

Oxidation Induced Enhanced Magnetic Susceptibility of Co Islands on Pt(111)[†]

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We have studied the evolution of the magnetic properties of monolayer-high cobalt islands on a Pt(111) surface as function of their exposure to oxygen. We observe a sequential quenching of magnetic anisotropy and magnetic moment. For minute exposures to oxygen this leads to an enhancement of the maximum susceptibility of up to 66% for χ'' . We show that the reason for the reduction of the anisotropy before the one of the moment is due to preferential oxygen adsorption at the island edges, which are the main source of magnetic anisotropy. Our example shows how the enhanced chemical reactivity, combined with the enhanced anisotropy of low coordinated atoms, leads to surprising changes of magnetic properties upon exposure to oxygen.

Introduction

Due to their reduced dimensions, small metallic magnetic particles created by metal epitaxy at surfaces are very sensitive to pollution, in particular to oxidation. The effect of oxidation on magnetic properties can be quite complex. Therefore partial oxidation may provide helpful insight into the origin of magnetic properties, such as magneto-crystalline anisotropy. Generally, oxidation degrades the magnetic properties; for instance, it reduces the anisotropy.¹ However, in some particular systems it may dramatically increase the anisotropy, e.g., due to exchange coupling with an antiferromagnetic CoO shell.²

One of the major questions coming up when dealing with very small nanoparticles is the influence of their shape and interfaces on the anisotropy.^{3–7} For supported cobalt chains,⁸ and for very small cobalt islands,⁹ the anisotropy per atom K is increased with respect to bulk or thin film values. In the limit of single adatoms this increase is more than 2 orders of magnitude.¹⁰ Due to the reduced atomic coordination the atoms recover part of their gas phase properties; e.g., their orbital moment is significantly larger than in bulk, where it is almost entirely quenched due to crystal field and delocalization effects. The higher orbital moments are related to a larger anisotropy of orbital moments, which in turn causes by spin–orbit coupling a higher magneto-crystalline anisotropy energy.⁶ As a consequence of this strong coordination effect, the anisotropy of two-dimensional cobalt islands grown on Pt(111) is principally determined by the edge atoms.⁶ On the other hand, the overall magnetic moment of an island is determined by all atoms approximately to equal parts because the spin moment is largely independent of coordination and it overwhelms the orbital moment. As the anisotropy is strongly dependent on the particular structure of the islands, the effect of oxidation on K should strongly depend on the island dimensionality. In particular, monolayer-high islands should be very sensitive to pollution because all atoms are interfacial. There are two interfaces to be considered, the two-dimensional (2D) island and its one-dimensional (1D) perimeter. It is the scope of this paper to study how these different interfaces are affected by oxidation and what the consequences for magnetism are.

In this article we study the early stage of oxidation of 2D cobalt islands grown on Pt(111) with focus on the evolution of their magnetic properties as function of progressing oxidation. We choose the Co/Pt system because it presents a strong perpendicular anisotropy; i.e., the average magnetization is perpendicular to the substrate and the blocking temperature is quite high. By measuring the zero field susceptibility, we are able to follow the evolution of the island's moment and anisotropy during oxidation. We show that the magnetic properties of Co islands are strongly affected by dosing minute amounts of oxygen and that the magnetic anisotropy diminishes more rapidly than the moment. Using variable temperature STM measurements, we have been able to follow the early stage of oxidation, which indicates that oxygen contamination begins selectively at the island edges. In the frame of a simple model, we show that the rapid decrease of the anisotropy is due to the fact that perimeter atoms are more rapidly affected by oxidation than core atoms. This leads to a quite astonishing effect, namely, to the increase of the maximum zero field susceptibility induced by oxidation.

Experimental Section

The experiments were carried out in a UHV chamber (base pressure 3×10^{-11} mbar), equipped with an Auger electron spectrometer (AES), a variable temperature scanning tunneling microscope (STM), and an optical system for the magneto-optical Kerr effect (MOKE). All of this equipment operates with the sample located at a common stage, operating in a temperature range of 40–1400 K. Because our system does not require sample transfer, the morphological and magnetic properties are characterized in situ, without a rise of temperature or pressure. The oxygen exposure was determined by measuring the oxygen partial pressure with a quadrupole mass spectrometer. The magnetic properties were measured with MOKE using a 780 nm laser diode as a light source. For polar Kerr measurements the laser beam was polarized in the plane of incidence, and incident on the surface at 45°. The reflected light passes through another polarizer, set to 0.5° from extinction, and is detected by a photodiode. Magnetic fields of up to ± 500 Oe and perpendicular to the surface are used for polar Kerr measure-

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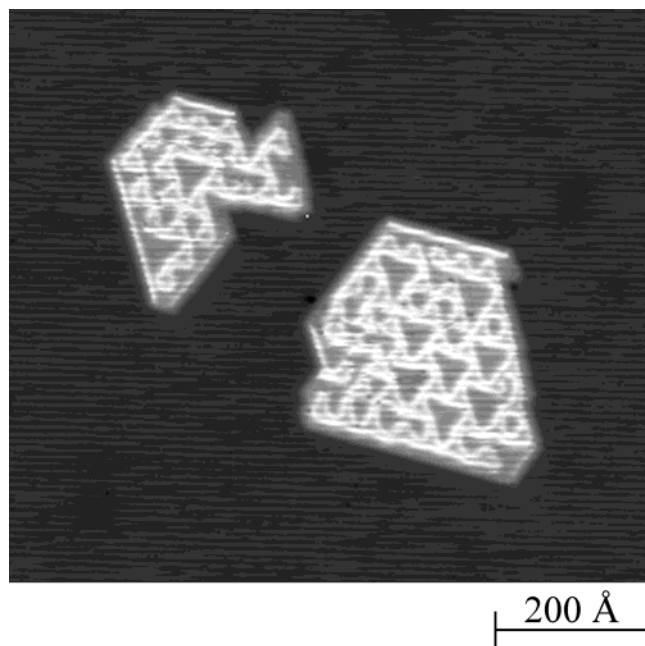


Figure 1. STM image of one monolayer-high pure cobalt islands on Pt(111) showing a triangular pattern of partial surface dislocations appearing bright and marking Co atoms adsorbed on bridge sites.

ments. The reported MOKE measurements of the zero-field susceptibility $\chi(T)$ are fully reversible with rising or lowering the temperature.

The Pt(111) substrate was prepared by cycles of 1000 eV Ar^+ sputtering at 800 K, followed by exposure to 3×10^{-8} mbar oxygen and flash annealing at 1400 K. The sample was free of contamination, as determined by AES and STM. Co was deposited by e-beam evaporation from a high purity rod (99.998%). The pressure during evaporation and annealing was lower than 5×10^{-11} mbar. The islands were grown by deposition of 0.3 ML Co at $T_{\text{dep}} = 130$ K with a deposition flux of $F = 0.3$ ML/min, and subsequent annealing to $T_{\text{ann}} = 290$ K to obtain compact islands. This two-step procedure allows us to obtain the desired island density and shape and to avoid insertion of adatoms into the first Pt plane. In addition, we thereby avoid decoration of surface steps, which is essential because a continuous Co seam forming at the steps upon deposition at 300 K turned out to dominate the magnetic signal of the sample. The islands obtained in the two-step process are essentially one monolayer-high whereas their mean size is of the order of $n = 1200$ atoms. The morphology of the ensemble of islands, namely, the island size and perimeter length distributions inferred from statistical analysis of many STM images, enables the quantitative analysis of the magnetic properties of partly oxidized islands in terms of the properties of perimeter and surface atoms in the very same way as previously shown for clean Co islands.⁶

Morphology

To see how the island morphology is modified during the oxidation process, in particular at the early stage of oxidation, we have taken STM images for different oxygen exposures, from 0 to 0.3 langmuir of oxygen, at 190 K sample temperature. The pure Co islands (i.e., 0 langmuir of O_2) shown in Figure 1 are compact monolayer-high islands with a triangular strain relief pattern of surface partial dislocations introduced to relieve part of the 10% lattice mismatch between platinum and cobalt.¹¹ In the pure Co islands the reconstruction is present everywhere on the islands, even in the close vicinity of the edges.

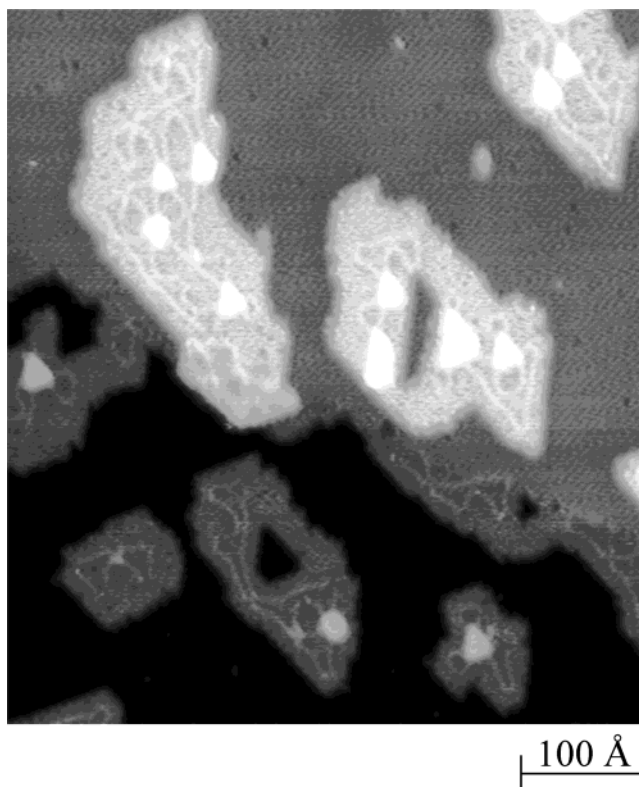


Figure 2. STM image of Co islands after the exposure to 0.05 langmuir of O_2 showing selective oxygen adsorption starting at the steps.

After the exposure to 0.05 langmuir of O_2 , the islands begin to become oxidized as shown in Figure 2. The triangular reconstruction pattern is still present at the island's center but has disappeared at the edge.

By adding more and more oxygen, the initial strain relief pattern is progressively replaced by a novel superstructure. After exposure to 0.3 langmuir of O_2 , the dislocation pattern characteristic of clean Co remains only in the center of the largest islands, as shown in Figure 3. The superstructure induced by oxidation can approximately be described as a 3×3 superstructure with a periodicity of 10 ± 1 Å. If one associates the replacement of the Co/Pt(111) reconstruction by the 3×3 superstructure to the island's progressive oxidation, then the STM images show clearly that the oxidation process begins at the island's edge.

The initial sticking coefficient of O_2 on clean Pt(111) at 200 K is $s_{0,\text{Pt}} = 0.03$.¹² This is much smaller than the one on cobalt $s_{0,\text{Co}} \approx 0.6\text{--}0.8$.^{13–15} Therefore molecules directly impinging onto Co islands will dissociate there and lead to chemisorbed oxygen atoms.^{13,16} However, because there is a weakly bound and highly mobile molecular precursor on Pt(111),^{12,17} a partly Co covered Pt(111) surface will capture oxygen molecules landing on Pt terraces more efficiently than a clean Pt surface, if their mean free path is sufficient to reach the edges of the Co islands, where the molecules dissociate with high probability. Therefore the initial sticking coefficient on Co/Pt(111) is anticipated to be significantly higher than $s_{0,\text{Pt}}$. This reaction pathway is also the first explanation of the observed selective oxidation of Co edges. The second possible reason is that O_2 molecules may also be mobile on Co islands and thus be able to reach the Co step from the top, where they are dissociated more readily due to the higher reactivity of steps.^{18–20} Therefore O_2 dosage leads first to an oxygen seam at the steps of the Co islands. As the oxygen exposure is increased, oxygen covered Co areas at the steps spread out laterally toward the island center

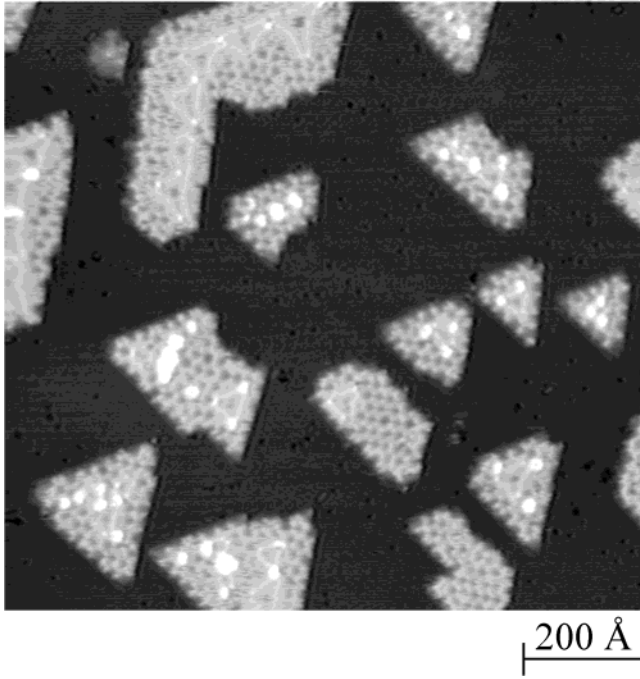


Figure 3. STM image of Co islands after the exposure to 0.3 langmuir of O₂. Only a small fraction of the larger islands have still the native strain relief pattern in their center; the remaining Co covered surface is transformed into an oxygen induced 3 × 3 structure.

until they finally encompass the whole island.²¹ Note that for an exposure to 0.3 langmuir of O₂ one has not yet the coverage required to form a stoichiometric oxide. For this exposure there is on average about one oxygen atom for 6 cobalt atoms. Even if we consider that the biggest islands are only 50% oxidized, the oxygen/cobalt ratio in the oxidized part is still low, about 1/3.

Magnetism

In a previous study we showed that the magnetic anisotropy of Co/Pt(111) islands is dominated by the perimeter atoms, whereas the islands magnetic moment is given to a good approximation by equal contributions from all constituent atoms.⁶ Thus, we expect the preferential contamination of the edge at the early stage of oxidation to have a dramatic effect on the magnetic anisotropy, whereas the moment remains high. Before showing the experimental results, we recall some results about the thermodynamics of an ensemble of uniaxial magnetic particles to introduce the necessary tools to interpret the experimental data.

Formalism Describing the Transition from the Blocked to the Superparamagnetic State. The total magnetic moment of a ferromagnetic monodomain particle containing n ferromagnetically coupled atoms can, for all practical purposes, be thought of as a single macrospin $M = n\mu_{\text{at}}$, where μ_{at} is the magnetic moment per atom. The macrospin has preferential orientations in space. Our cobalt particles have uniaxial out-of-plane anisotropy. Thus, the magnetic energy of a Co island of moment M , anisotropy K , in an applied magnetic field H parallel to the easy axis (i.e., perpendicular to the substrate), is given by $E(\theta) = -MH \cos(\theta) + K \sin^2(\theta)$, where θ is the angle between the macrospin and the easy axis.

Superparamagnetism occurs when the thermal energy is sufficient to overcome the anisotropy barrier K many times during the measurement time. In the small field limit, the probability per unit time for the macrospin to cross the

anisotropy barrier is given by the Arrhenius law $\nu = \nu_0 \exp(-(K \pm HM)/k_B T)$, where $\nu_0 \sim 10^{10}$ Hz is a typical value of the attempt frequency.

At zero field, the relaxation time τ is given by $\tau = \tau_0 \exp(K/k_B T)$, with $\tau_0 = 1/(2\nu_0)$. The barrier is readily overcome on the time scale of the measurement if $T > T_B = K/[k_B \ln(1/\omega\tau_0)]$, where ω is related to the observation time $t = 2\pi/\omega$. In our case, ω is the angular frequency of the ac-magnetic field used to measure χ . On the contrary, if the temperature is below the blocking temperature T_B , there is not enough thermal agitation to flip the magnetization during the measurement time, the particles are blocked in a fixed magnetization state (up or down), and hence $\chi(T) = 0$.

As at $T > T_B$, the magnetization has time to explore all the magnetization directions; the system is assumed to be in thermal equilibrium. Hence, $\chi(T > T_B) = \chi_{\text{eq}}$, where χ_{eq} is the thermodynamic equilibrium susceptibility. In the equilibrium state, the partition function, the magnetization, and the susceptibility can be calculated analytically.^{22,23} For the zero field susceptibility, $\chi = k_B T \partial^2 \ln Z / \partial H^2$, we obtain

$$\chi_{\text{eq}} = \frac{M^2}{k_B T} \left[\frac{\exp(K/k_B T)}{\sqrt{\pi K k_B T} \text{Erfi}(\sqrt{K/k_B T})} - \frac{1}{2K} \right] \quad (1)$$

where $\text{Erfi}(x) = \sqrt{2/\pi} \int_0^x \exp(x^2) dx$ is the imaginary error function.

At an intermediate temperature $T_B < T \ll K/k_B$, the real part of the susceptibility can be approximated by $\chi' \approx M^2/k_B T$, which corresponds to a two-state model (up-down) due to the fact that the macrospin is confined near the minima of energy obtained for $\theta = 0$ and $\theta = \pi$. Conversely, for high temperature ($k_B T \gg K$) the anisotropy is negligible and $\chi' \approx M^2/3k_B T$, which is the Langevin formula corresponding to the isotropic case where all directions of macrospin are occupied with a probability given by the Zeemann energy.

The imaginary part of the susceptibility, contrarily to the real one, is very peaked around T_B , in the region where the system goes from blocked to superparamagnetic. Hence, in the vicinity of T_B the system is determined by the kinetics of barrier crossing. In the limit of small fields ($MH < k_B T$) linear response theory gives the following analytical expression for the in-phase (real) and out-of-phase (imaginary) susceptibility:⁶

$$\chi'(T) = \frac{1}{1 + \omega^2 \tau^2} \chi_{\text{eq}}(T) \quad (2)$$

$$\chi''(T) = \frac{\omega \tau}{1 + \omega^2 \tau^2} \chi_{\text{eq}}(T) \quad (3)$$

The width of the transition from blocked to superparamagnetic, which corresponds also to the width of χ'' , is typically $\Delta T_B = 2k_B T_B^2/K \approx T_B/10$. The maximum of χ'' is reached at T_B and is given, to a good approximation, by $\chi''_{\text{max}} = M^2/(2k_B T_B)$. The maximum of χ' is located just above T_B and its value is approximately $\chi'_{\text{max}} = 2\chi''_{\text{max}} = M^2/k_B T_B \propto M^2/K$. Note that, as the width of the χ'' peak is almost proportional to T_B and its height to $1/T_B$, we deduce that the area of the χ'' peak depends neither on T_B nor on the anisotropy. Thus, two islands with the same macrospin M and relaxation time τ_0 , but different anisotropies, will have the same area for their χ'' peaks.

Maximum of the Real Susceptibility. We now focus on the expected effect of oxygen exposure on the maximum of the magnetic susceptibility of an ensemble of monodisperse islands. In the following the subscripts 0 and 1 designate the pure and

oxidized Co islands, respectively. If one assumes that the attempt frequency ν_0 stays constant during oxidation, then the ratio between the maximum of susceptibilities $\chi'_{\max,0}$ and $\chi'_{\max,1}$ of pure and oxidized Co island is given by

$$\frac{\chi'_{\max,1}}{\chi'_{\max,0}} = \frac{M_1^2 T_{B,0}}{M_0^2 T_{B,1}} = \frac{M_1^2 K_0}{M_0^2 K_1} \quad (4)$$

At the early stage of oxidation, the susceptibility χ can either increase or decrease depending on the origin of the magnetic anisotropy. Basically, there are two limiting cases: the first supposes that the magnetic anisotropy energy is mainly determined by the perimeter atoms (we always refer to the outer perimeter of the island and not to the borderline between oxidized and clean part); the second, that each Co atom of the non-oxidized part of the islands contributes equally to the anisotropy (i.e., the anisotropy is proportional to the particle's ferromagnetic volume). As we will see below, these two limiting cases give opposite results concerning the evolution of the maximum in-phase susceptibility.

First of all, consider an island for which the magnetic anisotropy energy K depends strongly on the perimeter atoms. For such an island the anisotropy should be rapidly affected even with a very small amount of oxygen due to the selective oxidation of the island edge. Concerning the island magnetic moment, it should decrease proportionally to the oxidized fraction of the island. Thus, for a very small amount of oxygen, for which only the island border is contaminated, the anisotropy should drop strongly whereas the macrospin should decrease only slightly. In the first approximation, we can suppose that K decreases, i.e., $K_1 < K_0$, whereas the macrospin stays constant: $M_1 = M_0$. Then, we obtain

$$\frac{\chi'_{\max,1}}{\chi'_{\max,0}} \simeq \frac{K_0}{K_1} > 1 \quad (5)$$

This means that the maximum of the susceptibility should *increase* at the beginning of oxidation, when only the perimeter atoms are bound to oxygen.

On the contrary, if the anisotropy is proportional to the ferromagnetic volume, then it is also proportional to the island magnetic moment M . In other words, the shrinking magnetic core should have a continuously decreasing anisotropy barrier. The magnetic moment of an oxidized island can be written as $M(x) \simeq (1 - x)M_0$, where M_0 is the macrospin of a pure Co island and x is the oxidized fraction of the island. Due to the proportionality between K and M , we also have $K(x) \simeq (1 - x)K_0$, where K_0 is the anisotropy of the pure Co island. From this we obtain $\chi'_{\max}(x) = M^2(x)/k_B K(x) \propto (1 - x) \propto T_B(x)$, which signifies that the maximum susceptibility should *decrease* continuously with oxidation.

To conclude this theoretical part, from the fact that steps are first covered by oxygen we obtain a criterion to evaluate the role of perimeter atoms in the anisotropy by dosing oxygen. If every atom in the island plays the same role, then the maximum of susceptibility must decrease linearly to zero. If the anisotropy energy is strongly dependent on perimeter atoms, then the maximum susceptibility should increase. These two models, though quite simple, catch the overall behavior of the two limiting cases.

Measurements. Figure 4 shows the experimental temperature dependence of the in-phase susceptibility of a sample exposed to three amounts of oxygen (0, 0.05, and 0.15 langmuir). The susceptibility measurements have been performed with a field

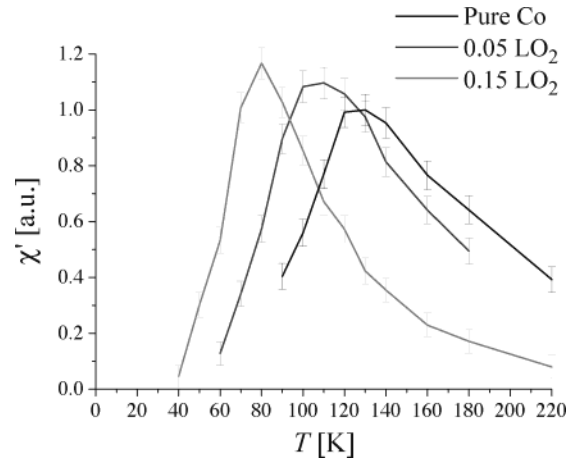


Figure 4. Zero field in-phase susceptibility χ' as a function of temperature for pure and oxidized Cobalt islands. The lines are guides for the eye.

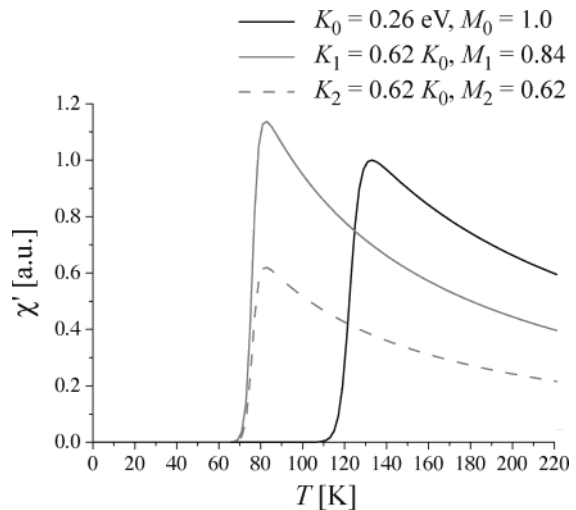


Figure 5. Simulated curves of the zero field in-phase magnetic susceptibility χ' of three types of islands. The black curve corresponds to islands with a blocking temperature of 130 K, which give a rough approximation of the experimental susceptibility of the pure Co islands. The continuous gray curve is obtained with the parameters extracted from the susceptibility of the islands exposed to 0.15 langmuir of O_2 . The dashed curve corresponds to the susceptibility expected for the anisotropy being proportional to the magnetic volume.

modulation frequency of 0.1 Hz and an amplitude of 500 Oe and by taking the zero-field slope of the $M(H)$ curve within the linear regime at ± 50 Oe with respect to the origin. The three curves have typically the same shape, which agrees qualitatively to what is predicted by the simple model discussed above (see also Figure 5). At low temperature the susceptibility goes rapidly to zero, when the temperature rises, the susceptibility increases to a maximum and then decreases slowly. Experimentally, the susceptibilities we measure present a wide transition from zero (blocked regime) to the maximum due to the island's size and perimeter length dispersion,⁶ which induce a broad range of blocking temperatures. But, for simplicity, we will consider a unique blocking temperature defined here as the temperature corresponding to the maximum of susceptibility. For pure cobalt islands, the blocking temperature is $T_{B,0} \simeq 130$ K and the maximum of real susceptibility is set to $\chi'_{\max,0} = 1.0$ (au). When the islands are exposed to oxygen, the blocking temperature decreases and the maximum of χ' increases. For 0.05 langmuir of O_2 one obtains $T_{B,1} \simeq 105$ K and $\chi'_{\max,1} = 1.1$, and

for an exposure to 0.15 langmuir of O₂ one obtains $T_{B,2} \approx 80$ K and $\chi'_{\max,2} = 1.15$.

The maximum susceptibility increases at the first stages of oxidation, which is expected considering the anisotropy being dominated by perimeter atoms.⁶ The explanation of the increase of χ' we gave previously was for monodisperse islands, but it also holds in the case of a polydisperse distribution of islands, as we will see in detail below. To give first quantitative estimates, we make the assumption that the curves of Figure 4 can be interpreted by considering the monodisperse case. Although this is a crude approximation, it should illustrate the overall behavior. Using this approximation, and supposing that the attempt frequency ν_0 is not modified by oxidation, we obtain

$$\frac{M_1}{M_0} = \sqrt{\frac{\chi'_{\max,1} T_{B,1}}{\chi'_{\max,0} T_{B,0}}} \quad (6)$$

Using the values of T_B and χ'_{\max} of pure and oxidized cobalt we found before, we obtain $M_1 = 0.94M_0$ and $M_2 = 0.84M_0$, where M_0 is defined as the magnetization of a pure Co island. Hence, due to the exposure to 0.05 langmuir of O₂ the anisotropy decreases by about 20%, whereas the macrospin lowers by only 6%. Similarly, for an exposure to 0.15 langmuir of O₂ the anisotropy decreases by 40%, whereas the macrospin lowers by only 16%. Therefore the anisotropy drops about three times faster than the macrospin, and this is why the maximum of susceptibility increases by 10–15%. This is in perfect agreement with the picture of the anisotropy being predominantly caused by perimeter atoms.⁶ On the contrary, supposing that the anisotropy is proportional to the magnetic volume, we should have $\chi'_{\max,1}/\chi'_{\max,0} = T_{B,1}/T_{B,0}$. Taking into account the blocking temperatures $T_{B,1}$ and $T_{B,2}$, this model predicts that $\chi'_{\max,1} \approx 0.8$ and $\chi'_{\max,2} \approx 0.6$. Experimentally, we find $\chi'_{\max,2} = 1.15$, which is about 100% more than what this model predicts (see Figure 5). Hence, we can exclude the anisotropy being just proportional to the magnetic volume.

The comparison between the measured susceptibility corresponding to an exposure of 0.15 langmuir of O₂ (Figure 4) and the simulated curve in Figure 5 ($K_1 = 0.61K_0$, $M_1 = 0.84M_0$) clearly shows that the decrease of χ' is much too fast compared with the theory. In the temperature range of the measurements, the decrease goes as $1/T$, consequently the value of the susceptibility at 200 K should be approximately $\chi' = 0.4$ (see Figure 5), but in fact the measured value is $\chi' \approx 0.1$. The faster than $1/T$ decrease at high temperature is also observed for the pure cobalt islands but the effect is less pronounced in this case.⁶ We associate this rapid lowering of χ' to the temperature dependence of the island's magnetic moments, which actually decrease upon approaching the islands Curie temperature. In the pure cobalt islands the Curie temperature is lowered compared to the bulk value due to the island's dimensionality.²⁴ This lowering is expected to be more pronounced for the oxidized islands due to the disorder induced by the oxygen impurities.

Taking the Size Distribution into Account. In the previous analysis, we have assumed that the behavior of the overall collection of particles was roughly the same as for a perfectly monodisperse collection. In fact, a deeper analysis shows that the increase of χ' upon oxidation for a real polydispersed system is qualitatively well described by this approximation. However, in the case of the imaginary susceptibility, one must take the dispersion into account, as we will show below.

In Figure 6 we show real and imaginary susceptibilities, acquired as a function of T using a LockIn and working with a

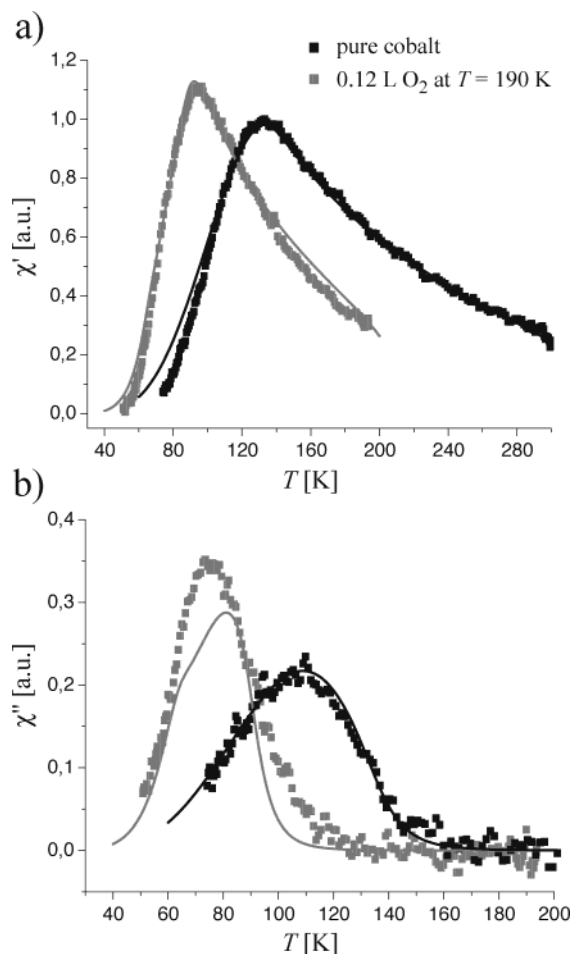


Figure 6. In-phase zero field susceptibility χ' (a) and out-of-phase zero field susceptibility χ'' (b) as function of temperature for pure and oxidized cobalt islands.

11 Hz, 50 Oe sinusoidal field modulation. This field amplitude is given by optimization of the signal-to-noise ratio while still staying in the linear response regime. All the curves have been normalized with respect to the maximum of χ' of the pure Co islands. The real susceptibility, which increases by 11% at an exposure of 0.12 langmuir, shows the same behavior as in Figure 4. However, the imaginary susceptibility increases by 66%, which is a much greater enhancement than for the real susceptibility.

For a monodisperse ensemble, χ'' is a narrow peak localized around the blocking temperature and the ratio between the maximum of χ'' and χ' should stay constant and equal to $\chi''_{\max}/\chi'_{\max} = 1/2$. For an ensemble of differently sized particles, χ'' is a sum of peaks localized at different positions depending on the anisotropy of each of the islands. As a result, χ'' has a broad peak, the shape of which reflecting the distribution of anisotropy energies. As explained previously, the area under χ'' does not depend on the particular anisotropy of each island. Therefore, a broadening of χ'' would necessarily be associated with a reduction of its amplitude χ''_{\max} . The effect of the broadening is much less pronounced on χ'_{\max} , hence for a system with a K distribution $\chi''_{\max}/\chi'_{\max} < 1/2$. The lower this ratio, the wider is the distribution of K values. Thus, the ratio $\chi''_{\max}/\chi'_{\max}$ allows a direct evaluation of the anisotropy energy distribution.

Due to the finite width of our actual size dispersion the ratio is indeed much lower than 50%. It varies from 21% in pure cobalt to 32% after the dosage of 0.12 langmuir of oxygen. The more the ratio approaches 50%, the more narrow is the

anisotropy distribution. The increase from 21% to 32% shows that the anisotropy distribution has been narrowed upon oxidation, and this squeezing of the anisotropy can induce a much stronger enhancement of χ'' than χ' .

The narrowing of the K distribution is expected because the proportion of perimeter to surface atoms decreases with increasing island size. Assuming now that the oxygen capture is proportional to the island area and that the oxygen diffuses and sticks at edges having higher reactivity, we deduce that the largest islands have their edges contaminated much more rapidly than the smallest ones. As a consequence, the anisotropy decreases much more rapidly for the large islands and the anisotropy distribution becomes more narrow.

This qualitative argument is supported, and absolute numbers for K can be attributed, if we use the measured size and perimeter length distributions as input to fit the real and imaginary susceptibilities for the ensemble of islands as shown in Figure 6. For the fitting procedure, we have summed over the ensemble of islands; for each island the susceptibilities are given by eqs 2 and 3. The anisotropy is given by a sum of two terms, one due to the perimeter atoms with amplitude pK_p where p is the number of perimeter atoms and $K_p = 0.91$ meV/atom.⁶ The other anisotropy term is a surface contribution nK_s , where $K_s = -0.033$ meV/atom; note that this term is the sum of the demagnetizing energy (negative) and of the magnetocrystalline surface anisotropy (positive).⁶ Here we have taken a temperature-dependent macrospin $m(T) = m_0(1 - T/T_c)^{1/8}$, given by the 2D Ising model. One could also take a temperature dependent anisotropy; but as the precise value of the anisotropy is solely needed near the blocking temperature, which is between 70 and 130 K (see χ'' of pure Co islands), it is safe to assume a constant anisotropy in this range. As seen in Figure 6, the fit is very good for χ' as well as for χ'' in the clean Co case.

For fitting the data of the oxidized Co islands, we have to find an appropriate procedure to describe how the anisotropy is modified upon oxidation. The macrospin of an oxidized island can be written as $M(x) = (1 - x)M_0$, where M_0 is the macrospin of the island before oxidation, and x is the oxidized fraction of the island. We will assume that for a given exposure, all the islands have the same oxidized fraction due to the fact that the oxygen capture rate is almost proportional to the island area. The surface anisotropy K_s is affected in the same way as the macrospin; therefore we take $E_s(x) = (1 - x)nK_s$. For the perimeter anisotropy, we consider that the oxidation begins at edges until the edges are completely oxygen covered, and then the oxidation progresses toward the center of the islands. If the edge is not fully saturated, the number of edge atoms contaminated is simply given by $p_{ox} = nx$, $\forall nx < p$, whereas if the edge is completely oxidized $p_{ox} = p$, $\forall nx \geq p$, where n and p still refer to the number of surface and perimeter atoms in the clean island. Then the most natural expression for the perimeter anisotropy is $E_p(x) = (p - p_{ox})K_p + p_{ox}K_p^{ox}$ for the unsaturated case, and for the saturated one $E_p(x) = pK_p^{ox}$, where K_p^{ox} stands for the anisotropy of the edge after oxidation. Naturally, we keep the same K_s and K_p as for pure Co. As we explained earlier, the macrospin seems to decrease more rapidly with temperature when the particles are contaminated; therefore we have to take a lower Curie temperature for the macrospin. For the fit of the oxidized island we have taken $T_c = 220$ K, slightly lower than the typical value of 350 K for clean Co islands.

With this model, the best fit is obtained with $K_p^{ox} = 0.72$ meV/atom and $x = 0.11$. The fact that K_p^{ox} is only 21% lower than K_p seems surprising at first sight, because it signifies that the contamination of edge atoms lowers their anisotropy only a

little. However, we believe that the oxygen covered step atoms have indeed much less anisotropy than their clean counterparts, but the new interface between them and the still clean Co atoms situated one row behind may augment the anisotropy of the second species far beyond the former surface value. Therefore in total the 1D interface located in close vicinity to the island border has an appreciable anisotropy, which we model by lowering the step anisotropy only by a small amount. Note that because the anisotropy is the sum of a surface and perimeter term, its reduction when all the perimeter atoms are contaminated can be higher than 21%. With our set of parameters, we find that the anisotropy of an island of 500 atoms has decreased by 12%, whereas the anisotropy of an island of 5000 atoms has decreased by 30%. This clearly shows that in the frame of our model the anisotropy of the bigger islands decreases much more rapidly than the anisotropy of the smaller ones. This leads to a compression of the K distribution and induces a strong enhancement of χ'' . As we can see from Figure 6b, the experimental enhancement of 66% is beyond the value predicted by our model. We note that our model was driven by the desire to reduce the number of free parameters to a minimum (K_p^{ox} and x); therefore perfect fitting of χ'' cannot be expected. Nevertheless, the fact that the χ'' peak is very high is a direct confirmation of the narrowing of the K distribution resulting from the preferential contamination of edge atoms.

Higher Oxygen Exposure. After an exposure to 0.3 langmuir of O_2 corresponding to the case of Figure 3, the magnetic susceptibility at 200 K is nearly zero to the precision of the measurements. The fact that such a small amount of oxygen is sufficient to entirely kill ferromagnetism is quite surprising and in striking contrast with previous experiments on 3D cobalt nanoparticles. In particular, Hill et al.¹ show that for half spherical nanoparticles of 2200 atoms, the magnetic signal begins to decrease only after exposure to 2 langmuir of O_2 and vanishes at a total oxygen amount of 30 langmuir of O_2 . These exposures are about 100 times more than the ones required for our islands. In the case of Hill et al., the slow oxidation process is due to the fact that for spherical particles the bulk is protected from contamination by the outer shell. Conversely, in the case of our monolayer-high 2D islands, all atoms are directly exposed to the dosed oxygen. We note that apart from oxygen also the residual gas strongly influences the island's magnetic properties. After a 1 h exposure to the residual gas of our vacuum chamber (essentially H_2) with a pressure of 3×10^{-11} mbar, the susceptibility at 200 K is generally reduced by 20%. Thus, the study of 2D islands requires us to work with base pressures below 10^{-10} mbar. Moreover, any manipulation of the sample between the preparation and the measurement should be avoided, and the magnetic measurements have to be done quickly.

Conclusion

We have shown that the magnetic signal from one monolayer-high cobalt islands on a Pt(111) surface is extremely sensitive to very small amounts of oxygen. An exposure to 0.3 langmuir of O_2 suffices to entirely suppress the island's ferromagnetic moment. The STM images show that the oxidation begins at the edges and progresses with increasing oxygen exposure toward the center. The susceptibility measurements show that the maximum susceptibility increases with oxygen exposure. This effect is explained by the magnetic anisotropy originating from the island edges and the moment being proportional to the area. As a consequence, oxygen exposure reduces first the anisotropy and only at a later stage the moment. This induces an enhancement of the susceptibility, and in addition the distribution of anisotropy energies is compressed.

References and Notes

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