rev.* B **47** 12 874
[16] Chen C T, Idzerda Y U, Lin H-J, Meigs G, Chaiken A, Prinz G A and Ho G H 1993 *Phys. Rev.* B **48** 642
[17] Lauhoff G, Lee J, Bland J A C, Schille J Ph and van der Laan G 1998 *J. Magn. Magn. Mater.* **177** 1253
[18] Thole B T, Carra P, Sette F and van der Laan G 1992 *Phys. Rev. Lett.* **68** 1943
[19] Billas I M L, Châtelain A and de Heer W A 1994 *Science* **265** 1682
Billas I M L, Châtelain A and de Heer W A 1997 *J. Magn. Magn. Mater.* **168** 64
[20] Tauxe L, Mullender T A T and Pick T 1996 *J. Geophys. Res.* **101** 571
[21] Childress J R and Chen C L 1991 *Phys. Rev.* B **43** 8089
[22] Waldfried C, McAvoy T, Welipitiya D and Vescovo E 1998 *Europhys. Lett.* **42** 685
Waldfried C, Welipitiya D, McAvoy T and Dowben P A 1998 *J. Appl. Phys.* **83** 7246
[23] Allan G A T 1970 *Phys. Rev.* B **1** 352
[24] Domb C 1973 *J. Phys. A: Math. Gen.* **6** 1296
[25] Barber M N 1983 *Phase Transitions and Critical Phenomena* vol 8, ed C Domb and J L Lebowitz (New York: Academic) ch 2
[26] Ou J T, Wang F and Lin D L 1997 *Phys. Rev.* E **56** 2805