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Magnetic properties of gold-encapsulated Co0.5Pd1–x self-organized nano-clusters on Au(111) are analyzed by x-ray magnetic circular dichroism for x = 0.5, 0.7, and 1.0. The clusters are superparamagnetic with a blocking temperature decreasing with increasing Pd concentration, due to a reduction of the out-of-plane anisotropy strength. No magnetic moment is detected on Pd in these clusters, within the detection limit, contrary to thick CoPd films. Both reduction of anisotropy and vanishing Pd moment are attributed to strain. © 2013 AIP Publishing LLC.

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I. INTRODUCTION

Combining alloy and dimensionality effects is expected to offer new engineering possibilities to optimize magnetic properties in nanoclusters, aiming at increased storage density. Presently, at the nanoscale, no stable magnetic information can be stored at room temperature because of too low superparamagnetic blocking temperatures, which scale with the product of magnetic volume and anisotropy. Therefore, magnetic alloy nanoparticles associating magnetic transition metals with high spin-orbit 4d and 5d elements are explored with the aim producing nanoparticles with enhanced anisotropy. Different routes of controlled-size nanocluster fabrication are explored today, mainly gas-phase cluster fabrication separately the pure elements in a sub-monolayer coverage on Au(111). The coverage was estimated by Scanning tunneling microscopy (STM). The evaporation rates of Co and Pd were adjusted to obtain the desired composition. Three samples were prepared, 0.25 monolayer (ML) of pure Co, 0.3 ML Co0.3Pd0.7, and 0.4 ML Co0.5Pd0.5. After characterization, they were covered by 2.5 nm gold, ensuring a continuous protective film of several monolayers, as verified by STM. As an XMCD reference for Pd L2,3 edges, we fabricated in a separate installation by molecular beam epitaxy a 40 nm thick Co0.5Pd0.5 film deposited on a silicon substrate (bottoming sequence was used: Cr(3 nm)/Co0.5 nm)/Co0.5 Pd0.5(40 nm)/Co(0.5 nm)/Cr(20 nm)/Si).

X-ray absorption and XMCD spectra at the L2,3 Co edges were measured at the DEIMOS beamline at SOLEIL in total electron yield mode for light incidences from normal to grazing (70°) in a 6.5 T field applied along the photon beam. Magnetization loops at the maximum dichroism of the Co L3 edge were recorded as a function of temperature, and averaged over the two light helicities (recording time: ≈40 min). Absorption and XMCD spectra at Pd L2,3 edges were recorded at ID 12 at ESRF using an energy resolved fluorescence detector, with grazing light incidence onto the sample (75°), under an applied field of 6.0 T and at 7 K.

Ab initio spin-polarized calculations were performed within the standard Kohn-Sham self-consistent density functional theory (DFT) using the SIESTA method11 in the generalized gradient approximation (GGA) with a Perdew Burke Emzerhof exchange–correlation potential.12 For the ion-electron interactions, the core electrons are replaced by norm-conserving pseudopotentials,13 while valence states are described using numerical atomic orbital basis sets (NAO). The electronic population is sorted for each orbital on each atomic site, using a Mulliken analysis.

To disentangle strain and hybridization effects, we have considered the following model configurations: the bulk

II. EXPERIMENTAL AND CALCULATION DETAILS

Bimetallic clusters were prepared by co-deposition of Co and Pd on Au(111) single crystals held at 300 K in ultra-high vacuum. Electron-beam evaporators with integrated flux monitors were used to evaporate Co and Pd from high purity rods. The flux monitors were calibrated by depositing separately the pure elements in a sub-monolayer coverage on Au(111). The coverage was estimated by Scanning tunneling microscopy (STM). The evaporation rates of Co and Pd were adjusted to obtain the desired composition. Three samples were prepared, 0.25 monolayer (ML) of pure Co, 0.3 ML Co0.3Pd0.7, and 0.4 ML Co0.5Pd0.5. After characterization, they were covered by 2.5 nm gold, ensuring a continuous protective film of several monolayers, as verified by STM. As an XMCD reference for Pd L2,3 edges, we fabricated in a separate installation by molecular beam epitaxy a 40 nm thick Co0.5Pd0.5 film deposited on a silicon substrate (following sequence was used: Cr(3 nm)/Co0.5 nm)/Co0.5 Pd0.5(40 nm)/Co(0.5 nm)/Cr(20 nm)/Si).

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To disentangle strain and hybridization effects, we have considered the following model configurations: the bulk
phase L1_0 of a CoPd alloy, a chemically ordered CoPd(111) atomic layer inserted in a gold matrix in order to mimic the experimental Au/Co_{0.5}Pd_{0.5}/Au(111) sample, and a Co(111) bilayer inserted in a gold matrix. For the Au-embedded layers, the simulation slabs are 6×6 atoms supercells with 3 to 6 layers thickness corresponding to 108 to 216 atoms. Co and CoPd embedded layers were considered to be accommodated to gold lattice parameter (0.408 nm) as optimized with DFT.

III. RESULTS AND DISCUSSION

Let us first summarize the most important features of the growth of bimetallic CoPd clusters, which is analyzed in detail elsewhere. A Co clusters are known to grow in a self-organized way as bilayers, whereas Pd grows as single-layer clusters. For Pd, although there is preferential nucleation on the kinks of the gold reconstruction, the organization of the cluster array is not as good as for Co. This is due to the fact that adsorption of Pd on Au(111) strongly disrupts the reconstruction, and hence nucleation sites. However, very few amounts (∼3%) of cobalt co-deposited with Pd allow to stabilize the reconstruction and favor self-organization of Pd. It is therefore possible to obtain a high quality of self-organization of CoPd alloys for a very large composition range.

Concerning the cluster height, Co forms bilayer whereas Pd forms single-layer high clusters, although the thermodynamically stable shape should lead to formation of bilayers for both elements. It was shown that for Pd on Au(111) atom hopping from first Pd to second layer is kinetically blocked by high energy activation barriers, whereas for Co, hopping is favored due to strain relaxation allowing clusters to reach the equilibrium shape. For alloy clusters, the height of the clusters depends on their composition but Pd has a strong tendency to stabilize the single-layer configuration. Up to about x = 0.5, Co_{1−x}Pd_x clusters are essentially single-layer high. Above x = 0.5, bilayer clusters start to appear. At x = 0.7, monolayer and bilayer clusters coexist (Fig. 1).

Figure 2 (left) shows the absorption spectra at the Co L_{2,3} edges for the three samples, and the XMCD signal of the Co_{0.5}Pd_{0.5} clusters. From the angular dependence of the XMCD, the spin and orbital moments are deduced using the so-called sum rules. They are reported in Table I, together with the orbital moment anisotropy ∆m_l = m_l^⊥ − m_l^∥. The number of d holes (N_d) necessary to extract the absolute values of moments is determined by the DFT calculations (see Table II).

Looking at the right panel of Fig. 2, one notices that the Pd L_{3} edge is much broader and less intense for the Co_{0.5}Pd_{0.5} clusters than for the 40 nm thick Co_{0.5}Pd_{0.5} reference film. The Pd L_{2} edge (not shown) is hardly detectable for the clusters: due to the very small quantity of Pd and to the overlap with the strong gold substrate background, we are at the limit of the detection possibility of the instrument. There is however no sizable XMCD signal at the Pd L_{3} edge in the clusters. Given the signal to noise ratio, we estimate by comparison with the reference film that the Pd magnetic moment in the clusters is below ∼0.1 μ_B. In the thick Co_{0.5}Pd_{0.5} film, the Pd spin moment is 0.4 μ_B, comparable to the one obtained earlier in similar alloy films.

Figure 3 shows XMCD magnetization loops at the Co L_{3} edge for the three samples at grazing and normal light incidence for various temperatures. From the shape of the loops at 4 K, one deduces that the easy magnetization axis is perpendicular to the surface for all samples. The loops were recorded along the easy axis as a function of temperature to estimate the blocking temperature, i.e., when there is a transition from a vanishing to a sizable coercive field. Loops

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_B (K)</th>
<th>m_l^⊥</th>
<th>m_l^∥</th>
<th>∆m_l</th>
<th>m_s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 ML Co/Au(111)</td>
<td>35 K</td>
<td>0.22</td>
<td>0.21</td>
<td>0.01</td>
<td>2.1</td>
</tr>
<tr>
<td>0.30 ML Co_{0.7}Pd_{0.3}/Au(111)</td>
<td>25 K</td>
<td>0.29</td>
<td>0.41</td>
<td>−0.12</td>
<td>2.0</td>
</tr>
<tr>
<td>0.40 ML Co_{0.5}Pd_{0.5}/Au(111)</td>
<td>10 K</td>
<td>0.44</td>
<td>0.34</td>
<td>0.10</td>
<td>1.7</td>
</tr>
</tbody>
</table>

TABLE I. Blocking temperature, Co orbital moment perpendicular and parallel to the surface, orbital moment anisotropy, spin moment (μ_B/atom). The number of d holes obtained by DFT is N_d = 2.6 (see Table II). The error on magnetic moments is in the order of 10%.
TABLE II. DFT calculations of Co and Pd spin magnetic moments ($\mu_B/\text{atom}$) for various model situations and number of $d$ holes.

<table>
<thead>
<tr>
<th>Model situation</th>
<th>Lattice constant (nm)</th>
<th>$m_{Co}^d$</th>
<th>$m_{Pd}^d$</th>
<th>$N_{Co}^d$</th>
<th>$N_{Pd}^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Co</td>
<td>0.353</td>
<td>1.51</td>
<td>...</td>
<td>2.49</td>
<td>...</td>
</tr>
<tr>
<td>Co (stretched)</td>
<td>0.375</td>
<td>1.72</td>
<td>...</td>
<td>2.51</td>
<td>...</td>
</tr>
<tr>
<td>Bulk Pd</td>
<td>0.400</td>
<td>...</td>
<td>0.00</td>
<td>...</td>
<td>1.19</td>
</tr>
<tr>
<td>Bulk CoPd</td>
<td>0.382</td>
<td>1.96</td>
<td>0.25</td>
<td>2.59</td>
<td>1.10</td>
</tr>
<tr>
<td>Bulk CoPd (stretched)</td>
<td>0.410</td>
<td>2.20</td>
<td>0.19</td>
<td>2.63</td>
<td>1.08</td>
</tr>
<tr>
<td>Au/2MLCo/Au</td>
<td>0.410</td>
<td>1.98</td>
<td>...</td>
<td>2.60</td>
<td>...</td>
</tr>
<tr>
<td>Au/CoPd/Au</td>
<td>0.410</td>
<td>2.32</td>
<td>0.09</td>
<td>2.62</td>
<td>1.08</td>
</tr>
</tbody>
</table>

The decrease of the blocking temperature with Pd concentration, although unexpected, is in line with recent work which did neither evidence enhanced blocking temperatures in nano-alloy clusters combining transition metals with high spin-orbit coupling. The orbital moment anisotropy is no more a monotonous function of magnetic anisotropy. It is therefore not possible to deduce magnetocrystalline anisotropy tendencies by comparing the orbital moments of the different situations analyzed. We must therefore rely on the magnetization loops.

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Within the comparison of these results with DFT, some tendencies can be clearly identified. From Table II, we note that the magnetic moments are sensitive to both strain and chemical environment (see also Ref. 25): DFT predicts a larger moment for Co atoms either when stretched or in chemical vicinity of Pd. For Pd, we observe a vanishing moment, and this is rather unexpected, since Pd and Pt behave quite similarly and bear a large spin magnetic moments when alloyed with Co or Fe, even in nanoparticles.4,21,23,24

Considering the spin moments, for Co we observe in all cases a spin moment larger than in bulk Co (1.59 $\mu_B$), and comparable to the one in bulk CoPd alloys (1.95 $\mu_B$).22 For Pd, we observe a vanishing moment, and this is rather unexpected, since Pd and Pt behave quite similarly and bear a large spin magnetic moments when alloyed with Co or Fe, even in nanoparticles.4,21,23,24

Turning to the orbital moment, we note that although magnetization loops all indicate out-of-plane anisotropy, the orbital moment anisotropy $\Delta m_B$ is either positive or negative. The simple correlation observed usually between the orbital moment anisotropy and the magnetocrystalline anisotropy27,28 no more applies in strongly hybridized systems with large spin-orbit coupling, as emphasized by Andersson et al.29 In such systems, as is the case for CoPd, the magnetocrystalline anisotropy is no more a monotonous function of magnetic anisotropy. It is therefore not possible to deduce magnetocrystalline anisotropy tendencies by comparing the orbital moments of the different situations analyzed. We must therefore rely on the magnetization loops.

The decrease of the blocking temperature with Pd concentration, although unexpected, is in line with recent work which did neither evidence enhanced blocking temperatures in nano-alloy clusters combining transition metals with high spin-orbit coupling.3,7 We obtain roughly the same order of magnitude for the anisotropy ($\approx$50 $\mu eV/\text{atom}$) as the one in CoPt nano-clusters,3 much less than in ordered bulk alloys. The decrease of the magnetic volume by replacing the magnetic Co atoms by weakly magnetic atoms like Pd or Pt is not compensated by a sufficient increase of anisotropy. In our particular case, a tentative explanation for the blocking temperature decrease for the mixed clusters with respect to pure Co clusters is the reduction of the out-of-plane anisotropy strength consecutive to a modified strain upon Pd incorporation. An increased in-plane parameter of Co leads to a reduced out-of plane anisotropy, as was demonstrated recently for Pt-Co and Au-Co core-shell clusters grown on Au(111).31,32 In case of pseudomorphic Co layers, the anisotropy was even predicted by calculations to be in-plane,33 and later verified for low-temperature grown Co films.34 In this latter case, the films are formed by small grains which may be able to accommodate high in-plane strain. Here, introducing Pd in the clusters tends to force Co in an environment with larger in-plane lattice constant, as shown by molecular dynamic calculations.14 Compared to pure Co clusters, which are almost relaxed, mixed clusters are much more strained. An indirect experimental evidence for this is the fact that the single-layer high clusters are favored with respect to pure Co clusters. Magneto-elastic effects hence favor in-plane magnetization, and the net result is a decrease of the out-of-plane anisotropy strength. Comparable effects were theoretically identified in CoPt nanostructures.35

IV. CONCLUSION

In conclusion, we showed that in self-organized gold-protected Co$_x$Pd$_{1-x}$ nanoclusters on Au(111) the blocking temperature decreases with increasing Pd concentration. We attribute this effect to the decrease of the out-of-plane anisotropy strength consequently to high in-plane strain appearing in the clusters upon Pd introduction. The strain also strongly reduces the Pd spin moment with respect to bulk CoPd alloys, as supported by DFT calculations. Seeking enhanced

FIG. 3. XMCD magnetization loops at the Co $L_3$ edge at 4 K (blue) and a temperature close to the blocking temperature (red). Full lines: normal incidence; dashed lines: grazing incidence ($70^\circ$).
anisotropy in nanoparticles will therefore require a fine tuning of strain and alloying effects to avoid antinomic behaviors.

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14F. Scheurer et al. (to be published).
26H. Reichart, private communication (unpublished); In the case of NiPd$_{1-x}$ alloys, the Pd L$_{2,3}$ edges have been recently shown to be very sensitive to the chemical composition.