

ENHANCEMENT OF THE ANISOTROPY OF Co NANOPARTICLES BY CAPPING WITH Cu AND Au NOBLE METALS

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The sequential sputter deposition of alumina Al₂O₃ and Co layers on a Si substrate is a method of producing nanometric-sized Co cluster granular layers. The distribution of clusters in the layer is quite regular, and by successive deposition of the Co/Al₂O₃ bilayers a quasi-crystal of Co clusters is built (see Fig. 1). It has the advantage of allowing a close control of Co average diameter, by modifying the Co deposition time, while the interparticle distances remain nearly constant. In previous work we have shown that the particle anisotropy increases strongly as the diameter decreases, as a result of the enhanced anisotropy at the Co surface atoms. [1]

Therefore, it may be expected that modifying the nature of the matrix in contact with the cluster surface could modify the particle anisotropy. Capping with a noble metal like Cu or Au the pre-deposited Co granular layer allows us to modify the matrix without changing any other geometrical or structural condition of the Co cluster distribution, and so assess the modification of the Co particle magnetic properties induced only by the different matrix.

Three series of samples were prepared, uncapped, capped with a 1.5 nm thick Cu layer, and with the same thickness of Au. Each series consisted of samples with average diameter $\langle D \rangle = 1.8, 3, \text{ and } 3.5$ nm. The ac magnetic susceptibility measurements showed that all the samples behave as superparamagnets, with the blocking temperature T_B increasing with decreasing size, and, for a given diameter increasing in the trend uncapped, Cu- and Au-capped. This is a direct proof that the particle anisotropy increases by varying the Al₂O₃ insulating matrix by a metallic one, and that the effect is more pronounced in the case of Au capping.

From the fit to Langevin curves of the magnetization measurements as a function of applied field, performed at temperatures above T_B , i.e. in the unblocked region, the average diameters could be determined. In all cases, irrespective of the capping type, the same diameters for the same Co depositing time were found, proving the statement that capping does not modify the geometry of the clusters.

The ac imaginary component gives direct information of the average value of the activation energy U for the reversal of the cluster magnetic moment, and its statistical distribution. The magnetic anisotropy is derived from the ratio $K = 6\langle U \rangle / \pi \langle D \rangle^3$. The increase of K on decreasing cluster diameter is proportional to the inverse of $\langle D \rangle$ in the three series, proving that the Co atoms at the surface contribute predominantly to the Co cluster anisotropy. Moreover, for Cu-capped clusters, the surface anisotropy becomes about 40 times stronger than in the bulk, i.e. about 60% larger than for the clusters in pure alumina, whereas capping with Au makes it almost three times larger.

It has been proposed that the mechanisms giving rise to the increase in K for the case of an insulating matrix is the reduction of symmetry at the surface Co atoms because of the lack of nearest neighboring Co atoms in the vacuum side of the interface, on one hand, and to

the departure of Co cluster from regular polyhedral shape [2]. Of course, both mechanisms are present in the capped samples, so the additional enhancement in them is essentially produced by the metallic nature of the matrix. By extrapolation of the similar effects observed in Co thin layers capped with noble metals, it is proposed that hybridization of the 3d electronic states of Co with the conduction bands of Cu or Au has the effect of broadening the out-of-plane d electron band [3]. As a consequence the orbital moment component perpendicular to the interface should increase.

The existence of the hybridization at the interface between the Co clusters and the metal is confirmed by XMCD data (see Fig. 2). These spectra were obtained at 5 K and an applied field of 1 T, with average particle diameter of $\langle D \rangle = 3$ nm. The Co-L_{2,3} XMCD in the upper plot (normalized to the L₂ edge) show the increase of m_L/m_S in the trend uncapped, Cu- and Au capped. The K-Cu and L₃-Au -edge XMCD spectra show clear peaks, which prove the polarization of the Cu s-p, respectively, Au d electrons. This result puts in evidence the proposed hybridization mechanism to enhance the orbital moments at the Co cluster surface atoms, and the increase of the magnetic anisotropy, in turn, because of its direct proportionality with m_L .

References:

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Figures:

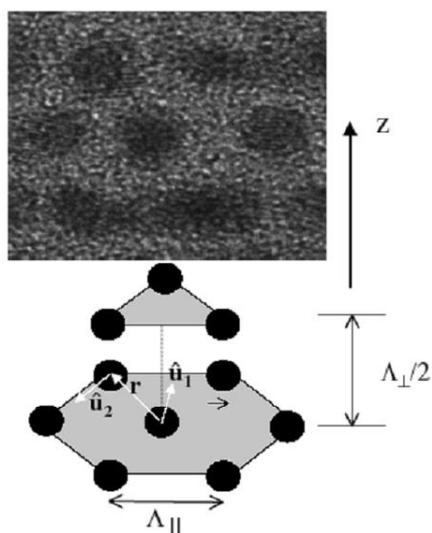


Fig. 1. Upper panel; TEM cross section of a Co/Al₂O₃ multilayer. Lower panel; schematic view of two layers (shown in perspective).

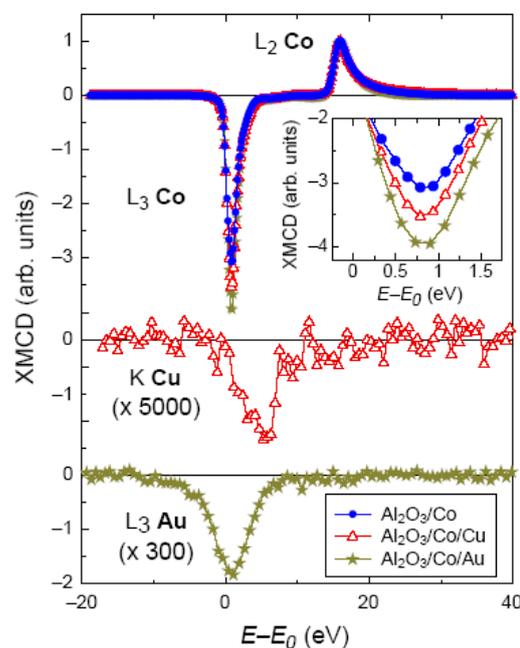


Fig. 2. XMCD spectra of multilayer samples (see text). The origin of the energy scale is taken at the inflection point of the corresponding absorption edge.